

Acetone and Ethanol Sensors Based on Nanocrystalline SnO₂ Thin Films with Various Catalysts

E.Y. Sevastyanov¹ · N. K. Maksimova¹ · L.S. Khludkova¹ · E.V. Chernikov¹ · N.V. Sergeychenko¹

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Abstract The electrical and gas-sensitive characteristics of sensors based on nanocrystalline SnO₂ thin films with noble metals (Pt, Pd, Au) and 3d-transition metals (Co, Ni) additives in the bulk and on the surface have been studied. Thin (~100 nm) tin dioxide films were grown in magnetron by DC sputtering of a tin–antimony alloy target in oxygen–argon plasma. It was shown that the obtained sensors can detect acetone and ethanol vapors at 1 ppm level. The detecting of acetone vapors needs higher temperatures than detecting of ethanol. In a temperature range $T < 650$ K, responses to ethanol exceed responses to acetone for all studied samples. For higher operating temperatures $T > 700$ K, the sensors with deposited Pt, Pd catalysts on the surface as well as the sensors with Ni and Co additives in the bulk are characterized by a higher sensitivity to acetone than to ethanol. The use of different operating temperatures allows detecting selectively acetone and ethanol vapors.

Keywords Gas sensors · Tin dioxide · Acetone · Catalysts

1 Introduction

Recently, increasing interest has been expressed about early diagnosis of some diseases based on human breath analysis. It has been discovered that some compounds in human breath can be used as biomarkers of the presence of diseases [1, 2].

Acetone in the human breath is an important marker for non-invasive diagnosis of type-1 diabetes. For diabetic patients, the acetone concentration in the breath exceeds 1.8 ppm. The researchers have proposed different methods to detect acetone in exhaled breath for early diagnosis of diabetes using gas analysis equipment such as gas chromatography/mass spectrometry (GC/MS) [3] and optical spectroscopy [4]. Although these types of analyzers are very sensitive to detect ppb level of biomarker components in breath, critical limitations such as bulky size, high cost, and difficulty in use hindered the practical application. In addition, these methods often require time-consuming preconcentration steps. Semiconductor metal oxides are promising materials for the highly sensitive and selective acetone sensors. In several papers [5–8], the possibilities of acetone detection using nanostructured films of tin dioxide and tungsten trioxide with various catalytic additives are considered. However, thick film technology of sensor fabrication proposed in these papers will slow the organization of industrial production of cheap portable devices that can be used in the home and can replace invasive blood glucose meters. In contrast, thin film technology has a number of advantages. Thin films have a high stability, high sensitivity because the high response needs a small grain size and for the thin films this condition is easier performed. The thin-film technology using the methods of microelectronics gives a possibility of miniaturization for integration in portable devices. The repeatability of properties of thin films is significantly higher than for thick films. For acetone detecting in human breath, it is necessary to use gas sensors that are highly selective to acetone in the presence of the other gases, containing in breath; the main of them being ethanol and water vapor. To improve the selectivity of semiconductor gas sensors, the sensor materials are modified with various catalysts. In this paper, the electrical and gas-sensitive characteristics of sensors based on nanocrystalline SnO₂ thin

✉ N. K. Maksimova
nkmax3@yandex.ru

¹ Kuznetsov Siberian Physical Technical Institute, National Research Tomsk State University, Sq. Novosobomaya., 1, Tomsk 634050, Russia

films with noble metals (Pt, Pd, Au) and 3d-transition metals (Co, Ni) additives in the bulk and on the surface have been studied.

2 Materials and Methods

SnO₂ thin films (about 100 nm) were deposited in oxygen–argon plasma by magnetron sputtering of a tin–antimony alloy target with antimony content 0.49 at.%. To introduce additives into the film bulk, pieces of corresponding metals were placed onto the target surface. The additive content was estimated by the ratio of the areas of the metal pieces S_m and the sputtered part of the target S_{Sn} . Sapphire wafers 150 μm thick were used as substrates. Contacts to the SnO₂ layers and a heater on the substrate's underside were formed by the sputter deposition of platinum followed by photolithographic engraving before the deposition of tin dioxide films. The sample size is 0.7 × 0.7 mm with an area of the sensitive element 0.3 × 0.3 mm². As many as 500 sensors were obtained on one substrate. The same DC magnetron sputtering technique was used to deposit ultrathin catalyst layers (Pt, Pd, Au) on the film surface. All fabricated wafers were subjected to stabilizing annealing in air at 723 K for 24 h. Four types of sensors, differing by additives on the surface and in the bulk of SnO₂ thin films, were investigated. The sensors of series (1) were fabricated by sputtering of a Sn + Sb target followed by deposition of ultrathin Pd layer and then Pt layer on the film surface. The target Sn:Sb + Au ($S_{Au}/S_{Sn} = 3 \cdot 10^{-3}$) was used for fabrication of the sensors of series (2) and then a dispersed Au layer was deposited on the SnO₂ surface. The sensors of series (3) and (4) differed from the sensors of series (2) by the additive of Ni (3) or Co (4) in the bulk of SnO₂ film ($S_{Ni}/S_{Sn} = S_{Co}/S_{Sn} = 3 \cdot 10^{-3}$). We introduce the following designations for films with various bulk additives and deposited catalysts: (1)—Pt/Pd/SnO₂:Sb; (2)—Au/SnO₂:Sb, Au; (3)—Au/SnO₂:Sb, Au, Ni; (4)—Au/SnO₂:Sb, Au, Co.

To measure the gas-sensitive characteristics, four sensors were placed in a quartz chamber with a volume of 1 L. Laboratory air purified using a sorption zeolite filter was pumped through the chamber, then the chamber was sealed. The necessary amount of ethanol or acetone vapors was injected into the testing chamber by a syringe. Two air streams with regulated speeds were used to change humidity: air dried with zeolite and humidified with a bubbler. The humidity was controlled using an HIH-4000 capacitive sensor placed in the chamber. The sensor conductivity in pure air (G_0) and in a gas–air mixture (G_1) were measured using an automatic bench, which made it possible to set and stabilize the operating temperature in the range of 300–700 K and record the conductivity values every second. The ratio G_1/G_0 was taken as the sensitivity (the adsorption response). The electrical and

gas-sensitive characteristics of sensors were measured at relative humidity RH = 30%.

3 Results and Discussion

The resistances in pure air at 300 K are $R_0 = 0.5$ –10 MΩ for films (1), $R_0 = 0.1$ –0.2 MΩ for films (2), and $R_0 = 0.5$ –2 GΩ for films (3), (4). Thus, introduction of Ni and Co additives into the bulk of SnO₂ thin films results in an increase in the film resistance by three orders of magnitude compared with the resistance of the films modified by only gold. In air ambient, the oxygen molecules adsorb on the semiconductor surface and create chemisorbed oxygen ions. For n-type SnO₂, negatively charged oxygen species result in a formation of space-charge region (SCR) on the surface, the sensor conductivity decreases. High resistances R_0 for the samples with Ni and Co additives are indicative of a high density of chemisorbed oxygen resulting in an increased space-charge region.

The temperature dependencies of the sensor resistance R_0 in pure air are presented in Fig. 1. During heating from room temperature to $T = 420$ –520 K, the resistance of all studied samples decreases mostly due to the ionization of shallow and deep centers in the film bulk, and the dependences $\ln R_0$ on $1000/T$ can be approximated by Arrhenius curves (Fig. 1). We can see that Arrhenius curves contain two linear portions from which the activation energies ΔE_1 and ΔE_2 were determined. These energies depend on the additive type in the bulk of SnO₂ film and deposited catalysts on the surface (Table 1). The resistance-increase portion in the region of $T > 470$ K is caused by an increase in the negative surface charge due to water molecule desorption from the surface and the transition of chemisorbed oxygen from the molecular form to the atomic form. The temperature T_{min} at which R_0 is minimal depends on the sensor type (Table 1). The lowest values of T_{min} are characteristic of films of series (1) with deposited Pd and Pt catalytic layers (Table 1). High resistance samples of series (3)

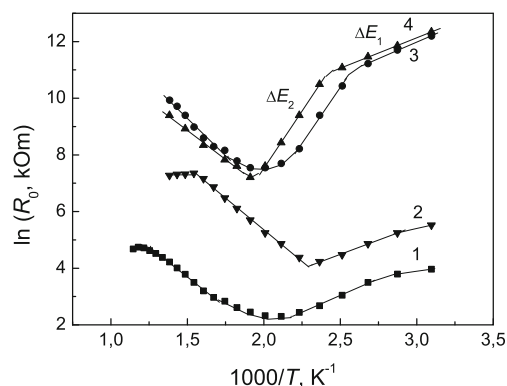


Fig. 1 Temperature dependences of the resistance R_0 in pure air for sensors of series (1)–(2), (2)–(1), (3)–(3), and (4)–(4)

Table 1 Sensor resistances R_0 in pure air at 300 K, conductivity activation energies ΔE_1 and ΔE_2 , and temperatures T_{\min} at which R_0 is minimal

Sensor type	R_0 (M Ω)	ΔE_1 (eV)	ΔE_2 (eV)	T_{\min} (K)
Pt/Pd/SnO ₂ :Sb (1)	0.5–2	0.11	0.17	420
Au/SnO ₂ :Sb, Au (2)	0.1–0.2	0.07	0.26	470
Au/SnO ₂ :Sb, Au, Ni (3)	500–2000	0.20	0.68	500
Au/SnO ₂ :Sb, Au, Co (4)	100–1500	0.19	0.70	520

and (4) with Ni and Co additives are characterized by higher temperatures $T_{\min} = 500$ – 520 K, the Fermi level shifts deep into the band gap, ΔE_2 corresponds to the ionization of deep centers.

Temperature dependences of sensor response to 8 ppm acetone (a) and ethanol (b) are presented in Fig. 2. The sensors modified only by gold have the lowest values of response both to acetone and ethanol. The other three types of sensors are much more sensitive and are characterized by similar values of response to acetone but differ in the response to ethanol. The response to ethanol of the sensors with Ni and Co additives reaches maximum at lower temperatures 600–620 K than the response of the sensors with deposited Pd and Pt layers. In a temperature range $T < 650$ K, the responses to ethanol exceed the responses to acetone for all studied samples (Table 2).

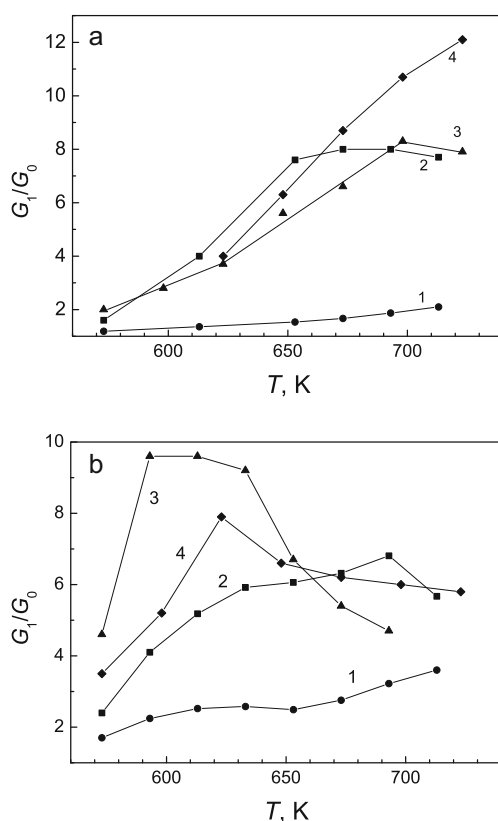


Fig. 2 Temperature dependences of the response to 8 ppm acetone (a) and ethanol (b) for sensors of series (1)–(1), (2)–(2), (3)–(3), and (4)–(4).

For higher operating temperatures $T > 700$ K, the sensors of series (2–4) are characterized by a higher sensitivity to acetone than to ethanol. The fact that the detecting of acetone vapors needs higher temperatures than detecting of ethanol may be caused by accumulation of acetone oxidation products on SnO₂ surface, blocking oxygen adsorption centers [9]. A desorption of such compounds, some of them having the more molecular mass than acetone, requires higher temperatures.

We can assume (basing on the ratio of the areas of the additive metal pieces and the sputtered part of the target $S_{Ni}/S_{Sn} = S_{Co}/S_{Sn} = 3 \cdot 10^{-3}$) that the concentration of additives of nickel and cobalt in the investigated thin films does not exceed approximately 0.3 at.%.

The study of the SnO₂ films obtained by different methods of thick-film technology [5, 10–12] showed that optimal concentrations of Ni and Co, in which the responses to a number of reducing gases (CO, H₂ etc.) reached the maximum values, varied from 0.2 to 2–4 wt%. Oleksenko et al. [12] concluded that electrical resistance, sensor response to hydrogen, catalytic activity towards hydrogen oxidation, and cobalt concentration in SnO₂ films correlate with each other, exhibiting maxima corresponding to the sensor material with 0.2 wt% Co. It is important to note that in all the works, X-ray diffraction analysis did not show the presence of the metal oxide second phase in SnO₂ films with optimal concentrations of 3d-metals. Korotcenkov et al. investigated Co-doped SnO₂ thin (50–400 nm) films deposited by spray pyrolysis [13]. They suppose that substitution of tin by cobalt in the SnO₂ lattice can be accompanied by forming of tin interstitial associations with oxygen vacancy, which may work as catalytically active adsorption centers, without forming defects related to cobalt interstitial. Comparison with the data for films with Pt and Pd additives in the bulk of SnO₂ [14] indicates a similar influence of noble and transition metals introduced in the volume. In the course of stabilizing, annealing during the crystallization of SnO₂ thin films in samples of series (3) and (4) Ni and Co atoms are mainly arranged on the surface of microcrystals. As a result of the interaction of additives with lattice oxygen, the increased density of superstoichiometric tin, which generates oxygen adsorption centers, increases the density of chemisorbed oxygen and, hence, increases the sensor's resistance.

The most accepted mechanism for gas sensing in semiconductor materials is based on the fact that reversible chemisorption of the active gases on the surface is accompanied by reversible changes in conductance. When the sensors are exposed to the reducing gases such as acetone and ethanol, dissociative adsorption of molecules is accompanied by the release of atomic hydrogen and other dissociation products. The most active atomic hydrogen reacts with the surface oxygen species, decreasing the density of the negative charge on the surface and the SCR width and resulting in an increase of the sensor conductivity. The samples with Ni and Co additives in

Table 2 Responses G_1/G_0 to 8 ppm acetone and ethanol at an operating temperature of 620 and 700 K for sensors of different types

Sensor type	G_1/G_0 (620 K)		G_1/G_0 (700 K)		η (ppm ⁻¹)	
	Acetone	Ethanol	Acetone	Ethanol	Acetone	Ethanol
Pt/Pd/SnO ₂ :Sb (1)	4–6	5–8	8–12	6–8	0.01	0.001
Au/SnO ₂ :Sb, Au (2)	1.5–2.5	2.5–4	1.8–3	3–4.5	0.02	0.004
Au/SnO ₂ :Sb, Au, Ni (3)	3.5–5	7–10	8–11	4–6	0.01	0.002
Au/SnO ₂ :Sb, Au, Co (4)	3.5–6	7–9	9–13	5–7	0.03	0.004

the bulk of SnO₂ are characterized by high density of chemisorbed oxygen and even minor changes in the negative charge density on the semiconductor surface, caused by oxidation of the reduction gases, have a significant effect on the film’s resistance that results in an increased sensor response.

Different temperature dependences of the sensor’s responses to acetone and ethanol give a possibility of the selective detection of acetone and ethanol vapors. The response times upon exposure to 8 ppm acetone and ethanol are 3 s for all types of sensors. The response time was defined as the time taken by the sensor to achieve 90% of the total resistance change. Figure 3 shows the typical concentration dependences of responses to acetone (a) and ethanol (b) in the range 1–10 ppm at an operating temperature 670 K. We can see that

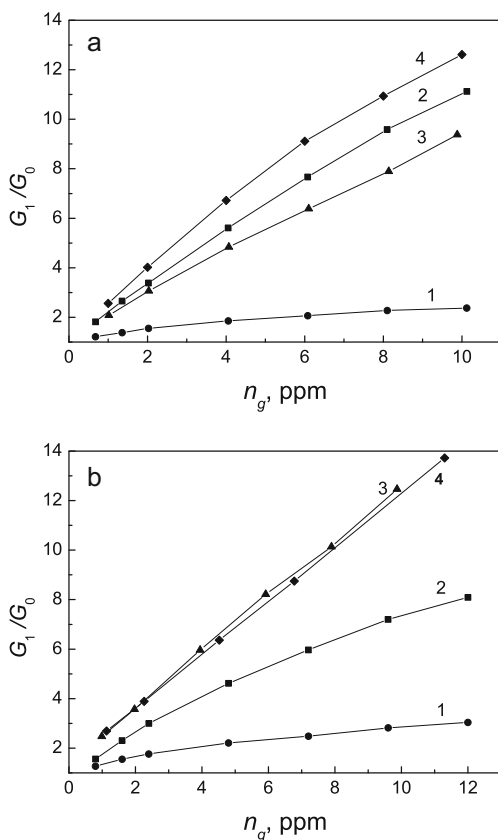


Fig. 3 Concentration dependences of the sensor responses to acetone (a) and ethanol (b) at an operating temperature 670 K for sensors of series (1)–(1), (2)–(2), (3)–(3), and (4)–(4)

the concentration dependences are linear or sublinear for all types of sensors. Previously, it has been showed [15] that such dependences correspond to a model according to which the tin dioxide film consists of microcrystals connected by conductive bridges of the same composition. For this case the conductance increment upon exposure to reduction gases is described by the following expression [15]:

$$\Delta G = G_1 - G_0 = G_{0M} 2d_0 \eta n_g / d_M (1 + \eta n_g) \tag{1}$$

Here, d_0 is the SCR width, d_M is the conductive bridge thickness, G_{0M} is the maximum possible film conductance, when $d_0 = 0$; and the parameter $\eta \sim \exp(\Delta E/kT)$ is defined by the adsorption heat ΔE . The value of η can be determined based on experimental data by the formula:

$$\eta = (tg\alpha \cdot n_g - \Delta G) / \Delta G / n_g \tag{2}$$

Here, $tg\alpha$ corresponds to $d(G)/dn_g$ at low gas concentrations, when $\eta n_g < 1$ and a linear dependence ΔG from n_g is observed. Concentration dependence of the sensor conductance increment upon exposure to acetone at an operating temperature 670 K was measured in a wide concentration range (Fig. 4). From an analysis of this experimental data, it was shown for all types of sensors in the case of ethanol adsorption $\eta \approx (1-4) \cdot 10^{-3}$ ppm⁻¹. These values correlate with previously obtained values for hydrogen adsorption [15]. In the

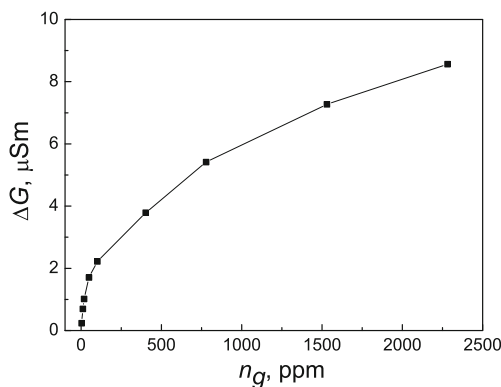


Fig. 4 Concentration dependence of the sensor conductance increment upon exposure to acetone at an operating temperature 670 K for the sensor of series (3)

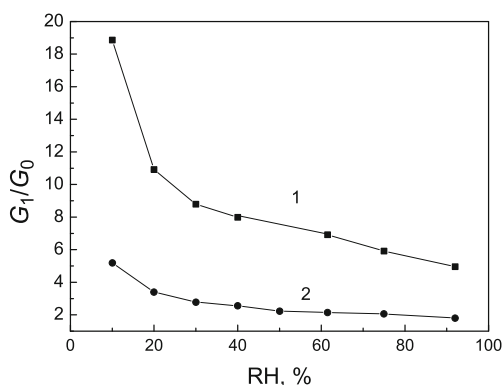


Fig. 5 Dependences of the response to 8 ppm acetone on relative humidity for the sensors of series (2)–(2) and (3)–(1) at an operating temperature 670 K

case of acetone adsorption, the parameter η is larger by an order of magnitude (Table 2). This is possibly indicative that acetone dissociation on SnO_2 surface occurs not only with producing of atomic hydrogen as in the case of ethanol but more complicated reactions take place [7].

The results of investigation of humidity influence on sensor responses to acetone are presented in Fig. 5 for an operating temperature 670 K. The most rapid decrease of sensor responses with increasing of relative humidity is observed at low humidity levels ($\text{RH} < 30\%$). A further increase in the relative humidity no longer reduced the response significantly. The relative humidity of the human breath is around 90%. So, gas sensors for breath analysis must detect acetone vapors at a high humidity level. The sensors with Ni and Co additives meet these requirements because they reveal a high sensitivity to acetone vapors even in the high humidity ($G_1/G_0 = 5$ for 8 ppm acetone and $\text{RH} = 90\%$). After the calibration of the sensitivity of the sensor in the range of 1–100 ppm acetone at $\text{RH} = 90\%$, the high measurement accuracy will be ensured.

4 Conclusion

Four types of sensors based on SnO_2 thin films grown by magnetron deposition with various catalysts in the bulk and on the surface have been studied. Sensors with deposited Pt, Pd layers on the surface as well as the sensors with Ni and Co additives in the bulk are characterized by a high sensitivity to acetone and ethanol and can detect these vapors at 1 ppm level. The detecting of acetone vapors needs higher temperatures than detecting of ethanol. The use of different operating temperatures allows detecting selectively acetone and ethanol vapors. Gas sensors for breath analysis must detect acetone vapors at a

high humidity level. The sensors with Ni and Co additives reveal a high sensitivity $G_1/G_0 = 5$ for 8 ppm acetone at $\text{RH} = 90\%$ and they are most promising for the analysis of acetone in exhaled breath of diabetic patients.

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