Determination of chlorine concentration using single temperature modulated semiconductor gas sensor

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ABSTRACT

A periodic temperature modulation using sinusoidal heater voltage was applied to a commercial SnO₂ semiconductor gas sensor. Resulting resistance response of the sensor was analyzed using a feature extraction method based on Fast Fourier Transformation (FFT). The amplitudes of the higher harmonics of the FFT from the dynamic nonlinear responses of measured gas were further utilized as an input for Artificial Neural Network (ANN). Determination of the concentration of chlorine was performed. Moreover, this work evaluates the sensor performance upon sinusoidal temperature modulation.

Keywords: gas sensor, metal oxide, temperature modulation, feature extraction, neural networks

1. INTRODUCTION

Environmental pollution is one of the most serious problems with which humanity is in contact today. There is continues need to design reliable devices for the detection of the volatile compounds present in the air. Today, sophisticated equipment is available on the market allowing precise measurements of the samples, e.g. mass spectrometers or gas chromatographs. Those two groups of devices and many others allow performing continuous monitoring, but despite their high accuracy, they have some drawbacks. They are referred to very high price, expensive operation costs and the need to operate only in the stationary condition. The ever-increasing air pollution forces the need for the continuous monitoring. Therefore, the utilization of semiconductor gas sensors is one of the alternative solutions for the detection and determination of the composition of the volatile gas mixtures. Metal oxide semiconductor (MOS) gas sensors are actually one of the most popular groups of gas sensors, widely used in domestic safety, air quality control, automotive, appliance control, industrial safety and other fields. They feature a relatively low price and a quite long life time. Consequently, they have attracted the attention of many users due to large number of possible applications and a great variety of detectable gases. Moreover, the advantages of semiconductor gas sensors are the simplicity of use, uncomplicated design, small size and mechanical strength. On the contrary, the main disadvantages of these sensors concern their lack of long-term stability, high energy consumption and low sensitivity and selectivity [1].

Although gas sensors have been developed to achieve high selectivity for a particular chemical species, their sensing properties are limited, due to the fact that they usually also respond to some interfering molecules coexisting in an ambient gas (e.g. humidity or oxygen concentration) [2-4]. Therefore, the most semiconductor gas sensors have low selectivity and are not able to detect a single chemical species in a mixture. This fact is related to the oxidation reactions taking place on a sensing layer. These reactions do occur not only with a specific gas presented in a gaseous mixture, but with every gaseous component of the mixture. Another problem is that in the most cases different gases often produce very similar sensors responses.

Hence, to overcome those drawbacks several approaches have been studied, including certain strategies in material science (doping, catalysts, filters) and the modification and optimization of the structure of the sensor. Furthermore, methods for improving the sensing parameters of MOS type sensors were based also on the application of signal processing algorithms for feature extraction of the data and the use of sensor arrays [5, 6]. Promising results over the years were obtained using the analysis of transient sensor responses to changes in analyte concentration or sensor temperature.

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Of the last group of techniques, the most commonly used method includes controlling the temperature of the semiconductor surface in order to gain more information from sensors resistance response. In 1973 Eicker patented a method of carbon monoxide and methane detection using temperature variation of metal oxide semiconductor [7]. This technique, called temperature modulation, was developed for improving the selectivity of gas sensors. It was proven that both, sensitivity characteristics of semiconductor gas sensor and the kinetics of adsorption reactions on the sensing surface, are affected by the operating temperature [8, 9]. Later, among others, it was reported that using commercial Taguchi Gas Sensors, the amplitudes of the higher harmonics of the DFT (Discrete Fourier Transform) response exhibit characteristic changes depending on the chemical structure and concentration of gases, which enable the distinction among concentration of gases [3,10]. Recently it was shown that gas sensor working under a closed loop control resulted in a reduced response time. It was obtained by periodically monitoring the resistivity of the sensing layer and generating temperature waveforms to enforce constant resistivity of sensing layer [11].

Among the variety of metal oxides that are used, tin oxide (SnO$_2$) is the most widely applied in semiconductor gas sensors. This is due to its fast response time and high surface tendency for gas adsorption. The phenomenon of metal oxide sensor response is based on the mechanism of the chemical reactions, which take place on the surface of a semiconductor. Up to 400°C the reaction of oxygen adsorption occurs on the surface of the metal oxide in the presence of clean air. Adsorbed oxygen causes withdrawing of the free electrons inside the metal oxide, due to its high electron affinity. That leads to a foundation of a potential barrier at the grain boundaries of metal oxide crystals. Therefore the electron flow through the conjoined parts (grain boundary) is limited by this potential barrier, which causes high resistance. In the situation when sensor is exposed to e. g. reducing gas, the reaction of oxidation of the adsorbed oxygen with gas takes place. Consequently, this leads to reduction of the height of the potential barrier at the grain boundaries, due to decreased density of adsorbed oxygen on the surface of metal oxide. Hence electrons can flow freely through the reduced potential barrier and the resistance of the sensor decreases accordingly [12]. Therefore, the change of resistance (or conductance) of MOS-type gas sensor can lead to detection of the gas concentration. The SnO$_2$ gas sensor electrical conductance $G(T)$ can be expressed as [10]

$$G(T) = G_0 \exp\left(\frac{-e V_s}{kT}\right)$$

where $G_0$ is the pre-exponential factor, $k$ represents the Boltzmann’s constant, $V_s$ denotes the surface barrier height which depends on the surface concentration of ionosorbed oxygen, the semiconductor permittivity and the volumetric density of an electron density. Surface barrier height $V_s$ is directly related and depends on the rate of reactions taking place on the surface adsorption site of the sensing layer. The reaction rate constant $k_r$ is dependent on the temperature according to the Arrhenius equation [12]

$$k_r = F \exp\left(\frac{-E}{RT}\right)$$

where $F$ denotes the pre-exponential factor, $E$ represents the activation energy and $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ is the ideal gas constant. Consequently, according to the Eq. (1), the conductance of a MOS-type gas sensor depends on the surface potential barrier height $V_s$ and the temperature of the sensor operation. Therefore, changing (modulating) the operating temperature of the MOS-type sensor affects the rate of the desorption and adsorption reactions (Eq. 2). That can provide more information from sensor response about the gas species. Moreover, more accurate detection and determination of the composition of atmosphere in the vicinity of the sensor is possible.

In this study, temperature modulation of a semiconductor gas sensor was performed. Measurement stand was designed and constructed. The responses of commercial Umwelt semiconductor gas sensor to different concentrations of chlorine were examined, under the application of a periodic temperature change. It was demonstrated, that the amplitudes of the higher harmonics of the fast Fourier transformed (FFT) sensor response exhibit changes, that are characteristic for concentration of target gas. Furthermore, it was also shown that using Artificial Neural Network it is possible to distinguish between different gas concentrations and achieve reliable prediction of the concentration using one sensor.
2. EXPERIMENTAL

2.1 Gas sensor

Single semiconductor gas sensor GGS 10331 produced by Umwelt Sensor Technik (UST) company was used in this study. GGS 10331 is made of an Al₂O₃ substrate with a structured Pt-film, consisting of heater channels and electrodes. The sensitive semiconductor layer is deposited on the substrate and separated from the heater. Sensor is in a TO39-housing with a stainless steel cap.

To perform the measurements the heater voltage is adjusted to control the operating temperature between specified values. Therefore in order to estimate the operation temperature range of gas sensor, the temperature of the Pt-heater had to be calculated. It was done basing on the equation from the sensor technical documentation. Equation allows calculating the temperature of the heater \( T_H \) is presented below (Eq. 3) [13]:

\[
T_H = \left( \frac{A}{2B} + \sqrt{\frac{A^2}{4B^2} - \frac{R_{H0} - U_H}{I_H I_H}} \right)
\]

where \( U_H \) and \( I_H \) are the voltage and the current input, \( R_{H0} \) denotes the heater resistance at 0°C, \( A \) and \( B \) stands for the linear and the quadratic coefficients, respectively.

Figure 1. Experimental apparatus for measuring the resistance response of a semiconductor gas sensor in a sensor chamber.

2.2 Measurement stand

A sensor chamber was designed to provide separate connections to excite the heater and to measure the response of the sensor. Gas flow was obtained using mass flow controllers (Brooks GF Series). One sensor – GGS 10331 was placed in the chamber. Figure 1 shows the experimental apparatus. A sinusoidal voltage with a frequency \( f = 0.025 \) Hz was generated using Arbitrary Power Supply Hameg 8143 and applied to the heater of the semiconductor sensor. The parameters of voltage signal were selected to modulate the temperature of the sensing layer from 300°C to 500°C during each period of 40 seconds. The resistance of the sensing layer was measured with a digital Multimeter Keithley 2400. The synthetic air and mixture containing target gas during the measurements were kept at a constant flow of 100 cm³/min. Exemplary results of sensor response in presence of different concentrations of chlorine and synthetic air are presented in Fig.2. The sensor response in the presence of synthetic air reaches a higher maximum resistance than in 10 ppm of Cl₂. However, the highest maximum resistance was obtained in 20 ppm of Cl₂, suggesting that competitive reactions are responsible for the sensing mechanism. In the reference atmosphere (synthetic air) oxygen adsorption occur on the sensing layer. Adsorbed oxygen withdraws the electrons from the semiconductor leading to increase of the resistance. When the metal oxide is in the presence of oxidizing gas (chlorine), the reactions involved are more complex. The chlorine reacts with ionsorbed oxygen, that results in forming gaseous oxygen, free electrons and chlorine ions.
causing decrease of the resistance. Besides that, chlorine alone also adsorbs and withdraws electrons from the sensing layer, which results in increase of the resistance. It is assumed that when sensor is exposed to 10 ppm of Cl₂, the reaction of chlorine adsorption have less impact on the resulting resistance. In the situation when sensor is in presence of higher concentration of target gas (20 ppm of Cl₂), the reaction of withdrawing electrons gain greater influence causing increase of the resistance.

![Resistances comparison](image)

**Figure 2.** Exemplary sensor resistance response of the sensor to synthetic air and chlorine in concentrations 10 and 20 ppm. Sampling frequency was set to 5 Hz. One modulation cycle was 200 samples.

### 2.3 Data acquisition

The sensor was heated with a sinusoidal voltage applied to the heater, which resulted in temperature modulating the heater from 300°C to 500°C. The sensor was exposed to specific concentration of target gas and thirty response cycles were collected when a quasi-stationary state was reached. Cleaning of the sensor chamber with synthetic air was performed after each gas mixture exposition. This was conducted until all air contaminants were cleaned from the sensor sensing surface and the response had reached again a quasi-stationary state. Depending on the concentration of target gas, the cleaning of the sensor chamber took from 40 to 100 minutes. Measurements were performed for different levels of target gas concentrations.

### 3. DATA ANALYSIS AND RESULTS

In the presented approach, the ANN was used to determine the concentration of target gas. Determination was performed on the features extracted using FFT, namely on basic and higher harmonics of resistance response of temperature modulated sensor. Measurements were conducted in the presence of synthetic air and volatile compound - chlorine, for different concentration levels.

#### 3.1 Feature extraction

The resistance responses of the gas sensor were successively stored in a PC. A frequency of the applied signal on the heater was \( f = 0.025 \) Hz, hence the duration of one modulation cycle was 40 seconds. The resistance sampling frequency was set to \( F_{\text{SAM}} = 5 \) Hz. Therefore, the resistance change over one temperature modulation period consisted of 200 samples. From each gas concentration of the measurement procedure thirty cycles were analyzed by the FFT, each cycle separately. This allowed to obtain thirty observations of the sensor for every gas concentrations. Each observation contained the dc value of sensor resistance, denoted as \( R_0 \), and amplitudes of the real \( \sum_{i=1}^{m} R_i \) and the imaginary
\[ \sum_{i=1}^{m} I_i \] harmonics (where \( m = 1, 2, \ldots, 8 \)). Additionally, the minimum and the maximum of the sensor resistance response cycle were used for analysis. The data set obtained for chlorine, contained 150 observations. That corresponded to 5, 10, 20, 30 and 40 ppm of that gas in a mixture. Additionally, a set of 60 observations from the measurement in synthetic air as a reference was analyzed. Therefore the final data set, marked as a features set, had the dimension of 19x210. The composition of the features set is showed below (\( N = 210 \)).

\[
\text{Features Set} = \begin{bmatrix}
R_{\theta_1} & R_{\theta_2} & \cdots & R_{\theta_{18}} & I_{1} & \cdots & I_{8} & \min_1 & \max_1 \\
R_{\theta_2} & R_{\theta_2} & \cdots & R_{\theta_{18}} & I_{2} & \cdots & I_{8} & \min_2 & \max_2 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
R_{\theta_{18}} & R_{\theta_{18}} & \cdots & R_{\theta_{18}} & I_{18} & \cdots & I_{8} & \min_{18} & \max_{18}
\end{bmatrix}
\] (4)

3.2 Neural network

For the purpose of determining the concentration of measured compound, the artificial neural network (ANN) was applied. Artificial neural networks belong to the group of machine learning methods and are widely utilized in numerous applications, including gas-detecting problems [14, 15]. ANNs are utilized for two kinds of analyses, namely the qualification (recognizing the kind of measured compound) and quantification (estimation of the concentration of measured gas). In this work, the ANN was employed for the prediction of the concentration of chlorine. To perform this task, the training and test datasets had to be created. For the training of the network, 138 samples were utilized. The validation of the performance of the network was done with the 72 samples. All calculations were performed using MATLAB with Neural Network Toolbox. In the training stage, the Levenberg-Marquardt algorithm was used, and for examination of network efficiency, the root mean squared error was calculated. The architecture of the network was simple, with only one hidden layer with 10 neurons in it.

The results of determining concentration of chlorine are presented in Figure 3. The very good fitting was achieved with the root mean squared error of 0.12 ppm. The results are promising, however, they will be validated on consecutive measurements to investigate the robustness of the method. The future work is focused on the optimization of the features selection methods and employment of other methods for qualification and quantification of the results.

![Figure 3. The ANN results for the prediction of chlorine concentration.](http://proceedings.spiedigitallibrary.org/ on 11/21/2016 Terms of Use: http://spiedigitallibrary.org/ss/termsofuse.aspx)
4. CONCLUSION

In the present study, it was demonstrated that single sensor resistance response can be an important source of information for gas recognition. Responses of a single sensor to sample gas under the technique of temperature modulation changed characteristically. Therefore, the introduction of this technique provides useful information for the analysis of a sample gas. Additionally, it was shown that characteristic differences in sensors response to chlorine, are reflected by the higher harmonics of FFT. Moreover, the results of determining the concentration of target gas using artificial neural networks and single gas sensor, indicate that the use of neural networks for the analysis of Fourier transformed responses may be promising.

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REFERENCES