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THE METHOD OF THE SENSITIVITY COMPARISON OF THE TIN DIOXIDE GAS SENSOR IN PERIODIC STEADY STATE

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Abstract. The formulas for the time dependency of the electrical conductivity of the sensor in thermal periodic steady state in the clean air atmosphere were derived herein. The created model of the sensor was experimentally verified and enables to compare the sensitivity to the tested substance at the frequencies at which the tests were carried out. The experiments were carried out with the sensors MQR 1003, SP 11, and TGS813. The sensors were tested in the clean air atmosphere and subsequently in the presence of ethanol, acetone and toluene vapour in the air at three different frequencies.

Keywords

Semiconductor gas sensor, temperature modulation, thermal cycling, thermal inertia, tin dioxide.

1. Introduction

Sensors are often operated in periodic time variable heating regimes, because of better detection properties compared to the constant heating regime [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11] and [12]. The overview of used types of time dependent heating of the sensor can be found in [13]. The theoretical models of the sensor response at the thermal modulation were presented in [14], [15], [16], [17], [18] and [19]. But in these works thermal inertia properties of the sensor were not considered. This is carried out herein. A heating system of the sensor has thermal inertia properties and that is why the detection properties of the sensor are dependent on the frequency of the heating voltage as well. The simple model of the behaviour of the sensor described herein can help to decide if the sensor is more or less sensitive to the given compound at given frequency.

2. Experiments

The commercial sensors of type MQR 1003, SP 11, and TGS813 were operated in the clean air of 31 % relative humidity and then in the vapour of the single compound of concentration 100 ppm in the clean air. Ethanol, acetone, and toluene were used in the experiments. The sensor response, which is the electrical conductivity of the detection layer, was sensed in periodic steady state. The heating voltage was realized by a function in the following way:

\[ U(t) = \sqrt{U_0 + U_A \sin(\omega t)}, \]

\[ U_0 = \frac{U_M^2 + U_m^2}{2}, \quad U_A = \frac{U_M^2 - U_m^2}{2}, \]

where \( t \) is the time, \( \omega \) is the angular frequency, \( U_M \) is the maximum value of heating voltage and \( U_m \) is the minimum value of the heating voltage. For the experiments \( U_M = 5 \text{ V}, U_m = 2 \text{ V} \). The response of the sensor was sampled in 32 points in every period of the heating voltage. The sampling rate \( t_s \) was chosen by experimental experience \( t_s = 1000 \text{ ms}, t_s = 500 \text{ ms} \) and \( t_s = 200 \text{ ms} \). Theses values are related to the frequencies of the sine component of the heating voltage \( f = 0.0312 \text{ Hz}, f = 0.0625 \text{ Hz}, f = 0.156 \text{ Hz} \), respectively.

3. Theory

A sensor consists of a heating system made of a heating resistance conductor covered by a ceramic insulator layer. The ceramic layer is covered by a metal oxide layer on which a pair of measuring electrodes is placed.
to measure the electrical conductivity of the metal oxide layer. The conductor is heated by an electrical voltage and heat penetrates through the ceramic layer into the detection layer. A gas detection does not occur until a specific temperature of the detection layer is reached, which is manifested by a change of the electrical conductivity of the detection layer. Each of these layers has its specific thermal properties. All these layers can be considered as one fictive layer of the thermal diffusivity \( a \) to simplify the mathematical solution. The heating voltage \( U \) generates the electrical power:

\[
P = \frac{U^2}{R},
\]

where \( P \) is the electrical active power, \( R \) is the electrical resistance of the heating system of the sensor and \( U \) is the electrical voltage. This power is converted according to Joule - Lenz law into heat, which heats up the detection layer of the sensor to the temperature \( \vartheta \),

The temperature can be designated as \( \vartheta \) and the electrical conductivity of the detection layer. The electrical conductivity is related to the temperature according to [20] by the following formula:

\[
\vartheta = \vartheta_0 + \vartheta_A \sin(\omega t),
\]

where \( \vartheta_0 \) is the constant component and \( \vartheta_A \) is the amplitude of the sine component of the driving temperature of the detection system of the sensor. Joule heat is conducted through the sensor and affects the temperature of the detection layer in the point \( x \) at the time \( t \).

This temperature can be designated as \( \vartheta(x,t) \). But we do not measure the temperature \( \vartheta(x,t) \) directly; we measure its manifestation, which is the electrical conductivity of the detection layer. The electrical conductivity of the detection layer is related to the temperature of the sensor to the temperature \( \vartheta \) according to the Fourier - Kirchhoff equation. Heat conduction inside the layer can be solved by the Fourier - Kirchhoff equation. Heat conduction is considered in the halfplane \( x > 0 \) in the direction of the axis \( x \):

\[
\frac{\partial^2}{\partial x^2} \vartheta + \frac{\partial}{\partial t} \vartheta = 0,
\]

where \( a \) is the thermal diffusivity of the material (m\(^2\)/s\(^{-1}\)), \( \vartheta \) is the temperature and \( t \) is the time. The heating system is supposed to be placed in the origin \( x = 0 \). We assume the initial condition in the following form to calculate the solution of Eq. (9) for sine component of Eq. (7):

\[
\vartheta(0, t) = \vartheta_A \sin \omega t.
\]

The periodic steady state solution is desired. The solution is supposed in the form as the product of two functions:

\[
\vartheta(x,t) = g(x) \cdot f(t), \quad \text{where} \quad f(t) = e^{j\omega t}.
\]

Substituting Eq. (11) into Eq. (9) we obtain:

\[
a \frac{\partial^2 g}{\partial x^2} e^{j\omega t} = \partial \vartheta (g e^{j\omega t}) = j\omega g e^{j\omega t}.
\]

Since the term \( \exp(j\omega t) \) cancels on both sides of Eq. (12), we obtain:

\[
a \frac{\partial^2 g}{\partial x^2} = j\omega g.
\]

We rewrite Eq. (13) into the form:

\[
\frac{d^2 g}{dx^2} - \frac{1}{a} j\omega g = 0.
\]

We find the solution with the use of the relevant characteristic equation:

\[
\lambda^2 - \frac{1}{a} j\omega = 0, \quad \Rightarrow \quad \lambda^2 = \frac{j\omega}{a}.
\]

The number \( \lambda \) equals:

\[
\lambda_{1/2} = \pm \sqrt{\frac{j\omega}{a}} = \pm (1 + j) \sqrt{\frac{\omega}{2a}} = \pm (1 + j) h.
\]

The solution of Eq. (13) equals:

\[
g(x) = K_1 e^{\lambda_1 x} + K_2 e^{\lambda_2 x}.
\]

Since \( \vartheta(x,t) < \infty \) is valid, we consider the solution only in the form:

\[
g(x) = K_1 e^{\lambda_1 x}, \quad \text{where} \quad \lambda_1 = -(1 + j) h \cdot
\]

Considering Eq. (11) the solution is written in the form:

\[
\vartheta(x,t) = g(x) \cdot f(t) = K_1 e^{-j(1+j)hx} e^{j\omega t},
\]

\[
\vartheta(x,t) = K_1 e^{-jhx} e^{j(-hx + \omega t)}.
\]
in the solution i.e. the imaginary part of Eq. (15). We can write:

\[ \vartheta(x, t) = K_1 e^{-hx} \sin(-hx + \omega t). \]  

(21)

Regarding Eq. (10) in case that Eq. (1) reaches non-zero temperature at the frequency \( \omega = \infty \). The sensor heated by the voltage described by Eq. (1) reaches non-zero temperature at the frequency \( \omega = \infty \). This is why Eq. (21) is to be modified by introducing the constant \( \vartheta_0 \). We obtain:

\[ \vartheta(x, t) = \vartheta_0 + A e^{-hx} \sin(-hx + \omega t). \]  

(23)

Equation (23) is also the solution of Eq. (9), because Eq. (23) contains only additional constant \( \vartheta_0 \) compared to Eq. (21). If the heating voltage is described by Eq. (1), the temperature of the detection layer in the place \( x \) at the time \( t \) is described by Eq. (23). With the use of Eq. (4) we obtain the conductivity of the detection layer in the following form:

\[ G(t) = G_0 e^{-\frac{hx}{\sqrt{f}}}, \quad \text{where} \]

\[ \vartheta(x, t) = \vartheta_0 + A e^{-hx} \sin(-hx + \omega t). \]  

(24)

The term \( hx \) can be modified with the use of Eq. (16) and Eq. (23) into the following form:

\[ hx = x \sqrt{\frac{\omega}{2a}} = x \sqrt{\frac{\pi f}{a}} = h_1 \sqrt{f}, \quad h_1 = x \sqrt{\frac{\pi}{a}}. \]  

(25)

The coefficient \( h_1 \) is dependent on the construction of the sensor, \( x \) is the thickness of the heated fictive layer. Then it is possible to write the electrical conductivity of the sensor in the following form:

\[ G(t) = e^{-\frac{hx}{\sqrt{f}}}, \quad \text{where} \]

\[ \vartheta(x, t) = \vartheta_0 + A e^{-hx} \sin(-hx + \omega t). \]  

(26)

Then the maxima of the heating voltage \( U(t) \) occur in the time \( t_i \). When considering following in Eq. (24):

\[ -h_1 \sqrt{f} + \omega t_j = (2n + 1) \frac{\pi}{2}, \quad n = 0, 1, 2, \ldots, \]  

(28)

then the maxima of the electrical conductivity \( G(t) \) occur at the time \( t_i \). It follows from Eq. (27) and Eq. (28), that the following equation must be satisfied for two matching maxima of \( U(t_i) \) and \( G(t_j) \):

\[ -h_1 \sqrt{f} + \omega t_j = \omega t_i. \]  

(29)

We express from Eq. (29):

\[ h_1 = \frac{\omega t_j - \omega t_i}{\sqrt{f}} = 2\pi \frac{\sqrt{f}(t_j - t_i)}{2\pi \Delta t \sqrt{f}}, \]  

(30)

where \( \Delta t \) is the time delay between the heating voltage and the electrical conductivity. \( \Delta t \) can be calculated from the experimental values of \( G(t) \) and \( U(t_i) \). Then \( h_1 \) can be calculated from Eq. (30).

We designate in Eq. (30) that:

\[ u = e^{-h_1 \sqrt{f}}. \]  

(31)

With the use of Eq. (30) and Eq. (31), the following expressions can be defined as:

\[ G_M = e^{-\frac{\pi h_1}{\sqrt{f}}}, \quad G_m = e^{-\frac{\pi h_1}{\sqrt{f}}}, \]  

(32)

where \( G_M \) represents the maximum and \( G_m \) represents the minimum value of the electrical conductivity. The constants \( A \) and \( B \) can be expressed from Eq. (32). Substituting \( u \) from Eq. (31) we obtain:

\[ A = \frac{1}{2} \left( \frac{1}{-\ln G_M} + \frac{1}{-\ln G_m} \right), \]  

(33)

\[ B = \frac{1}{2} \left( \frac{1}{-\ln G_M} + \frac{1}{-\ln G_m} \right) e^{h_1 \sqrt{f}}. \]  

(34)

Equation (33) and Eq. (34) enable to calculate \( A \) and \( B \) from the experimental values of \( G_M \) and \( G_m \). The coefficient \( h_1 \) is calculated by Eq. (30).

The percent deviation \( \delta \) was defined by the following formula:

\[ \delta = \frac{S_e - S_{a}}{S_{a}} \cdot 100, \]  

(35)

where \( S_e \) is the difference \( S_e = G_M - G_m \) taken from the experimental values and \( S_{a} \) is the difference \( S_{a} = G_M' - G_m' \), where \( G_M' \) and \( G_m' \) designate the theoretical values given by Eq. (26). The quantity \( S_e \) can also call the swing of the experimental sine component whereas \( S_{a} \) the swing of the theoretical sine component. The quantity \( \delta \) enables to compare magnitudes of the alternating sine components of the sensor response at given frequency.
4. Results

The values of the time difference $\Delta t$ were found in the experimental values of the measurement carried out in the clean air. It was found, that the maximum of $G$ is delayed behind the maximum of $U(t)$ as expected according to heat conduction theory. The value $h_1$ was calculated from Eq. (30). The overview of the calculated values is in Tab. 1.

<table>
<thead>
<tr>
<th>$f$ (Hz)</th>
<th>$\Delta t$ (s)</th>
<th>$h_1$ (m$^2$·s$^{-1}$·K$^{-1}$)</th>
<th>Average of $h_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0312</td>
<td>4.0</td>
<td>4.142</td>
<td></td>
</tr>
<tr>
<td>0.0625</td>
<td>3.0</td>
<td>4.712</td>
<td>4.209</td>
</tr>
<tr>
<td>0.156</td>
<td>2.4</td>
<td>3.474</td>
<td></td>
</tr>
<tr>
<td>0.208</td>
<td>1.0</td>
<td>1.110</td>
<td></td>
</tr>
<tr>
<td>0.0625</td>
<td>1.5</td>
<td>2.356</td>
<td>1.982</td>
</tr>
<tr>
<td>0.156</td>
<td>1.4</td>
<td>2.481</td>
<td></td>
</tr>
</tbody>
</table>

The constants $A$ and $B$ were calculated from Eq. (33) and Eq. (34) at the frequency $f = 0.0312$ Hz with the use of the average value of $h_1$ from Tab. 1. When two near maxima of $G_M$ or two near minima of $G_m$ occurred, their average value was used instead them. The calculated values are in Tab. 2.

<table>
<thead>
<tr>
<th>$G_M$ (µS)</th>
<th>$G_m$ (µS)</th>
<th>$A \cdot 10^{2}$ (1)</th>
<th>$B \cdot 10^{2}$ (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.12</td>
<td>0.93</td>
<td>7.668</td>
<td>2.159</td>
</tr>
<tr>
<td>9.82</td>
<td>0.30</td>
<td>7.665</td>
<td>1.429</td>
</tr>
<tr>
<td>10.07</td>
<td>0.49</td>
<td>7.810</td>
<td>1.745</td>
</tr>
</tbody>
</table>

The data in Tab. 2 were considered as input data used in Eq. (26) and only the frequency $f$ was changed. Then Eq. (26) was used as the model of behaviour of the sensor.

An example of the results is in Fig. 1, Fig. 2 and Fig. 3. At the beginning the theoretical curves were calculated at the frequency $f = 0.0312$ Hz. The curves fit the experimental data well. The example is in Fig. 1. The accordance is a bit worse in Fig. 2 where the frequency $f = 0.0625$ Hz was used. The curve is even shifted compared to the measured data in Fig. 3 where the frequency $f = 0.156$ Hz was used. Heat is conducted from the heating system faster into the sensor compared to convection of heat away of the sensor into its surrounding at higher frequency. This phenomenon can elevate the temperature of the sensor and shift the theoretical curve compared to measured data.

heat exchange between the sensor and its surrounding was not considered in the derivation of Eq. (26). Despite this the neglecting of the phenomenon is acceptable for the purpose of which Eq. (26) is used herein.

Table 4 includes the deviation $\delta$ calculated for the clean air. From it follows that the deviation $\delta$ does not exceed 23%.

The sensors were further tested in the concentration $x = 100$ ppm of the single tested vapour in the air at the same heating voltage as in the clean air case. The conductivities $G_M$ and $G_m$ were found out in the experimental data of the tested vapour and average of $h_1$ from Tab. 1 was used to calculate the constants $A$ and $B$ with the use of Eq. (33) and Eq. (34) at the frequency

![Fig. 1](image-url)  
**Fig. 1:** The electrical conductivity $G(t)$ of the sensor TGS 813 at frequency $f = 0.0312$ Hz in the clean air. $U(t)$ is the heating voltage.

![Fig. 2](image-url)  
**Fig. 2:** The electrical conductivity $G(t)$ of the sensor TGS 813 at frequency $f = 0.0625$ Hz in the clean air. $U(t)$ is the heating voltage.
Fig. 3: The electrical conductivity $G(t)$ of the sensor TGS 813 at frequency $f = 0.156 \text{ Hz}$ in the clean air. $U(t)$ is the heating voltage.

Tab. 3: The deviations of $\delta$ in % for the sensors in clean air at the used frequencies.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>MQR 1003</th>
<th>SP 11</th>
<th>TGS 813</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0312</td>
<td>5.0</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>0.0625</td>
<td>−1.8</td>
<td>2.0</td>
<td>17.2</td>
</tr>
<tr>
<td>0.156</td>
<td>2.5</td>
<td>14.5</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Tab. 4: The values of $\delta$ in % for the sensor in the tested vapours.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Frequency (Hz)</th>
<th>MQR 1003</th>
<th>SP 11</th>
<th>TGS 813</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>$f = 0.0312$</td>
<td>0.5</td>
<td>12.9</td>
<td>59.9</td>
</tr>
<tr>
<td></td>
<td>$f = 0.0625$</td>
<td>2.7</td>
<td>51.6</td>
<td>62.4</td>
</tr>
<tr>
<td></td>
<td>$f = 0.156$</td>
<td>4.0</td>
<td>19.5</td>
<td>−27.4</td>
</tr>
<tr>
<td>ethanol</td>
<td>$f = 0.0312$</td>
<td>0.8</td>
<td>−46.3</td>
<td>53.8</td>
</tr>
<tr>
<td></td>
<td>$f = 0.0625$</td>
<td>5.4</td>
<td>−14.6</td>
<td>−42.2</td>
</tr>
<tr>
<td></td>
<td>$f = 0.156$</td>
<td>0.9</td>
<td>6.7</td>
<td>−25.3</td>
</tr>
<tr>
<td>toluene</td>
<td>$f = 0.0312$</td>
<td>0.5</td>
<td>10.9</td>
<td>−45.7</td>
</tr>
<tr>
<td></td>
<td>$f = 0.0625$</td>
<td>7.6</td>
<td>−54.7</td>
<td>−79.7</td>
</tr>
<tr>
<td></td>
<td>$f = 0.156$</td>
<td>7.5</td>
<td>−37.8</td>
<td>−42.1</td>
</tr>
</tbody>
</table>

The deviations $\delta$ in the column at the frequency $f = 0.0312$ Hz are small, because of the constants $A$ and $B$ which were calculated from the experimental data at this frequency. This represents the reference column. The results in Tab. 3 show that the swing of the conductance of the sensor MQR 1003 is greater by 59.9 % at the frequency $f = 0.156$ Hz for the acetone case than expected. Similarly it is for the case when ethanol was used at the frequencies $f = 0.625$ Hz and $f = 0.156$ Hz. On the other hand the sensor SP 11 indicates for the acetone case and for the toluene case the swing smaller by −51.6 % or even less at the frequencies $f = 0.0625$ Hz and $f = 0.156$ Hz then expected. It follows that the parameter $\delta$ can serve as a decision criterion if the sensor is more or less sensitive to the compound at given frequency compared to the expected value. The curve calculated by Eq. (26) can be considered as a reference curve for which the parameter $\delta$ is calculated by Eq. (35).

An example of measured data and the dependency of Eq. (26) is in Fig. 2, Fig. 5 and Fig. 6. For the measured data, the maximum of $G$ is not always delayed behind the maximum of $U(t)$ as expected when a compound is detected. That is why the method of the calculation of $h_1$ by Eq. (30) fails here. The coefficient $h_1$ is related to the thermal properties of the sensor and it would be independent on a detected compound. The correct value of $h_1$ can be calculated when the experimental data of the clean air are taken.

It is general knowledge [21], [22] and [23], that during the detection of ethanol the maximum of the electrical conductance occurs at specific heating voltage between the values $U = 2 \text{ V}$ and $5 \text{ V}$. Hence the maximum of $G(t)$ for the ethanol case occurs earlier than the maximum of $G(t)$ for the clean air case. The corollary of this is less or even a negative delay $\Delta t$ between $G(t)$ and $U(t)$. The phenomenon can be seen in Fig. 2, Fig. 5 and Fig. 6. Ethanol is not only one compound with maximum electrical conductance at specific heating voltage and the negative delay $\Delta t$ can occur also during the test of other substances.

It follows from Eq. (26) that for $f = \infty$, the magnitude of the sine component tends to zero. The value

**Fig. 4:** The electrical conductivity $G(t)$ of the sensor MQR 1003 for ethanol of the concentration $x = 100 \text{ ppm}$ at frequency $f = 0.0312 \text{ Hz}$ of the heating voltage. $U(t)$ is the heating voltage.
5. Conclusion

The electrical conductivity of the tin dioxide gas sensor was derived herein. The model of the sensor is based on thermal inertia and it is valid for specific periodical heating voltage. The model was verified with the experimental data. It was found that the model can be used in the determination of sensitivity of the sensor to the tested substance at given frequency.

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References


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