Increasing the selectivity of semiconductor gas sensors working at sinusoidal-varying temperature for machine industry safety systems

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Abstract. The article considers the possibility of creating a sensor system on the basis of 50%In$_2$O$_3$–50%Ga$_2$O$_3$ thin films, functioning at sinusoidal-varying temperature, with high selectivity to a number of key industrial gases including ethanol, acetone, ammonia, and propane-butane. A study of temperature and time dependencies of resistance at a sinusoidal-varying operating temperature was conducted. The deviation of the dynamic dependencies of the resistance from the harmonic law was detected, the reason of which should be considered to be the non-linearity of the temperature dependencies of the gas-induced response and the response time constants. The complex shape of the obtained dynamic characteristics was analyzed using Fourier transform. It has been shown that the resultant Fourier images can be used as sources of a large number of information parameters, which are suitable for increasing the selectivity of the sensor system operating in the considered mode of operation. It has been demonstrated that the selection of the amplitudes of the first three harmonics of Fourier images as information parameters allows the unambiguous identification of the type of the analyzed gas.

1. Introduction

Many technological processes in machine industry, heat-power industry and production of functional materials create a risk of getting chemically harmful substances or combustible industrial gases in the air of the working areas. The risk of these events is usually reduced by gas alarm systems and gas analyzers based on semiconductor gas sensors [1, 2]. The main advantages of semiconductor sensors over other types of sensors are simple design, low cost, high reliability, speed, excellent response as well as high stability and durability [3]. At the same time the main disadvantage of semiconductor gas sensors is low selectivity, or in other words the insufficient ability of such systems to recognize the type of analyzed gas [3]. Efforts of the last few years have allowed to develop an approach to increase the selectivity of gas sensor systems [4–12]. The essence of this approach is the increase in the number of information parameters of the sensor system, whereby it is possible to determine the type of the actuating gas by analyzing the combination of these parameters.

Receiving a large number of information parameters is possible when implementing:

- multi-sensor array of gas-sensitive films of various properties [4–7];
- multi-sensor array of identical films function at different temperatures [9];
- single-sensor systems operating with a stepwise supply of the analyzed gas-air mixture [10];
- single-sensor systems in which the sensitive film operates at a time-varying temperature profiles (exponential, linear, sinusoidal) [11, 12].
The advantage of the last of the presented approaches is the greatest simplicity of the design due to the use of a minimum number of gas sensitive films and the absence of necessity to implement the gas mixture supply system.

Investigation of the characteristics of the gas sensitivity of the thin oxide films at the time-varying temperature profiles shows the perspective of the use of the sinusoidal profile [12]. In this approach, it is possible to use Fourier analysis having low computational costs to obtain a large number of information parameters dependent on the type of the analyzed gas, but independent of its concentration. As shown below, the amplitudes of higher harmonics of Fourier images of the resistance time dependencies may be used as such information parameters. It is also assumed that the origin of that higher harmonics is the non-linearity of temperature and time dependencies of the response.

Among the various materials of the sensors for semiconductor gas sensors, the system of transition metal oxides with In$_2$O$_3$–Ga$_2$O$_3$ composition has attracted attention in recent years due to the promising characteristics of gas sensitivity [13]. The highest values of the gas response, the lowest working temperatures and the highest response speed, have the films of 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition, as shown in [13] for films obtained by pulsed laser deposition.

2. Problem statement

Thus, the purpose of this work is to investigate the possibility of increasing the selectivity of sensor systems based on thin films of 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition, functioning at sinusoidal-varying temperature. Its objectives:

- investigation of temperature and time dependencies of resistance at sinusoidal-varying temperature and under exposure of one of the following gases: ethanol, acetone, ammonia, propane-butane;
- determination of possible information parameters obtained by applying Fourier transform to experimental time dependencies of gas-induced resistance response at given temperature profile;
- investigation of the possibility to develop a sensor system featuring high selectivity to a number of industrial gases operating at a sinusoidal temperature profile.

3. Experimental

The 0.2 μm thin films with 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition were produced by pulsed laser deposition from powder targets in vacuum chamber with $10^{-2}$ Pa residual air pressure at 400 °C substrate temperature, 637.0 J·cm$^2$ laser beam energy density, followed by annealing at 800 °C for 5 minutes to stabilize their characteristics. A 0.5 mm thick glass ceramic was used as substrates.

The gas-sensitive properties of these films were studied by applying a sinusoidal-varying supply voltage to a flat resistive heater. The voltage profile was generated as the sum of the reference direct voltage from the stabilized voltage source B5-8 and the sinusoidal voltage from the signal generator G6-31. The amplitude of the alternating voltage component in all studies was 5 V. The constant component of the voltage was chosen such that the baseline temperatures on the surface of the film were $T_0 = 400 \, ^\circ\text{C}$, 450 °C, 500 °C, 550 °C, or 600 °C. The temperature on the surface of the gas-sensitive film was measured with a miniature chromel-copel thermocouple. These temperatures were chosen on the basis of typical operating temperatures of thin films of the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ composition. At these temperatures, substantial gas response values are obtained, but no self-ignition of the gas-air mixtures containing the test gases occurs. The minimum self-ignition temperatures are at 500° C. but self-ignition at such temperatures occurs at significant concentrations of combustible gases. As practice shows, at the test gases concentrations of about 25 ppm the operation of the miniature gas sensor does not produce a self-ignition hazard up to the temperatures of the working area of 750 °C.

Time and temperature dependencies of resistance were studied by feeding ethanol, acetone, ammonia or a propane-butane mixture with concentrations of 5 or 25 ppm into a closed experimental chamber. Frequency change rates $f = 50$ mHz, 20 mHz, 10 mHz, 5 mHz and 2 mHz were used.
Time relationships were obtained with a step $(1.00 \pm 0.04) \, \text{c}$, $\epsilon = 4.0\%$; temperature measurement was carried out with accuracy $\pm 0.1 \, ^\circ \text{C}$, $\epsilon = 0.15$–$0.25\%$, supply voltage – with accuracy $\pm 0.1 \, \text{V}$, $\epsilon = 0.15$–$0.28\%$; resistance – with accuracy $\pm 0.1 \, \text{kOhm}$, $\epsilon = 0.20$–$0.28\%$. The relative humidity in all measurements was $(50.0 \pm 3.5\%)$, $\epsilon = 7.0\%$.

The least squares and fast Fourier transform software implementations provided by the OriginPro2015 software were used to process the experimental data.

4. Theory

The mechanism of operation of semiconductor gas sensors was described in a variety of works, such as [3]. The principle of their action consists in changing the resistance of the thin polycrystalline oxide film when the composition of the gaseous medium acting on the surface changing. Microscopic processes resulting in a change in the resistance of a given film include processes of the adsorption and desorption of the oxygen, water vapor molecules, molecules of analyzed gas and products of catalytic oxidation of molecules of analysed combustible gas on the surface of oxide film.

The macroscopic resistance of the gas-sensitive film in the case of the most common mode of above-barrier conductivity depends on the values of the potential barriers between the crystallites, which arise due to the presence of chemosorbed oxygen on their surface. The concentration of oxygen particles chemisorbed on surface of crystallites is determined by dynamic equilibrium between temperature-activated processes of its adsorption, desorption and consumption for catalytic oxidation of molecules of reducing gas whose concentration is to be measured. Thus, when the concentration of the combustible gas is changed, the equilibrium oxygen filling of the crystallite surface changes, which results in a change of the value of potential barriers between the crystallites and finally, in the change of the macroscopic measured parameter – the resistance of the film.

At that, the selectivity of the semiconductor gas sensor is fundamentally small, since any reducing gas has a qualitatively similar effect on the film. The distinction of the different reducing gases is possible by using an array of sensors having unequal parameters defining the interaction with each of the gases:

- working temperature of oxide film,
- chemical composition of the film,
- presence and properties of surface catalysts that change the kinetics of interaction with gases,
- presence and properties of active or passive filtering coatings that alter the availability of the film surface for different gases.

Another way to achieve high selectivity for semiconductor gas sensors is the use of a single gas-sensitive film whose operating parameters are subject to changes in time:

- dynamically changing over a specified profile temperature of the film,
- dynamically and controllably varying concentration of analyzed gas.

When using any method of constructing a sensor system designed to recognize the type of gas to be analyzed, the following method of processing the output signals of such a system is applied:

- selection of a set of information parameters of signals with which it is possible to unambiguously identify analyzed gas,
- creation of discrete “images” of different gases – sets of information parameters corresponding to the given gas – in the “learning” mode of the sensor system,
- in the mode of “direct operation” – searching for coincidence of current image with known records obtained in training mode and determination of the type of analyzed gas.

In the development of gas-sensitive systems with high selectivity or designed for analysis of the composition of gas-air mixtures, it is possible to use various information parameters [13], but there remains an actual question about the selection of an algorithm which makes it possible to minimize the cost of the sensor system and the computational costs of the gas identification procedure, maximize the number of gases to be identified and the performance of the system. The method of using a single sensor operating at a sinusoidal-varying temperature has advantages of simple analysis of the set of
information parameters, low cost for its implementation, high degree of difference of gases from each other.

5. Results and discussion
When a sinusoidal-varying voltage is applied to the heater, the temperature on the surface of the gas-sensitive film also varies according to the harmonic law due to linearity of the heat transfer process through the substrate. Also there is some phase shift between time dependencies of voltage and temperature due to heat transfer inertia. The time shift value is characterized by a time constant which is equal 10 s for the test sample. This value was obtained by testing time dependencies of temperature when rectangular voltage pulses are supplied to the heater. The influence of delay can be neglected at the frequency of change of the supply voltage \( F = 2 \text{ mHz} \).

The time dependencies of the resistance of the gas-sensitive layer deviate from the harmonic law due to non-linearity of temperature dependence of its resistance. The non-linearity of these characteristics may be conveniently studied in the coordinates \( R(T) \). Examples of these relationships for frequencies of 50 mHz, 20 mHz, 10 mHz, 5 mHz and 2 mHz in the case of reference temperature \( T_0 = 450 ^\circ \text{C} \) and acetone as the test gas are presented in figure 1. It can be seen from these experimental dependencies that when the frequency is increased above 2 mHz, the amplitude of the resistance change is significantly reduced, which makes it difficult to analyze the data. The reason for decreasing the amplitude of resistance change is the presence of the inertia in the gas response processes. Previous studies of time dependencies of resistance when feeding rectangular voltage pulses to a heater show, that the time constants of these processes in the case of acetone at temperatures near 450 °C have a value of 78 s and exponentially decrease with temperature. The time constants of the gas response for the other test gases behave similarly having the difference in absolute values and activation energies on the temperature dependencies.

![Figure 1](image1.png)

**Figure 1.** Temperature dependencies of resistance at \( T_0 = 450 ^\circ \text{C} \), \( F = 50 \text{ mHz}, 20 \text{ mHz}, 10 \text{ mHz}, 5 \text{ mHz}, 2 \text{ mHz}, \) test gas – acetone (5 ppm).

The figure 2 shows the temperature dependencies of resistance at a sinusoidal-varying temperature at \( F = 2 \text{ mHz} \) and several reference temperatures \( T_0 = 400 ^\circ \text{C}, 450 ^\circ \text{C}, 500 ^\circ \text{C}, 550 ^\circ \text{C} \) and 600 °C in the case of acetone as a test gas. The dependencies for other studied gases are similar. It can be seen from the above relationships that at some temperature a maximum of the gas-induced resistance response for a given gas is reached. The previous studies show that for the investigated sample, the temperatures of the response maximum for different gases are:
- ethanol vapour – 530 °C;
- Acetone vapor – 528 °C;
- Ammonia vapors – 586 °C;
- Propane-butane mixture – 596 °C.

These results make it possible to determine the reference temperature, at which temperature dependence of resistance of the 50%In_2O_3-50%Ga_2O_3 film at sinusoidal-varying temperature for the set of investigated gases will have the greatest differences. This temperature was calculated as a mathematical expectation for the set of temperatures of the maximum resistance response. The obtained value of the optimal temperature is 560 °C.
Figure 2. Temperature dependencies of resistance at $F = 2 \text{ mHz}$, $T_0 = 400 ^\circ \text{C}$, $450 ^\circ \text{C}$, $500 ^\circ \text{C}$, $550 ^\circ \text{C}$, $600 ^\circ \text{C}$, test gas – acetone (5 ppm).

Figure 3 demonstrates the temperature dependencies of the resistance at a sinusoidal-varying temperature at $F = 2 \text{ mHz}$ and reference temperature $T_0 = 560 ^\circ \text{C}$ in the case of ethanol, acetone, ammonia or propane-butane mixture supply into the air of the experimental chamber. These dependencies have noticeable differences in the cases of different gases, which makes it possible to develop a highly selective gas-sensitive system based on single $50\% \text{In}_2\text{O}_3-50\% \text{Ga}_2\text{O}_3$ film, operating at sinusoidal-varying temperature near reference temperature $T_0 = 560 ^\circ \text{C}$. Possible information parameters may be:

- the temperature at which the twist of the hysteresis loop is observed – corresponds to the temperature of the maximum response,
- the ratio of the areas of the hysteresis to the left and to the right of the twist – is dependent on the temperature of the maximum of the response, on the response time constant and the concentration of the investigated gas,
- the total area of the hysteresis loop – depends on the time constants of the response, the concentration of the investigated gas.

Figure 3. Temperature dependencies of resistance at $F = 2 \text{ mHz}$, $T_0 = 560 ^\circ \text{C}$, test gases – Ethanol, Acetone, Ammonia or Propane-butane (25 ppm).

However, the above information parameters are not convenient. They weakly characterize the type of gas to be analyzed, strongly depend on its concentration and require substantial computational costs to be determined. Paper [12] shows that Fourier transform can be used for processing signals of gas sensors having harmonic law in their basis, but deviating from it due to the presence of non-linear distortions. The Fourier spectrum contain information about non-linear processes which influence the
shape of the resultant time dependence of the response. This can be used to identify the type of gas acting on a gas sensor operating at a sinusoidal-varying temperature [12]. In addition, the use of a Fast Fourier transform algorithm makes it possible to significantly reduce the computational costs for processing the signals of such sensors.

Thus, a large number of information parameters were obtained, non-dependent on the concentration of the gas under investigation, by applying Fourier transform to time dependencies of resistance at a sinusoidal-varying temperature. Examples of the obtained frequency dependencies of the imaginary part of the Fourier transform applied to the dependencies given in figure 3 are presented in figure 4. The imaginary part of the Fourier images is more preferred for analysis since the study shows, that real part does not contain noticeable peaks corresponding to higher harmonics. The values of normalized peak intensities obtained from the given dependencies at frequencies of 2 mHz, 4 mHz and 6 mHz are presented in Table 1. The normalization was made by the maximum value of peak amplitude.

![Figure 4](image_url)

**Figure 4.** Imaginary parts of Fourier-images. Experimental parameters: $F = 2 \text{ mHz}, T_0 = 560 °C$, test gases – Ethanol, Acetone, Ammonia or Propane-butane (25 ppm).

The dependencies presented in figure 4 have a number of features, which enables the identification of the type of analyzed gas. The dependencies for the cases of ethanol and acetone have a characteristic peak with a negative amplitude at a frequency of 2 mHz, not observed for ammonia and propane-butane. The dependence for ammonia has a peak at a frequency of 6 mHz which distinguishes it from other dependencies. The dependence for propane-butane mixture is characterized by a broad peak near 0 mHz. The difference in the dependencies for ethanol and acetone can be seen in the difference in peak heights at frequencies of 4 mHz and 6 mHz. For ethanol, the amplitude of the first peak is less than the amplitude of the second peak and for acetone vice versa. Thus the data presented in table 1 show that the selection of the amplitude of the two first harmonics as information parameters makes it possible to definitely identify the type of analyzed gas. The computational complexity of obtaining these parameters is not high.

| Table 1. Amplitudes of peaks of imaginary parts of Fourier images |
|---------------------|----------------|----------------|-----------------|----------------|
| $F$, mHz | Ethanol | Acetone | Ammonia | LPG |
| Normalized amplitude | -0.805 | -0.898 | -0.743 | -0.589 |
| 2 | 1.067 | 0.921 | 0.129 | 0.812 |
| 4 | 0.712 | 0.755 | 1.297 | 0.935 |

The results presented in table 1 demonstrate the possibility of using a Fourier transform to obtain information parameters with which it is possible to definitely identify the type of analyzed gas using a sensor system based on a single sensor operating in a thermocycling mode at a sinusoidal-varying temperature. In order to develop such a system, it is possible to use the common approach that consists in forming a set of “images” of the test gases in the “learning” mode and the following comparison of
the current values of the information parameters with the available “images” in the “direct” mode of operation of the sensing system. The advantage of using the amplitudes of the first three harmonics of Fourier-images as the information parameters of is the small volume of the processed and stored information and low computational costs for identification of gas type.

6. Conclusion
This results presented reveal that the time dependence of the resistance for the 50%In$_2$O$_3$–50%Ga$_2$O$_3$ thin film, which are functioning at a sinusoidal-varying temperature, deviate from the harmonic law, the reason of which is considered to be the non-linearity of the temperature and dynamic response curves. The complex shape of the received time dependencies can be analyzed by applying Fourier transform to them. The resultant Fourier images can be used as sources of a large number of information parameters, which are usable for increasing the selectivity of the sensor system operating in the mode under consideration. The selection of the amplitudes of the first three harmonics of the Fourier images as information parameters makes it possible to definitely identify the type of the analysed gas. Application of proposed information parameters enables developing a sensor system with high selectivity to a number of important industrial gases, at low computational cost required to identify the type of gas.

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