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Conductivity and response formation of semiconductor gas sensors based on tin oxide nanomaterials

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Actuallity: *The semiconductor sensors are widely used for detection of explosive and toxic gases leakages in air due to their high sensor response and low production cost [1]. Improvement of the main sensor characteristics (sensitivity, selectivity, stability, power consumption and other parameters) is a main task during development of new semiconductor nanosized gas sensitive materials for the sensor layers that are able to change amount of chemisorbed oxygen on their surfaces. The chemisorbed oxygen is known to be responsible for the sensitivity of the sensor because the oxygen is involved in the catalytic oxidation of the target gas molecules on the semiconductor surface [2].*

The aim of this work is to *analyze and describe the experimental dependences of responses to methane by the mathematical model based on the kinetics of heterogeneous catalytic oxidation of methane on the surface of gas sensitive layer of the sensor based on Pd- and Pt-doped nanosized tin dioxide. Methane has been chosen as a target gas due its significant economic importance and a variety of applications whereas studies of the sensors based on modified tin dioxide will make obtained results appropriate for the sensors that can found a practical use in gas alarm systems.*

Synthesis of the nanosized tin dioxide for sensor materials

Initial tin dioxide with an average particles size 10 – 11 nm was synthesized via a sol-gel method by using $SnCl_4 \cdot 5H_2O$ and ethylene glycol. Formation of the nanosized crystalline SnO_2 was performed by the heat treatment of the xerogel in air up to 600 °C. Sensors were made by depositing a paste obtained from the synthesized initial SnO_2 and 3% aqueous solution of carboxymethyl cellulose between the Pt measuring electrodes of the ceramic sensor plates. The plates with the paste were dried in air for 1 h at 20 °C and 1 h at 90 °C. Addition of Pd and Pt was performed by impregnation with solutions of $PdCl_2$ and $HPtCl_4$ with the concentrations from 0.21×10^{-2} to 35×10^{-2} M. Then the plates were dried in air for 30 min at 20 °C and 30 min at 90 °C. The plates with the applied materials were heated up to 600 °C.

Model for descriptin of dependences of the conductivities on CH_4 concentrations of the sensors based on nanosized SnO_2 materials

Kinetics of the methane oxidation on the obtained Pd/SnO_2 and Pt/SnO_2 gas sensitive materials was represented by a kinetic scheme where chemisorbed oxygen interacts with methane. The equation for gas sensitive layer surface coverage by the chemisorbed oxygen is:

$$\theta = \frac{1}{1 + \frac{(m+1)\cdot k_r^{ef}}{2\cdot k_a^{ef}}\cdot\frac{C_{CH_4}}{C_{O_2}}}$$

That allows to propose the model of the sensor response formation that describe dependences of the sensor conductivities on concentrations of CH_4. The main provisions of the model is follows: at a constant temperature the sensor conductivity is proportional to the gas sensitive layer surface coverage by chemisorbed oxygen ($\sigma=f(\theta)$), in turn $\theta = f(C(CH_4))$.The expression that approximate a dependence of the sensor conductivity (σ_g) on the methane concentration in air is:

$$\sigma_g = \sigma_0 + \frac{\sigma_{max} - \sigma_0}{1 + A/C_{CH_4}}$$

A linear form of this equation is:

$$\frac{1}{\sigma_g - \sigma_0} = \frac{1}{\sigma_{max} - \sigma_0} + \frac{A}{\sigma_{max} - \sigma_0}\cdot\frac{1}{C_{CH_4}}$$

where σ_0 - the electrical conductivity of the sensor in the absence of the reducing gas; σ_{max} - maximal electrical conductivity of the sensor; parametr A is equal:

$$A = \frac{2\cdot k_a^{ef}\cdot C_{O_2}}{(m+1)\cdot k_r^{ef}}$$

Approximated dependences of the sensor conductivities on the methane concentrations in linearized form (a, b) and normal scale (c) for sensors Pd/SnO_2 and Pt/SnO_2 are presented in Fig.1,2.

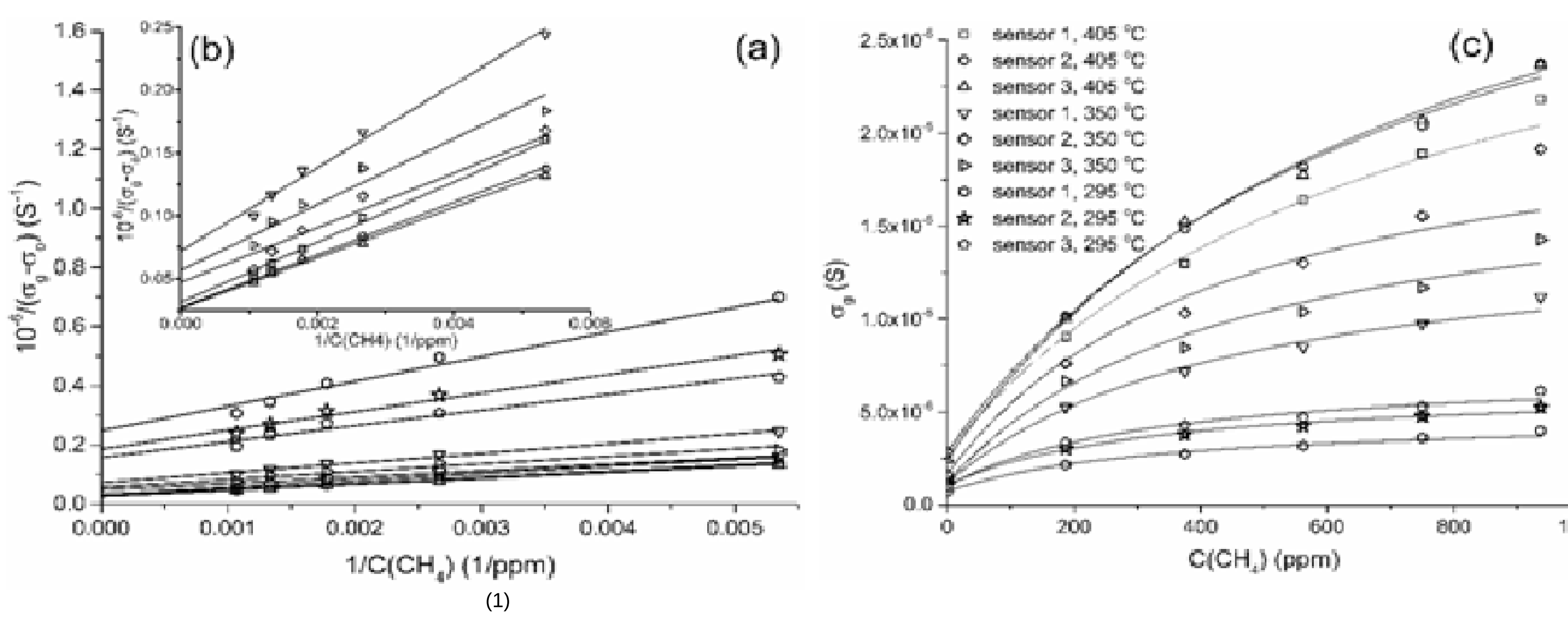

Fig. 1. Approximated dependences of the sensor conductivities on the methane concentrations in linearized form (a, b) and normal scale (c) for three different sensors with the same composition – 1.41 wt.% Pd/SnO_2.

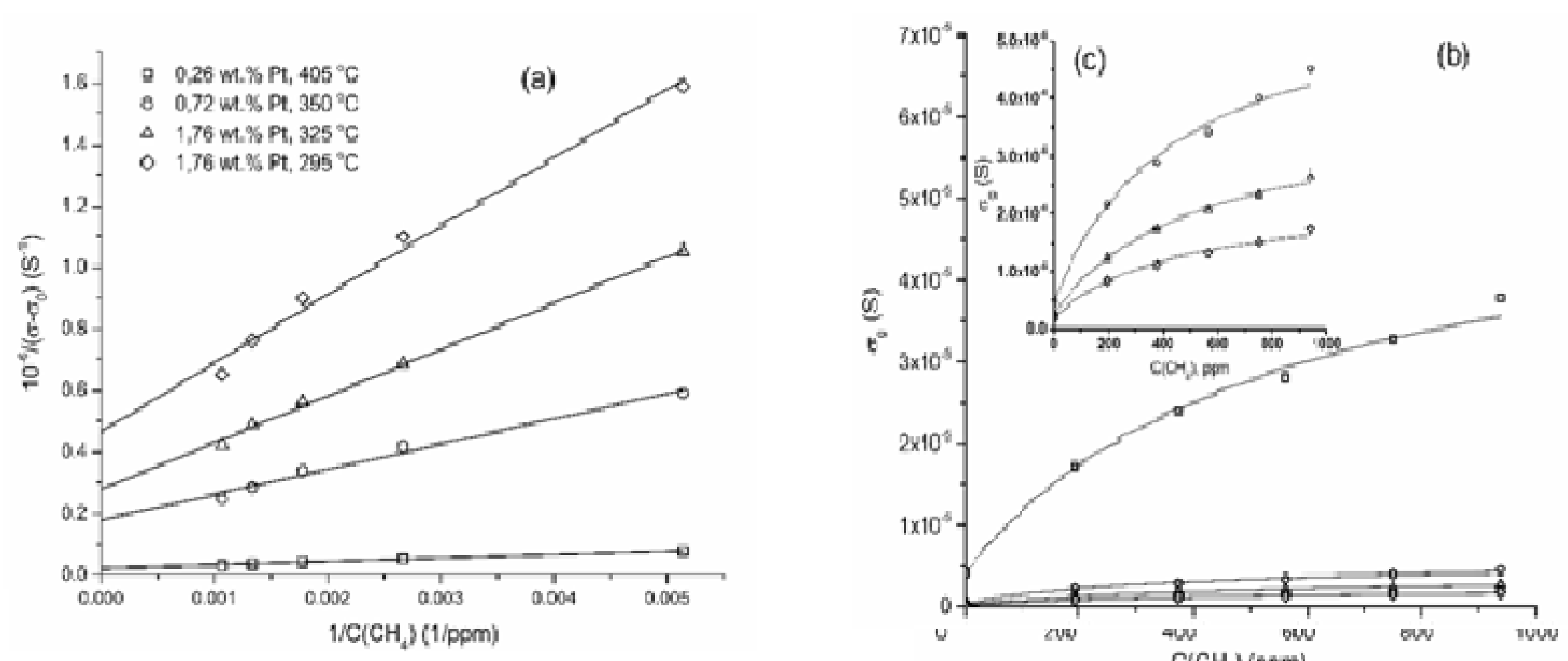

Fig.2. Approximated dependences of conductivities on CH_4 concentrations in linearized form (a) and normal scale (b, c) for Pt/SnO_2 sensors

Calculated parameters A and $\gamma_{max} = \sigma_{max}/\sigma_0$ are presented in Table. γ_{max} is related to the range of CH_4 concentration that could be detected by sensors because for all studied sensors based on different materials the scale of parameter *A* is the same.

Dopant loading	1.76 % Pt	1.41 % Pd
T (°C)	325	350
γ_{max}	13.8	15.4
A	544	458

Conclusion: It was established that the sensors based on the nanosized tin dioxide with average particle size 10 – 11 nm exhibit the wide range of methane concentration in air that can be detect. The proposed mathematical model was found to be appropriate for the description of the experimental dataset obtained for the sensors with different dopants (Pd or Pt), that indicates about the adequacy of the assumptions made in the model and their general nature.

[1]. *Marikutsa A., Rumyantseva M., Gaskov A., Samoylov A.* Nanocrystalline tin dioxide: Basics in relation with gas sensing phenomena. Part 1. Physical and chemical properties and sensor signal formation // Inorg Mater.-2015.-**51**, N 13.-P. 1329-1347.

[2].*Wang C., Yin L., Zhang L., Xiang D., Gao R.* Metal oxide gas sensors: sensitivity and influencing factors // Sens.-2010.- **10**.- P. 2088-2106.