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A logarithmic multi-parameter model using gas sensor main and cross sensitivities to estimate gas concentrations in a gas mixture for SnO_2 gas sensors

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Abstract

In a metal-oxide semiconductor gas sensor, the sensitivity of the metal-oxide resistance to concentrations of reducing gases in the surrounding atmosphere is known to be related to adsorption and desorption of gas on the redox reactions between the gas and oxygen. Changes in the electric conductance due to these reactions were measured for tin dioxide semiconductor gas sensors. In this study, we propose a model of gas sensor responding behaviour using a relationship between sensor conductance and gas concentrations in a mixture. A least-squares method fit of measured data was applied to determining the values of coefficients. The proposed method uses main and cross sensitivities the describing the response of a gas sensor. Applying two-gas sensors which show different characteristics, the gas concentrations in a gas mixture can be evaluated. The proposed method has been applied to the estimation of gas concentrations in a mixture of hydrogen–methane, carbon monoxide–methane, propane–methane, ethanol–ammonia and propane–ammonia. The concentrations determined from the response curves were accurate within a 5% error. The results indicate that the proposed model is feasible for recognition of calculated estimations in a gas mixture. This paper shows a significant result through utilization of the proposed model of gas sensor response.

Keywords: Main sensitivity; Cross sensitivity; Gas concentration; SnO_2 gas sensor; Gas mixture; Modelling

1. Introduction

Metal-oxide semiconductor gas sensors are suitable for the detection of oxidizing and reducing gases, since they react to their presence with a measurable change of their electrical conductivity [1–3]. Among the used semiconductor layers heated SnO_2-layers are best tested and furthest common [2]. However, a single semiconductor gas sensor is only conditionally suitable for the selective proof of certain gasses, since it exhibits cross sensitivities opposite to practically all oxidizing and reducing gases. These sensors do not have usually high gas selectivity, and its recognition characteristics are largely depending on changes in the environment, such as temperature and humidity [3]. Furthermore, metal-oxide gas sensors are non-linear systems which thereby cause considerable measurement errors. To the correction of these measuring errors, heuristic–mathematical or physical–chemical models can be used. The coefficients of these models must be determined with often significant effort by calibration and adaptation of the models to the calibrating data. For the determination of each parameter, value at least a measured value under exactly defined conditions must be acquired. The reaction of gas sensors to the measured gasses can be described by different models, which mostly indicate a power-law for the interrelation between partial pressure and sensor conductance. For the metal-oxide gas sensor, Clifford and Tuma [4,5] attempted to derive from experimental results an empirical formula which described the sensor resistance as a function of several gas concentrations. The model of Clifford was developed for application to sensors of the type Taguchi (TGS) [6]. Madou and Morrison [7] employed extensive theoretical considerations concerning the influence of oxygen and reducing gases on the sensor

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conductivity. At operating temperature, the resistance of semiconductor gas sensors follows a power-law dependence on the gas concentration in the environment air [4,7,8]. Hirobayashi et al. [9] proposed a logarithmic model for detecting the individual components of gas mixtures, demonstrating good approximation results for measured gas concentrations from 100 to 1000 ppm. Latterly, artificial neural network [10–13] and other pattern recognition methods [14] are employed with some success. Faglia et al. [15] used a neural network, to which information about the current humidity is supplied by separate measurement. Using an array of semiconductor gas sensors, they attempted to eliminate the humidity influence on the measurements. However, these methods require many gas concentration measurements for each object gas, which requires significant time and effort. Usually, gas sensor responses are obtained experimentally for each pure gas forming a mixture gas, and mixture gas concentrations are determined accurately using the sensor response equation.

The object of the present study is to test and expand the formulation and verification of a logarithmic model in detail and describe an accurate estimation procedure for five kinds of gas mixtures using our proposed model. The model is particularly suitable for describing the low concentration range from 0.00001 to 10 ppm. This is important for application scenarios with low gas concentrations (e.g. ozone or carbon monoxide). Our logarithmic model delivers also good accuracy for the complete gas concentration range from 0 to 1000 ppm. The results show that accurate estimation is feasible using this model through detailed exploration of sensor output resistance characteristics.

2. A model of sensor characteristic curve

A SnO_2 gas sensor is reliable for detecting combustible gases. The sensors GGS1470 and GGS4470, herein after referred to as sensor 1 and sensor 2, respectively, are reliable and stable, but have no gas selectivity and show cross sensitivities to several gases; i.e. they sense different gases at random. Both sensors GGS XXX0 are commercial SnO_2-thick film gas sensors of the company UST. They consist of an Al_2O_3-carrier substrate with a structured platinum layer on the front and back side for the contacts and the heater. As an electrode structure a standard structure (SS) with two wide electrodes or an interdigital structure (IDS) is used. The sensitive layer (SnO_2) is deposited via the screen printing technique on the Pt-contacts. The used sensors differ in their preparation of the sensitive layer, which leads to different main and cross sensitivities to the gases to be detected; for example, the sensor GGG1470 has main sensitivity to CH_4 and the sensor GGS4470 to NH_3. The gas sensors used in the present study were sensor 1 and sensor 2. In many applications, these two types of sensors are widely used due to their advantages such as small size, light weight and high sensitivity. The sensor 1 is cross sensitive to hydrogen (H_2), propane (C_3H_8) and carbon monoxide (CO); this sensor also has a main sensitivity to methane (CH_4) and it is especially suitable for the leakage detection of combustible gases. The sensor 2 is mainly sensitive to ammonia (NH_3) and cross sensitive to ethanol (C_2H_5OH), propane (C_3H_8) and other hazardous gases, and is often used in gas leakage alarms. The following combinations of testing mixture gases were chosen: (1) $CH_4 + H_2$, (2) $CH_4 + C_3H_8$, (3) $CH_4 + CO$, (4) $NH_3 + C_3H_8$, and (5) $NH_3 + C_2H_5OH$.

Table 1
Lower explosion limit (LEL) for the used gases

	C_2H_5OH	C_3H_8	CH_4	CO	H_2	NH_3
LEL (vol%)	3.3	2	5	10	17	4

In Table 1, the lower explosion limit (LEL) is shown for each gas we used. By different limit ranges of each gas, one could have obtained better results, but the analysis and modelling of the small concentration range in the close proximity to 0 ppm were the centre of attention.

Typically, semiconductor gas sensors react to different gases. Therefore, as a sensor signal the relative conductivity $S(c)$ is used [16,17]. It corresponds to the resistance value of the sensor under gas influence related to the sensor resistance in pure atmosphere.

$$S(c) = \frac{R_g(c)}{R_0} = \frac{G_0}{G_g(c)}, \tag{1}$$

where G_0 is the baseline conductance (i.e. in the presence of clean air) and G_g is the steady-state conductance of the sensor in the presence of a given gas or gas mixture. As previously mentioned, the function (1) applies only at constant temperature T of the sensor surface.

It is well known that the electrical resistance R_g (Ω) of a gas sensor decreases as the gas concentration c (ppm) increases. Therefore, the sensor relative conductivity can be expressed as:

$$S(c) = a - b\ \ln(c + 0.5), \tag{2}$$

where a and b are the coefficients and the constant 0.5 is used for the defining of the sensor response at the gas concentration of 0 ppm (i.e. in the presence of clean air). The Eq. (2) shows that the sensor resistance or relative conductivity is proportional to the logarithm of the concentration c, and is satisfied when the temperature and relative humidity of the environment are fixed. The condition for maximum value of sensor resistance is the sensor response at 0 ppm measurement in clean air and that of minimum value of sensor resistance is the lower limit of sensor response at high gas concentrations.

Gas sensor relative conductivity is shown in Fig. 1(a and b) as a function of the gas concentration for each object gas. The gas sensors 1 and 2 were measured to individual gas. For sensor 1 each object gas was varied from 1 to 1000 ppm (measured four times at 1, 10, 100, 1000 ppm) and for sensor 2 each gas was varied from 1 to 1000 ppm (measured seven times at 1, 3, 10, 30, 100, 300 and 1000 ppm). We took three measurements for each gas concentration, the mean value of which was used in the analysis. The solid line approximations connecting the experimental data were obtained from Eq. (2), using a least-squares method.