Aviation kerosene sensors based on nanocrystalline SnO$_2$ thin films with various catalysts

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Abstract. Gas-sensitive characteristics of aviation kerosene sensors based on nanocrystalline SnO$_2$ thin films with various catalysts have been studied as a function of the operating temperature and gas concentration in the air. Thin tin dioxide films were grown in magnetron sputtering of a tin–antimony alloy target in oxygen–argon plasma. It is shown that the sensors are characterized by a high sensitivity to aviation kerosene vapors and by a good stability of parameters during long-term tests and under the variation of humidity.

1. Introduction
One of the actual ecological problems is the pollution of the airfield and near-airfield territories due to leakages of aviation fuels. To prevent a harmful influence of aviation kerosene vapors on human health a continuous air monitoring is necessary. Thin-film metal oxide semiconductor gas sensors are promising devices for this purpose because of their low cost, high sensitivity, fast response time and simple electronic interface. Gas-sensitive characteristics of metal oxide sensors can be improved by introducing metal modifiers into the bulk and depositing catalytic layers on the surface. Noble metals are usually used as catalytic additives in gas sensing materials. Recently, in some studies 3d-transition metals such as Co, Ni, Cr are considered as the additives that can effectively modify adsorption properties of gas sensing materials and improve the parameters of gas sensors [1-4]. In this paper the electrical and gas-sensitive characteristics of sensors based on nanocrystalline SnO$_2$ thin films with noble metals (Pt, Pd, Au) on the surface and 3d-transition metals (Co, Ni) additives in the bulk have been studied.

2. Experimental
SnO$_2$ thin films (about 100 nm) were deposited in oxygen-argon plasma by magnetron sputtering of a tin–antimony alloy target. 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 metal pieces $S_m$ (m = Ni, Co, Au) and of the sputtered target $S_{Sn}$. The same DC magnetron sputtering technique was used to deposit ultrathin catalyst layers (Pt, Pd, Au) on the films surface. Sapphire wafers 150 μm thick were used as substrates. Contacts to the SnO$_2$ 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 mm$^2$. As many as 500 sensors were obtained on one substrate. All fabricated wafers were subjected to stabilizing annealing in air at 450 °C for 24 h. A detailed description of the technology of film deposition and fabrication of sensors is given in [5]. Three types of sensors, differing by additives on the surface and in the bulk of SnO$_2$ thin films were investigated.
The sensors Au/SnO\textsubscript{2};Sb, Au, Ni of series (1) were fabricated by sputtering of a target with gold and nickel additives (S\textsubscript{Au}/S\textsubscript{Sn} = S\textsubscript{Ni}/S\textsubscript{Sn} = 3\cdot10^{-3}) and then a dispersed Au layer was deposited on the SnO\textsubscript{2} surface. The sensors Au/SnO\textsubscript{2};Sb, Au, Co of series (2) differed from the sensors of series (1) by the additive of Co in the bulk of SnO\textsubscript{2} film (S\textsubscript{Au}/S\textsubscript{Sn} = 6\cdot10^{-3}, S\textsubscript{Co}/S\textsubscript{Sn} = 9\cdot10^{-3}). The sensors Pt/Pd/SnO\textsubscript{2};Sb, Au, Co of series (3) with gold and cobalt additives in the volume (S\textsubscript{Au}/S\textsubscript{Sn} = S\textsubscript{Co}/S\textsubscript{Sn} = 3\cdot10^{-3} ) were fabricated by deposition of ultrathin Pd layer and then Pt layer on the film surface. The thickness and microstructure of the films were controlled by atomic force microscopy.

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. 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 necessary amount of aviation kerosene vapors was injected into the testing chamber by a syringe. The sensor conductivity in pure air (G\textsubscript{0}) and in a gas–air mixture (G\textsubscript{1}) were measured using an automatic bench, which made it possible to set and stabilize the operating temperature and record the conductivity values every second. The ratio G\textsubscript{1}/G\textsubscript{0} was taken as the adsorption response.

### 3. Results and Discussion

Investigations showed that the thickness of the studied tin dioxide layers is 120-130 nm. The films contain nanocrystallites with sizes d\textsubscript{1}=8-15 nm and d\textsubscript{2}=150-250 nm (Table 1). The values of the sensors resistances in pure air at an operating temperature 450 °C vary in the interval 2-12 MΩ. The highest values of R\textsubscript{0} are characteristic of sensors from series (3) with gold and cobalt additives in the volume and Pt/Pd catalyst layers on the surface (Table 1).

#### Table 1. Typical sizes of grains d\textsubscript{1} and d\textsubscript{2} in tin dioxide films with various catalysts and sensors parameters at an operating temperature 450 °C: resistances R\textsubscript{0} in pure air and the values of the response G\textsubscript{1}/G\textsubscript{0} under exposure to 15 ppm of aviation kerosene vapors.

| The sensor type | Au/ SnO\textsubscript{2};Sb, Au, Ni series (1) | Au/ SnO\textsubscript{2};Sb, Au, Co series (2) | Pt/Pd/ SnO\textsubscript{2};Sb, Au, Co series (3) |
|-----------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| d\textsubscript{1}, nm | 40-50                                       | 125                                         | 8-16                                       |
| d\textsubscript{2}, nm | 150-250                                    | -                                           | 190-260                                    |
| R\textsubscript{0}, MΩ | 2-4                                        | 5-9                                         | 7-12                                       |
| G\textsubscript{1}/G\textsubscript{0} | 2,1-2,5                                    | 2,2-2,5                                     | 2,3-2,8                                    |

Temperature dependences of the sensor response to 15 ppm kerosene vapors are presented in Fig. 1(a). The response of the sensors of series (3) with Pt/Pd catalyst on the surface reaches maximum at 370 °C. The responses of the sensors of series (1) and (2) increase monotonically up to 450 °C. For all types of sensors the operating temperature in the range 400-450 °C provides relatively high response values G\textsubscript{1}/G\textsubscript{0}=2.1-2.7 upon exposure to 15 ppm kerosene vapors. The response time of the sensors is 5-6 s at 400 °C and 4 s at 450 °C. The response time was defined as the time taken by the sensor to achieve 90 % of the total resistance change.

Figure 1(b) shows concentration dependences of responses to aviation kerosene vapors in the range 5–75 ppm at an operating temperature 450 °C for sensors of different series. The response values to 45 ppm (this concentration corresponds to permissible exposure limit for aviation kerosene vapors in workplace air) are G\textsubscript{1}/G\textsubscript{0}=3-4. It should be noted that sensors can detect kerosene vapors at 5 ppm level which corresponds to 0.1 of permissible exposure limit for aviation kerosene.
Figure 1(a, b). Dependences of the response to 15 ppm of aviation kerosene vapors on the operating temperature (a) and concentration dependences of the response measured at an operating temperature 450 °C (b) for the sensors from series: (1) (1), (2) (2), (3) (3).

One of the significant sources of instability in the parameters of sensors based on metal oxide semiconductors is the change in the humidity of the environment. The previous studies of the humidity influence on the properties of SnO₂ thin films showed that the conductivity of sensors in pure air increases and the responses of sensors to reducing gases (hydrogen, carbon monoxide, etc.) decrease as the humidity level increases [6,7]. The results of investigations presented in this paper showed that the rate of conductivity increase with humidity level increasing is the same for pure air and gas–air mixture containing kerosene vapors. For all types of sensors both the conductivity in pure air $G_0$ and the conductivity in a gas–air mixture containing 15ppm of aviation kerosene vapors ($G_1$) increases by 4-6 times with increasing of relative humidity from 10 % to 70 % (Fig. 2 (a)). As a result the sensor response defined as the ratio $G_1/G_0$ is practically independent on humidity in the wide range of RH (Fig.2 (b)).

Figure 2(a, b). Dependences of conductivity in pure air (1) and in a gas–air mixture containing 15ppm of aviation kerosene vapors (2) on the humidity level for the sensor from series (3) (a) and dependences of the response to 15 ppm of aviation kerosene vapors on the humidity level for the sensors from series: (1) (1), (2) (2), (3) (3) (b). The sensors operating temperature is 450 °C.
To discuss the obtained results the mechanism for gas sensing in semiconductor materials is to be considered. The detection of aviation kerosene vapors is based on the oxidation reaction of adsorbed molecules with the participation of previously chemisorbed oxygen ions, which occurs at high temperatures, when atomic oxygen predominates on the surface. As a result, the density of oxygen ions decreases and the conductivity increases. Kerosene is a mixture of different hydrocarbons and oxidation of such molecules at the surface of metal oxide semiconductor is accompanied by the release of atomic hydrogen and other dissociation products \[8\]. Atomic hydrogen reacts with the surface oxygen species, decreasing the density of the negative charge on the surface and resulting in an increase of the sensor conductivity. The effect of humidity on the properties of sensors is determined by the fact that under adsorption on the surface of the SnO$_2$ microcrystal, the H$_2$O molecule dissociates into the proton and hydroxyl group and compensates the charge of one adsorbed oxygen ion \[6\]. The density of chemisorbed oxygen decreases, that leads to an increase of the sensor conductivity.

To study the stability of parameters at long-term operation of the sensors, the values of the response to aviation kerosene vapors were measured at intervals of 2-10 days. It was shown that only a slight attenuation in the sensing response was observed during 200 days.

4. Conclusion
Three 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. The all types of sensors are characterized by a high sensitivity to aviation kerosene vapors and can detect these vapors at 5 ppm level which corresponds to 0.1 of permissible exposure limit for aviation kerosene. The sensors revealed a good stability of parameters after the long-term tests and under the variation of humidity.

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References
\[1\] Korotcenkov G, Boris I, Brinzari V, Han S H, Cho B K 2013 Sensors and Actuators B 182 112
\[2\] Oleksenko L P, Maksymovych N P, Buvailo A I 2012 Sensors and Actuators B 174 39
\[3\] Sevastyanov E Y, Maksimova N K, Khudskova L S, Chernikov E V, Sergeychenko N V 2017 BioNanoSci. 7 654
\[4\] Sevastyanov E Y, Maksimova N K, Potekaev A I, Khudskova L S, Chernikov E V, Davydova T A 2018 Russ. Phys. J. 60 1739
\[5\] Sevastyanov E Y, Maksimova N K, Novikov V A, Rudov F V, Sergeychenko N V, Chernikov E V 2012 Semiconductors 46 801
\[6\] Gaman V I, Anisimov O V, Maksimova N K, Sergeychenko N V, Sevastyanov E Y, Chernikov E V 2008 Russ. Phys. J. 51 83
\[7\] Maksimova N K, Sevastyanov E Y, Sergeychenko N V, Chernikov E V 2016 Thin-Film Semiconductor Gas Sensors (Tomsk: Izd. Nauchn.-Tekh. Liter.)
\[8\] Carotta M C, Guidi V, Martinelli G, Nagliati M, Puzzovio D, Vecchi D 2008 Sensors and Actuators B 130 497