Selectivity of the gas sensor based on the 50\% In_2O_3–50\% Ga_2O_3 thin film in dynamic mode of operation

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Abstract. The article considers the gas sensor with the sensitive layer based on the 50\% In_2O_3–50\% Ga_2O_3 thin film. The temperature and concentration dependencies of gas-induced resistance response of this sensor and the dynamical dependencies of its resistance response on the test gases in air are investigated. The test gases were ethanol, acetone, ammonia and liquefied petroleum gas. The information parameters of the sensor in the dynamical mode of operation were considered to improve its selectivity. The presented results show that the selectivity of the sensor in this mode may be improved by using the following information parameters: gas-induced resistance response in steady state, activation energy of the response and pre-exponential factor of the temperature dependence of the response time constant.

1. Introduction
Semiconductor gas sensors based on oxide materials are widely used in the fields of safety, control and optimization of technological processes. Advantages of this type of sensor are high sensitivity to a large amount of combustible and oxidizing gases, simplicity of design, temperature and chemical stability, low cost [1].

An essential disadvantage of semiconductor sensors is their low selectivity, in other words their low ability to recognize the type of gas. Commonly used approach to overcome this difficulty is to increase the number of information parameters of the sensor. The information parameter is some parameter calculated from output signal of the sensor and used to identify a gas type or to quantify its concentration. In addition to the widely used amplitude of the gas-induced resistance response, following characteristics may be used to calculate information parameters: dynamics of response and recovery under exposure to abruptly changing concentration of sample gas [2], dynamics of response at a changing operating temperature [3–5], dynamics of gas diffusion along the thickness of a sensitive layer [6].

The best technical solution for applying these approaches is to use multi-sensor systems. The following trends can be distinguished in developing multi-sensor systems:
1) systems based on sensor arrays with a differently modified surface;
2) systems based on arrays of identical sensors with different operating temperatures;
3) systems based on sensor arrays with different electrode configurations;
4) systems based on sensor arrays with sensitive layers made of various semiconductor materials [2].

A promising approach from the point of view of the simplicity of design and fabrication of a multi-sensor system is the second approach based on identical sensors, which have different operating temperatures. One of the main trends in research in the field of semiconductor gas sensors is the search
for new gas-sensing materials that provide high selectivity. An important approach in this direction is the use of composite oxide materials.

Recently, among semiconductor composite oxide materials, a system based on indium and gallium oxides has attracted interest. The studies [7, 8] have shown that films of 50%In$_2$O$_3$–50%Ga$_2$O$_3$ have a high sensitivity to a number of gases. However, for the use of these films as sensitive layers of gas sensors, it is necessary to analyse their selectivity to the gases, and to suggest the most suitable operating mode for sensors based on them. As a perspective mode of operation one should consider the dynamic mode, for which there is a number of information parameters of the sensor allowing one to determine concentration of a gaseous medium.

Thus, the aim of the work is to study the selectivity of a semiconductor gas sensor based on the In$_2$O$_3$-Ga$_2$O$_3$ thin films under the dynamic mode of its operation.

2. Experimental
Semiconductor thin films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition for gas sensors were obtained in two stages. At the first stage, the target with desired composition was made from the powders of indium and gallium oxides. In the second stage, pulsed laser deposition of these films was performed from the obtained target to a glass ceramic substrates. The modes of the target preparation and the pulsed laser deposition of the films were considered in detail in [9].

The analysed gases were ethanol, acetone, ammonia and a mixture of liquefied petroleum gas (the LPG). As a characteristic of the gas-induced resistance response, the value of S was used

$$S = \frac{R_0 - R_g}{R_g},$$

(1)

where $R_0$ and $R_g$ – resistance of the film in the natural air and in the air with the sample of the analysed gas, respectively.

Temperature and concentration dependencies of gas-induced resistance response of the films and its dynamical resistance response on the analyzed gases in air were investigated experimentally. The research methodology was presented in [9].

3. Formatting the text
A Figure 1 represents the obtained normalized dynamic dependences of the resistance response for the sensor based on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film for 25 ppm of acetone in air, at different operating temperatures. The dynamic dependencies of the normalized resistance response for other analyzed gases have a similar form. All the obtained dependences can be approximated by functions

$$S(t)/S_0 = 1 - \exp(-t/\tau),$$

(2)

where $S(t)$ – gas-induced resistance response of the sensor at time $t$, $S_0$ – gas-induced resistance response of the sensor in steady state, $\tau$ – response time constant.
Figure 1. Normalized dynamic dependences of the gas-induced resistance response of the sensor based on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film for 25 ppm of acetone in air.

The response time constants ($\tau$) were calculated from the approximation of the experimental data by the functions (2) using the least squares method. The obtained values of the response time constants for 25 ppm concentration of the analysed gases at the different operating temperatures are presented in Table 1.

| Analyzed gas | Temperature ($T$), °C | Response time constants ($\tau$), s |
|--------------|-----------------------|----------------------------------|
|              | 386                   | 445                              |
|              | 504                   | 563                              |
|              | 623                   | 682                              |
|              | 742                   |                                  |
| Ethanol      |                       |                                  |
| Acetone      | 139                   | 41.1                             |
|              | 22.9                  | 9.00                             |
|              | 5.13                  | 2.62                             |
|              | 1.62                  |                                  |
| Acetone      | 277                   | 78.5                             |
|              | 38.7                  | 16.8                             |
|              | 8.80                  | 4.20                             |
|              | 2.38                  |                                  |
| Ammonia      | 342                   | 268                              |
|              | 212                   | 21.6                             |
|              | 10.8                  | 3.55                             |
|              | 1.35                  |                                  |
| LPG          | 4655                  | 968                              |
|              | 423                   | 143                              |
|              | 72.4                  | 24.0                             |
|              | 13.1                  |                                  |

As noted above, semiconductor gas sensors based on oxide materials have a low selectivity and the recognition of the type of an analysed gas by measuring only one information parameter with their help is nearly impossible. This is confirmed by the experimentally obtained temperature and concentration dependences of the gas-induced resistance response of the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film in steady state. For example, Figure 2a shows the temperature dependences of the resistance response of the studied film at 25 ppm ethanol (graph 1) and acetone (graph 2) in air. From the presented data, it can be seen that these dependences are insignificantly different in the whole investigated temperature range. Figure 2b shows the concentration dependences of the resistance response of the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film on ethanol and acetone. Analysis of these dependencies shows the ambiguity in determining the type of the gas probe. For example, the response value of the film resistance at 25 ppm of acetone in air is equal to its response at 40 ppm ethanol in air. The given examples clearly
demonstrate the impossibility of gas recognizing with the help of the In$_2$O$_3$–Ga$_2$O$_3$ thin film sensor, basing only on measurements of the resistance response in the steady state.

**Figure 2.** Temperature (a) and concentration (b) dependencies of the gas-induced resistance response for sensor based on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film for ethanol (1) and acetone (2): Fig. 2(a) – gas concentration is 25 ppm; Fig. 2(b) – working temperature is 563 °С.

The solution of this problem is possible when using the parameters of the dynamic characteristics of the sensor behaviour in the medium of the analysed gas. Figure 3 represents dynamic dependencies of the resistance response of the sensor based on the investigated film at 563 °С and at the step change of the test gas concentration (acetone) up to the specified values. The values of the response time constant determined from these dependences are the same for all the concentrations of the analysed gas and depend only on the gas type.

Thus, the value of the sensor response time constant at the certain operating temperature can be an information parameter that does not depend on the gas concentration and allows one to determine the type of gas being analysed. However, for each gas the value of the sensor response time constant depends on the operating temperature, and for some gases these values at the certain operating temperatures may be approximately equal. For example, according to the data presented in Table. 1, in the operating temperature range of 623–682 °C, the response time constant of the sensor resistance for ammonia and acetone is close, which reduces the selectivity of the sensor operating in dynamic mode. Thus, the complete consideration of the temperature dependence of the response time constant is required in order to unambiguously determine the type of a test gas.
Figure 3. The effect of gas concentration on the dynamics of the gas-induced resistance response: test gas – acetone, working temperature – 563 °C.

Figure 4 presents the temperature dependences of the response time constant for sensor on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film for all the tested gases. These dependences have a linear form in the coordinates of the inverse temperature and the logarithmic coordinates for the response time constant.

The obtained experimental temperature dependences of the response time constant for all the tested gases may be represented in an analytical form as follows

$$\tau = \tau_0 \exp(-E_a/kT),$$

where $E_a$ – activation energy of the response time constant, $\tau_0$ – pre-exponential factor [9, 10].

The parameters $\tau_0$ and $E_a$ included in (3) may be determined from the experimental dependences in the preliminary calibration of the sensor. These parameters are independent of the concentration of the test
gas and the working temperature of the sensor. They can be used as information parameters for identifying the type of test gas during real operation mode of the sensor.

The values of parameters $S_0$, $\tau_0$ and $E_a$ for sensor based on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film for the different operating temperatures and for the concentration of the test gases of 25 ppm are given in Table 2. The presented data show that this set of information parameters is unique for each of the test gases. They allow identifying the type of gas being analysed and determining its concentration. For example, as noted above, the response time constant of the sensor resistance in the operating temperature range of 623–682 °C for ammonia and acetone has similar values (Table 1). However, according to the data presented in Table 2, these gases can be identified by the information parameters $\tau_0$ and $E_a$.

**Table 2.** The values of parameters $S_0$, $\tau_0$ and $E_a$ for sensors on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film.

| №   | Temperature, °C | Parameter | Test gas |
|-----|----------------|-----------|----------|
|     |                |           | Ethanol  | Acetone | Ammonia | LPG |
| 1   | 445            | $S_0$     | 7.00     | 9.00    | 0.59    | 1.03 |
|     |                | $\tau_0$, μs | 495   | 512     | 0.548   | 308  |
|     |                | $E_a$, eV | 0.712    | 0.755   | 1.297   | 0.935 |
| 2   | 504            | $S_0$     | 20.5     | 24.4    | 0.8     | 1.80 |
|     |                | $\tau_0$, μs | 495   | 512     | 0.548   | 308  |
|     |                | $E_a$, eV | 0.712    | 0.755   | 1.297   | 0.935 |
| 3   | 563            | $S_0$     | 18.5     | 21.00   | 1.80    | 4.00 |
|     |                | $\tau_0$, μs | 495   | 512     | 0.548   | 308  |
|     |                | $E_a$, eV | 0.712    | 0.755   | 1.297   | 0.935 |
| 4   | 623            | $S_0$     | 6.47     | 7.85    | 2.15    | 3.78 |
|     |                | $\tau_0$, s | 495   | 512     | 0.548   | 308  |
|     |                | $E_a$, eV | 0.712    | 0.755   | 1.297   | 0.935 |

The considered approach to increase the selectivity of gas sensors based on 50%In$_2$O$_3$–50%Ga$_2$O$_3$ films requires the use of the more sophisticated measuring circuits that must ensure dynamic measurements at different operating temperatures. There are two options for implementing such a measurement process. In the first variant, one sensor is used the operating temperature of which is periodically varied. The second option is to use a multi-sensor system in which each sensor has its own operating temperature. In both cases, the parameters $S_0$, $\tau_0$ and $E_a$ are calculated, basing on the dynamic measurements of the gas resistance response. These parameters are used to identify the type of an analysing gas and to determine its concentration.

4. Conclusion
The presented results by the example of the gas sensor on the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ film show that the selectivity of semiconductor gas sensors can be improved by using the dynamic mode of measurement and determining, from the measurement results, the set of values of the following parameters: gas-induced resistance response in steady state ($S_0$), activation energy of response time constant ($E_a$) and pre-exponential factor ($\tau_0$). To determine these parameters, it is necessary to carry out dynamic measurements at different operating temperatures and use more sophisticated measuring schemes. The
choice of the optimal temperature operation conditions of the sensors for the dynamic measurements requires the additional studies.

Acknowledgments
This work was carried out within the project «Young scientist»; research effort № 17072B.

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