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Numerical and Experimental Analysis of the Response of a SAW Structure with WO_3 Layers on Action of Carbon Monoxide

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The paper presents the results of an analysis of gaseous sensors based on a surface acoustic wave (SAW) by means of the equivalent model theory. The applied theory analyzes the response of the SAW sensor in the steady state affected by carbon monoxide (CO) in air. A thin layer of WO_3 has been used as a sensor layer. The acoustical replacing impedance of the sensor layer was used, which takes into account the profile of the concentration of gas molecules in the layer. Thanks to implementing the Ingebrigtsen equation, the authors determined analytical expressions for the relative changes of the velocity of the surface acoustic wave in the steady state. The results of the analysis have shown that there is an optimum thickness of the layer of CO sensor at which the acoustoelectric effect (manifested here as a change in the acoustic wave velocity) is at its highest. The theoretical results were verified and confirmed experimentally.

Keywords: gas sensor, carbon monoxide CO, piezoelectric substrate, numerical modeling, surface acoustic waves, acoustoelectric effects, Ingebrigtsen's formula.

1. Introduction

The autumn-winter season is the period in which poisonings are observed resulting from incorrect ventilation installations. The poisoning results from a too high concentration of carbon monoxide (CO), influencing aggressively on the organism, which is of particular importance. Diagnostic methods with gas sensors ought to be installed in building objects, in houses and public institutions. Many modern gaseous sensors based on optical (Bielecki *et al.*, 2012; Pustelny *et al.*, 2004), plasmon (Maciak, Pustelny, 2013, Pustelny *et al.*, 2004) semiconductor (Urbanczyk *et al.*, 2011; Pustelny *et al.*, 2012) and electrochemical (Procek, Pustelny, 2013; Hossein-Babaei, 2003) effects have been investigated and are offered. The sensitivity of gaseous sensors reaches a concentration of 100–150 ppm CO in air. A very interesting alternative to sensors mentioned above may be SAW sensors based on surface acoustic waves with differential measurements of their frequency (Hejczyk *et al.*, 2010). These kinds of sensors are characterized by their simple construction, small dimensions and may detect concentrations in a higher range than standard gas sensors. In the work the main efforts devoted to appointing the optimal characteristics of the sensor in a wide range of concentration, thickness, temperature as well as porosity of the layer on the basis of the numerical model, and to check the range of adaptation of an analytical model compared. The results obtained by means of the numerical models were compared with experiment results. Sensors with an acoustic surface wave are used in many fields, especially in biochemical applications (Anisimkin, Verona, 2001), monitoring DNA (Reibel, Stahl, 2000) as well as monitoring the physical and chemical properties of solids (Pustelny *et al.*, 2008; Pustelny, Pustelny 2009), monitoring the quality of food (Ceeke *et al.*, 1999), and measurements of humidity (Kawalec *et al.*, 2008). New possibilities of applying surface acoustic wave sensors allow to detect the toxic gases, among others – carbon monoxide – silent killer.

2. Analytical model of a gas sensor

The analytical model of a SAW gas sensor having the described form was used in order to analyzed it numerically (Hejczyk *et al.*, 2010; 2012; Hejczyk, Urbańczyk, 2011; 2013). In order to analyze such a sensor layer in the SAW gas sensor we assumed that the film is a uniform stack of infinitesimally thin sheets with a variable concentration of gas molecules (Fig. 1) and that it influences the electric conductance (Hejczyk, Urbańczyk 2013).

$$\frac{\Delta v}{v_0} = -\operatorname{Re}\left\{\frac{\Delta k}{k_0}\right\} = -\frac{K^2}{2} \cdot \frac{a^*}{a^* + \left[1 + \sum\limits_{i=1}^{n-1} g(y_i, \sigma(y_i))\right]^2 (v_0 C_S)^2}, \qquad (1)$$

where

$$a^* = \left[\sigma_0(1 + aC_{A,y=0}) + \sum_{i=1}^{n-1} \sigma(y_i) f(y_i, \sigma(y_i))\right]^2,$$

$C_S = \varepsilon_0 + \varepsilon_p^{\mathrm{T}}$, $i = 1, 2, 3, \ldots, n$ (the sublayers index), $\Delta v/v_0$ and $\Delta k/k_0$ relative changes of velocity and wave vector of SAW, respectively, σ_0 – electrical conductivity of sensing layer in air, K – coefficient of electromechanical coupling.

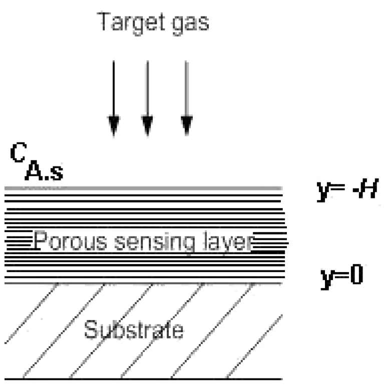

Fig. 1. Thin semiconducting layer on a piezoelectric substrate (Hejczyk, Urbańczyk, 2013).

The profile of the concentration in the steady-state takes the following form (Hejczyk *et al.*, 2010; 2012):

$$C_A(y_i) = C_{A,S} \frac{\cosh\left(y_i \sqrt{k/D_K}\right)}{\cosh\left(H \sqrt{k/D_K}\right)}$$

and $\sigma(y_i) = \sigma_0 \left[1 + a \cdot C_A(y_i)\right]$, where: a – sensitivity coefficient of sensitivity of the sensing layer [1/ppm].

In the expression (1) the functions $f(y, \sigma)$ and $g(y, \sigma)$ are the results of the transformation of the individual sublayer on the surface of a sensor waveguide (Fig. 1) and it has the form:

$$f(y_i, \sigma_S) = \frac{1 - [\tanh(ky_i)]^2}{[1 + \tanh(ky_i)]^2 + \left[\tanh(ky_i) \cdot \frac{\sigma_S}{\varepsilon_0 v_0}\right]^2} \qquad (2)$$

and

$$g(y_i, \sigma_S) = \frac{[1 + \tanh(ky_i)]^2 + \tanh(ky_i) \cdot \left(\frac{\sigma_S}{\varepsilon_0 v_0}\right)^2}{[1 + \tanh(ky_i)]^2 + \left[\tanh(ky_i) \cdot \frac{\sigma_S}{\varepsilon_0 v_0}\right]^2}. \qquad (3)$$

The conductivity of the semiconductive layer of sensor depends on the temperature:

$$\sigma_{T_2} = \sigma_{T_1} \exp\left(\frac{E_g}{2k_B} \cdot \frac{T_2 - T_1}{T_1 T_2},\right) \qquad (4)$$

where σ_{T_1} and σ_{T_2} are the conductance of the layer, respectively, at temperature the T_1 and T_2, k_B – the Boltzmann constant, E_g – the width of the energy gap of sensor layer material.

The expressions (1) to (4) make it possible to determine the use of the iteration method response of the surface acoustic wave in the steady-state ($t \to \infty$). The diagram of iterative calculation is presented in Fig. 2.

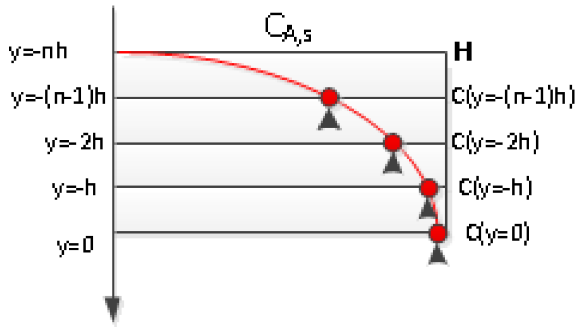

Fig. 2. Iteration takes into consideration the gas concentration in the next sub-layer SAW sensor.

Basing the above-mentioned means of the analysis a SAW gas sensor a patent announcement has been made (PATENT No P-394124, 07.03.2011).

3. Numerical analysis

For the assumed parameters of the sensor layer WO_3 a numerical analyses were carried out. The sensitivity coefficient $a = 1$ [/], gas concentration: 25, 50, 75, 100 [ppm], temperature 318 (40°C) [K], $r = 2$ [nm], surface conductivity $\sigma_S = 4.7 \times 10^{-7}$ [S], $k = 10^8$ [s^{-1}], $D_K = 10^{12}$ [nm^{2}s^{-1}], $E_g = 2.7$ [eV], $M = 28$ [g/mol] (CO), $\kappa = 1$ were established. For the graphic presentation of the results we use statement between relative changes of the differential frequency and velocity of the SAW wave as follows (Hejczyk, Urbańczyk, 2011).

$$\frac{\Delta f_{\max} - \Delta f}{\Delta f_{\max}} = \kappa \frac{\Delta v_{\max} - \Delta v}{\Delta v_{\max}}. \qquad (5)$$

Results of numerical analyses are presented in Fig. 3. We can see that for each concentration the optimal layer thickness is in the range from 40 nm to 60 nm. This range of thicknesses indicates the range of optimal thicknesses where acoustic-electrical effect is maximal. We also see a downward tendency due to the rise of the thickness and we observe the disappearance of the acoustic-electrical effect when the thickness sensor layer decreases (Hejczyk, Urbańczyk, 2011; 2013). The presented tendencies in the steady state are complying with experimental results.

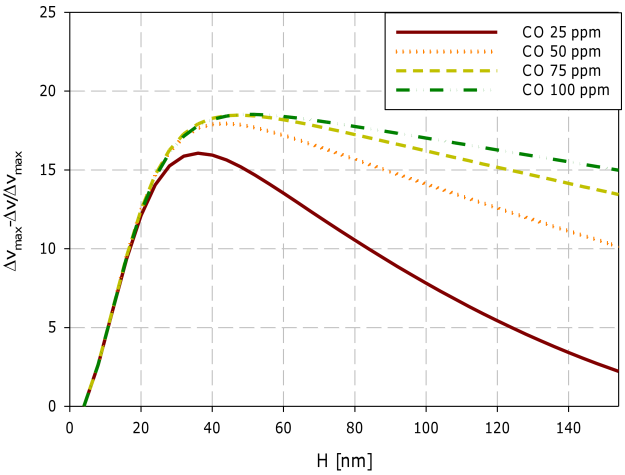

Fig. 3. Relative changes of velocity vs. sensor layer thickness – numerical results. Sensitivity coefficient a = 0.5 ppm^{-1}, $\sigma_S = 4.7 \times 10^{-7}$, $k = 10^8$ s^{-1}, $D_K = 10^{12}$ nm^{2}s^{-1}, $E_g = 2.7$ eV, $M = 28$ g/mol (CO) (Hejczyk, Urbańczyk, 2013).

4. Experimental results

The main aim of researches of selected structures of the sensor with a surface acoustic wave was an experimental verification of the response of numerical analysis sensor. We must emphasize that performing experimental researches was possible in limits, because of the wide range of work and the complex of technological processes connected with the practical feasibility of the sensor structure. In researches it was assumed that the sensor should be prepared with WO_3 for different thickness: ~50, ~100, ~150 nm and covered with the catalyst Pd (Pallad) on each of them. These structures were checked on carbon monoxide in synthetic air. The sensor layers and catalyst were prepared in the same technological process, warranting that the physicochemical parameters, and the morphology were the same.

The WO_3 + Pd sensor layer was prepared for carbon monoxide detection (at typical temperature 40°C of the semiconductor sensor). Experimental results are presented in Fig. 4. The results were normed to maximum change in differential frequency for selected layer. The results (in a relative scale) in Fig. 5 are shown. The influences of the thickness of the sensor layers on the values of the sensor responses are shown in Fig. 6. The experimental results revealed an increase of the

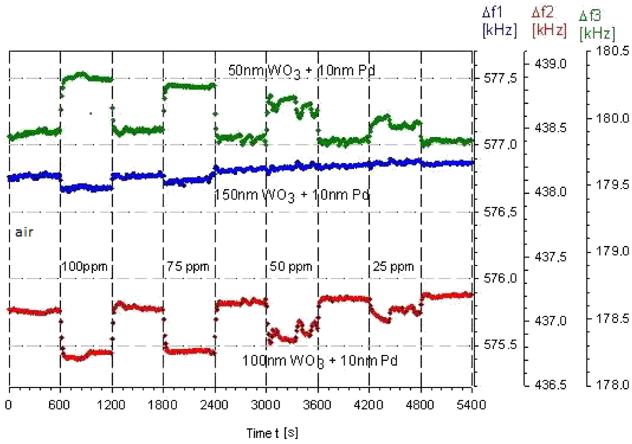

Fig. 4. Experimental results – response (Δf) sensor for thickness layers of the WO_3 + Pd: 50, 100, 150 nm CO gas (25, 50, 75, 100 ppm), $T = 40$°C.

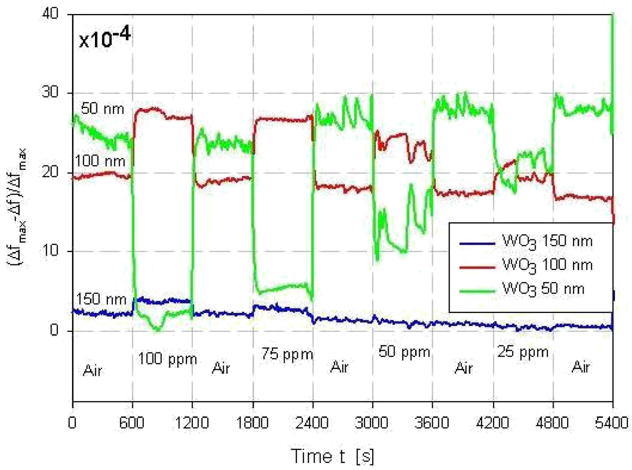

Fig. 5. Relative changes of the response of a sensor normed to maximum differential frequency for each WO_3 + Pd: 50, 100, 150 nm CO gas (25, 50, 75, 100 ppm), in synthetic air, $T = 40$°C.

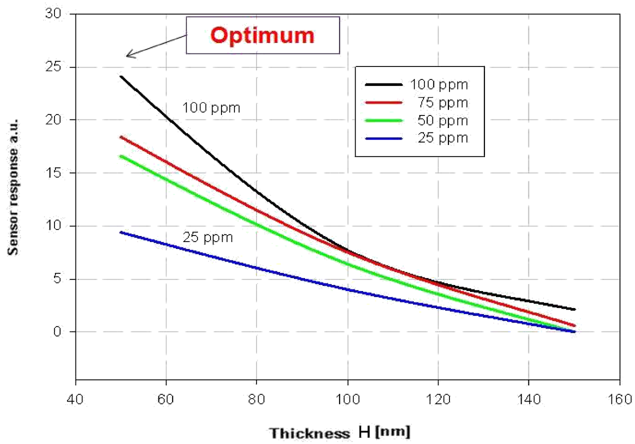

Fig. 6. Influence of the thickness of the WO_3 layer on the response of carbon monoxide vs. concentration: 25, 50, 75, 100 ppm) in $T = 40$°C.

thickness sensor layers caused the decrease of the sensor response (Hejczyk, Urbańczyk, 2011). The layers with a thickness exceeding 150 nm and larger cannot be applied for applications to detect carbon monoxide by means of a sensor with surface acoustic waves.

5. Numerical analysis in the steady state

Numerical analyses of the influence of gas concentrations on the responses of the carbon monoxide sensor were performed for the selected parameters: temperature and thickness layer. In the numerical analysis we found (Fig. 7) that the most intensive influence of the CO concentrations on the acoustoelectric effect occurs at the lowest thickness of the sensor layer, about 50 nm. In the case of thicker layers (about 150 nm) the sensitivity of the structure does not depend on the tested CO concentration.

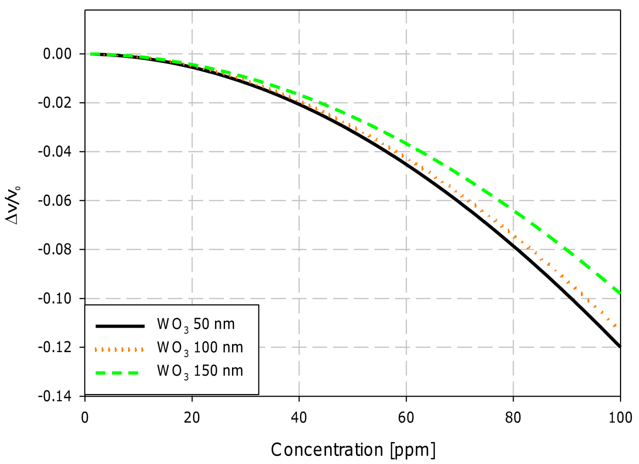

Fig. 7. SAW velocity changes on CO vs. concentration from 0 to 100 ppm in synthetic air in the case of three sensor layers WO_3 (50, 100, 150 nm) in $T = 40°$C. Calculations were performed for: the sensitivity coefficient $a = 0.5$ ppm^{-1}, $\sigma_S = 4.7 \times 10^{-7}$ S, $k = 10^8$ s^{-1}, $D_K = 10^{12}$ nm^{2}s^{-1}, $E_g = 2.7$ eV, $M = 28$ g/mol, $r = 2$ nm (CO).

The porosity of sensor layer for pore radius from 2 to 40 nm have been theoretically analysed. Exemplary results achieved for the 50 nm layer at a temperature of 40°C are presented in Fig. 8.

Numerical results of the acoustoelectric effect vs. temperature are shown in Fig. 9. We see that the largest acoustoelectric effect in the wide band of temperature occurs at the thickness of the layer amounting to 50 nm; the lowest effects are observed for the layer, 150 nm thick.

Very interesting results were obtained at the response of the SAW sensor to the presence of carbon monoxide depending on the thickness of the sensing layer (Fig. 10). It results from the analysis that the optimum is in the range from 40 nm to 60 nm (Fig. 6) (Hejczyk, Urbańczyk, 2013).

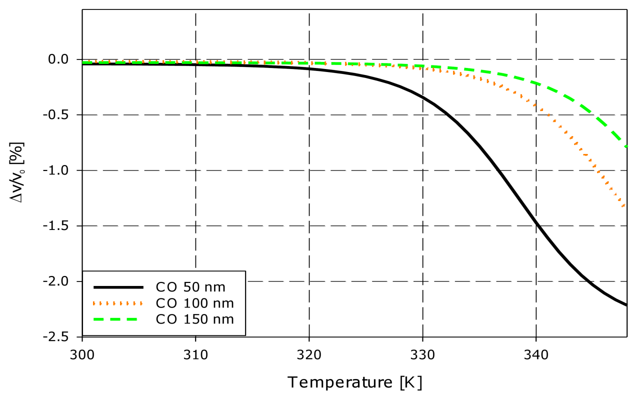

Fig. 8. SAW velocity changes on CO vs. porosity from 2 to 40 nm (pore radius) in synthetic air in the sensor layer WO_3 in $T = 40°$C. Calculations were performed for: the sensitivity coefficient $a = 0.5$ ppm^{-1}, $\sigma_S = 4.7 \times 10^{-7}$ S, $k = 10^8$ s^{-1}, $D_K = 10^{12}$ nm^2 s^{-1}, $E_g = 2.7$ eV, $M = 28$ g/mol, concentration = 100 ppm, thickness 50 nm (CO).

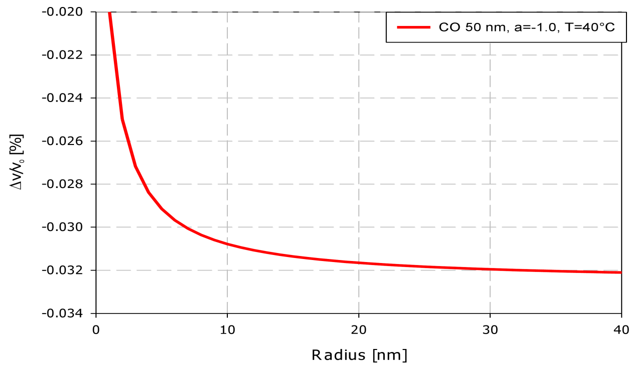

Fig. 9. SAW velocity changes in result of the effect of CO in synthetic air vs. temperature from 300 to 360 K (27–87°C) concerning three thicknesses of the sensor layer WO_3 (50, 100, 150 nm). Calculations were performed for: sensitivity coefficient $a = 0.5$ ppm^{-1}, $\sigma_S = 4.7 \times 10^{-7}$ S, $k = 10^8$ s^{-1}, $D_K = 10^{12}$ nm^{2}s^{-1}, $E_g = 2.7$ eV, $M = 28$ g/mol, $r = 2$ nm (CO).

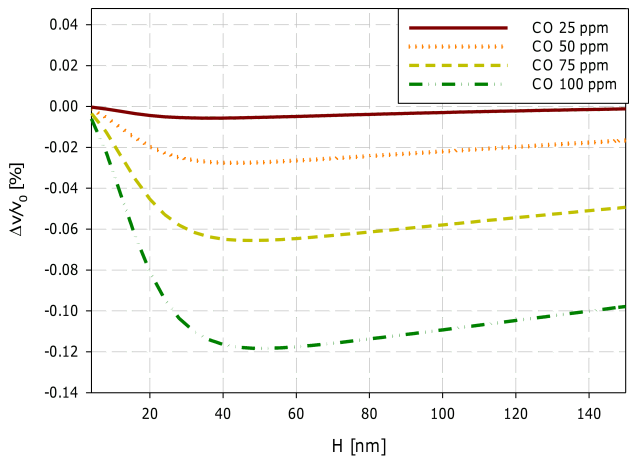

Fig. 10. SAW velocity changes of CO vs. thickness in the layer from 0 to 150 nm in synthetic air in 40°C at concentration: 25, 50, 75, 100 ppm. Calculations were performed for the sensitivity coefficient $a = 0.5$ ppm^{-1}, $\sigma_S = 4.7 \times 10^{-7}$ S, $k = 10^8$ s^{-1}, $D_K = 10^{12}$ nm^{2}s^{-1}, $E_g = 2.7$ eV, $M = 28$ g/mol, $r = 2$ nm (CO).

When the thickness decreases, the influence of the growth of CO concentration becomes smaller and smaller. We can observe an explicit tendency towards "0" in the characteristic. In the range of thicker layers above 100 nm the interaction grows smaller, which confirms the obtained experimental results. It can be noticed in the characteristics that at the small concentrations (below 25 ppm) measurements of carbon monoxide by means of the SAW sensor with a sensing layer above 150 nm and thicker will be useless (Fig. 6). This fact is confirmed explicitly by experiments mentioned above.

6. Conclusions

Extensive numerical analyses of the SAW sensor response depending on parameters like: concentration, porosity, temperature and thickness were conducted. Numerical researchers were performed in the steady state. (Numerical analyses were performed using proprietary software written in Python.)

The optimum thickness of the sensing layer depends on the porosity of the layer and the type (size) of gas molecules diffusing into the interior. Detailed analyses showed that the optimal thickness of the WO_3 layers for the detection of carbon monoxide molecules are about 40–60 nm. The layer thickness decides about the maximum range of the detected gas concentration. Thicker layers will be useful for the application at higher gas concentration (saturation occurs as the response of gas at higher concentrations). Also the choice of the temperature of the sensor is important – the optimal work temperature depends on the type of the sensor layer and its porosity. The change of temperature allows to determine the point of sensor work, and has also an impact on the speed of its response and the recovery time of the sensing properties of the sensor layer (Hejczyk, Urbańczyk, 2013). Experimental results of a SAW sensor with tungsten oxide were achieved for three thicknesses of the layers ($\sim$50, $\sim$100, $\sim$150 nm) and the same morphology. The main aim was to verify experimentally the analytical model of the SAW gas sensor affected on carbon monoxide in air. Experimental results confirmed the usefulness of the elaborated analytical model for researches of the SAW sensor in the design stage. In particular, the influence of the thickness of the layer and the size of gas particles were confirmed. The essential parameter of the sensor is the porosity of the sensing layer, which influences the response depending on the size of gas particles transported to its interior. This property can be utilized in pattern recognition methods in order to recognize gases and to determine the composition of gases in the mixture. In order to optimize the sensor construction for its practical application we always used results of its theoretical analysis (Szaszkowski, 2003). The results of numerical analyses of the SAW sensors, confirmed by means of experimental investigations showed that the optimum thicknesses of the sensing layers based on WO_3 for the detection of CO gas in air are equal to about 40 to 60 nm. The study has shown that the parameters of the sensor layer for the SAW sensor should be individually adjusted, according to the type of the detected gas and to the applied sensing layer.

Acknowledgments

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