Ammonia sensors based on resistive structures M–SnO$_2$:Sb–M

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Abstract. The paper presents a comparison of the responses of sensors to ammonia in continuous heating and thermal cycling modes, and also shows the dependence of the response time of the sensors on the content NH$_3$. Thin films of tin dioxide were obtained using RF magnetron sputtering, and then annealed in air at a temperature of 425°C for 24 hours. In thermal cycling, the temperature of the heating cycle remains constant $400 \, ^\circ C$ (duration of the heating cycle was 8 s). The temperature of the cooling cycle changes in the range $200 \, ^\circ C – 100 \, ^\circ C$, but duration of cooling of the cooling cycle was remained constant of 5 s. It was shown that the thermal cycling mode has several advantages over the constant heating mode. The experiments showed that sensors based on SnO$_2$:Sb have short response times – less than 3 seconds.

1. Introduction
At the moment, the demand for ammonia sensors is becoming more and more. This is due to the fact that ammonia is used in industry for the production of nitrogen fertilizers, which are widely used in agriculture. Almost every person in the medicine chest has a bottle of ammonia. The basis for its manufacture is NH$_3$. Ammonia is used in the production of explosives, where the control of the environment must be carried out strictly. In medicine, ammonia sensors can be used to determine various diseases of the digestive tract by the concentration of NH$_3$ in the exhaled gas mixture [1]. Every day the content of harmful substances in cities is increasing. So, for example, the daily excess of NH$_3$ in the environment can greatly affect human health, and this often leads to chronic diseases.

Sensors must have such important parameters as: short response time and high response. Modification of the sensors leads to the fact that they become selective to certain gases [2–6]. It was shown in the works that the thermal cycling mode positively affects the response of the sensors [7–11]. Catalysts on the film surface not only increase selectivity, but also increase the response of sensors. Palladium is the most suitable catalyst for ammonia. Thus, we are faced with the task of creating and improving ammonia sensors based on tin oxide thin films doped antimony.

2. Experimental
NH$_3$ sensors were obtained by RF magnetron sputtering of tin dioxide on a sapphire substrate. Finely dispersed platinum (catalyst) is applied to the surface of the films by the same method. Platinum electrical contacts and a heater are formed using photolithography. The film was annealed in a chamber filled with air for 24 hours at a temperature of 425 °C. The resulting plate was cut into many single sensors with an area of 1.4×1.4 mm$^2$. Then, a gold wire with a diameter of 50 μm was welded to the Pt
contacts, the heater, and the contact pads of the crystal holder. The manufacturing process of the sensors ended with the placement of structures in metal cases.

The experiments were carried out using a special measuring setup, which consists of an integrated circuit and a device transmitting a signal to a computer. This equipment allows you to take time and electrical characteristics, and also control the heating temperature of the sensors. All measurements were carried out in an insulated glass chamber, the volume of which was 1 liter. An integrated circuit was placed in the chamber, to which samples were attached using holders. The gas mixture N₂ / NH₃ (96.96 / 3.04) vol.% was supplied using a medical syringe. There is purge equipment in the chamber, which ensures uniform distribution of gas throughout the chamber, and a bubbler is connected to the air supply system to control humidity (RH = 32–34 %).

Response measurements were carried out in continuous heating and thermal cycling modes. In the constant heating mode, the temperature of the sensors remains unchanged (340 °C), but the content of ammonia increases by doses. The thermal cycling mode is a sequential alternation of heating and cooling cycles. During each cycle, a specific temperature and duration is set. In our work, the temperature of the heating cycle was 400 °C, the duration was 8 seconds, and the temperature of the cooling cycle was considered in the range of 200 °C – 100 °C using duration of cooling cycles of 5 seconds.

3. Results
In this paper, we consider the effect of thermal cycling on the response of ammonia sensors, compared with the response with constant heating.

For thermal cycling mode the response in the heating cycle was determined by the ratio of the conductivity of the sensors in the gas Gₖ to the conductivity without the gas G₀ (in the saturation region). The response in the cooling cycle was calculated in the same way, but the lowest conductivity G(t) value is taken as the calculated value.

In the experiment, 4 sensors from the same batch were considered. When the sensors are working on direct current, the operating temperature is \( T_m = 340 \) °C. The response values of the sensors, represented by the ratio of the conductivity in the gas Gₖ to the conductivity in the air G₀, with constant heating are shown in Figure 1.

![Figure 1. The dependence of the response of the sensors in continuous heating mode on the concentration of NH₃ (Gₖ is the sensor conductivity in gas, G₀ is the sensor conductivity in air, the character indicates the sensor number)](image-url)
in the cooling section it varied from 200 °C to 100 °C (for a duration of 5 s). Concentration dependences of the response with temperature variation in the cooling cycle are shown in Figure 2.

![Graph](image)

**Figure 2.** The dependence of the response of the sensors in thermal cycling mode in the cooling cycle at temperatures: 200 °C (a), 150 °C (b) and 100 °C (c)

As can be seen from the above dependences, the thermal cycling mode significantly increases the response of the sensors. The response increasing is explained by the fact that when the sensor is heated to 400 °C, molecular oxygen dissociates into atomic oxygen on its surface $\text{O}_2 \leftrightarrow \text{O}^+ + \text{O}^-$, which is
chemically active [8]. Then, with a sharp decrease in temperature, oxygen does not have time to associate back to molecular oxygen and reacts with hydrogen, which is the decomposition product of ammonia. This in turn leads to a decrease in the density of atomic oxygen on the surface of the sensor, which means that the width of the surface region of the space charge decreases, and the bulk conductivity of the films increases [12].

The most important parameter of the sensor is the response time. The examined samples were exposed to a mixture with an ammonia content of 300, 600 and 900 ppm, response times are presented in Table 1.

Table 1. The dependence of response time on an ammonia concentration

| NH₃, ppm | Sample № 1 | Sample № 2 | Sample № 3 | Sample № 4 |
|---------|------------|------------|------------|------------|
| 300     | 2.29       | 2.63       | 2.63       | 1.93       |
| 600     | 2.45       | 2.69       | 2.57       | 1.88       |
| 900     | 2.89       | 2.92       | 2.86       | 2.40       |

where \( \tau_r \) is response time

The table shows that the response times do not exceed 3 seconds for all sensors. It can also notice that with an increase in the ammonia content, the response time also slightly increases.

4. Conclusion

It was found that in the thermal cycling mode the response is much larger compared to the constant heating mode. As a result, we can say that the thermal cycling mode allows fulfilling two most important conditions for improving sensors - an increase in response and a decrease in power consumption. The most advantageous option for all parameters, from the considered modes, is the operation of the sensors in the regime of 400 °C (8 s) – 100 °C (5 s). Sensors based on SnO₂: Sb show short response times, which are weakly dependent on the ammonia content.

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