Platinum containing semiconductor nanomaterials based on SnO_2 with Pt-additives to analyze concentration of CH_4 in air

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Introduction

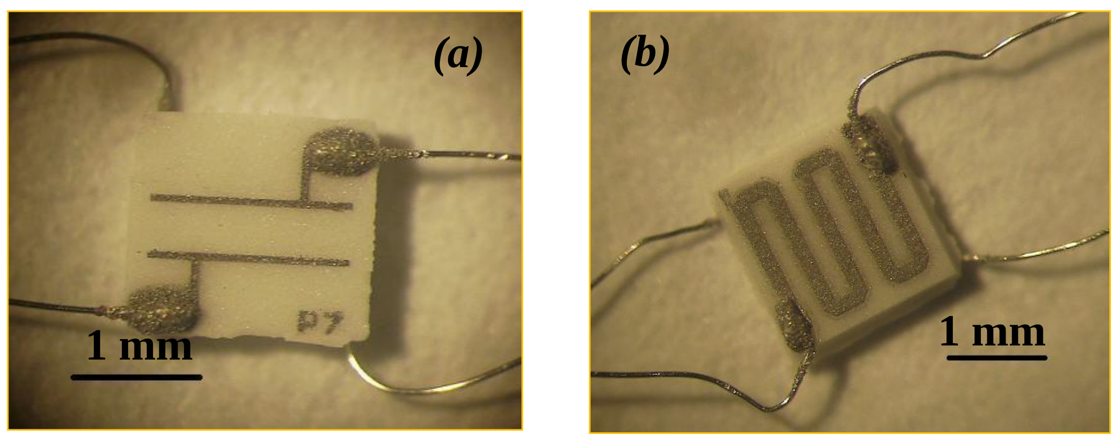
For detection of explosive gas leakages adsorption semiconductor sensors can be used due to their low cost, simple construction, low power consumption and high sensitivity. Their sensing mechanism is based on catalytic oxidation of an analyzed gas on the surface of the semiconductor gas sensitive layer. Chemisorbed oxygen oxidizes a detected gas (e.g. hydrogen, methane, carbon monoxide, ethanol vapor), that causes a change of the electrical resistance of the sensor. The most used material for the gas sensitive layer is tin dioxide because of its chemical stability. However, the oxidation of some widely used gases such as methane on undoped tin dioxide requires high temperatures (above 500^{0}C). That results in a large power consumption and low response of the sensors . To solve this problem catalytic active dopants can be added to the gas sensitive layer.

Target

The goal of this study was to investigate Pt doped nanosized tin dioxide materials and study gas sensitive properties of the sensors to methane based on them. To achieve the target next experimental methods and techniques were used:

- Transmission electron microscopy (TEM) to study morphology of Pt/SnO_2 (Selmi TEM – 125K)
- X-ray diffraction analysis (XRD) to investigate phase composition of the gas sensitive materials (Bruker D9 Advance, CuK_α radiation)
- Studies of gas sensitive properties to 930 ppm CH_4 (was performed on special electric stand)

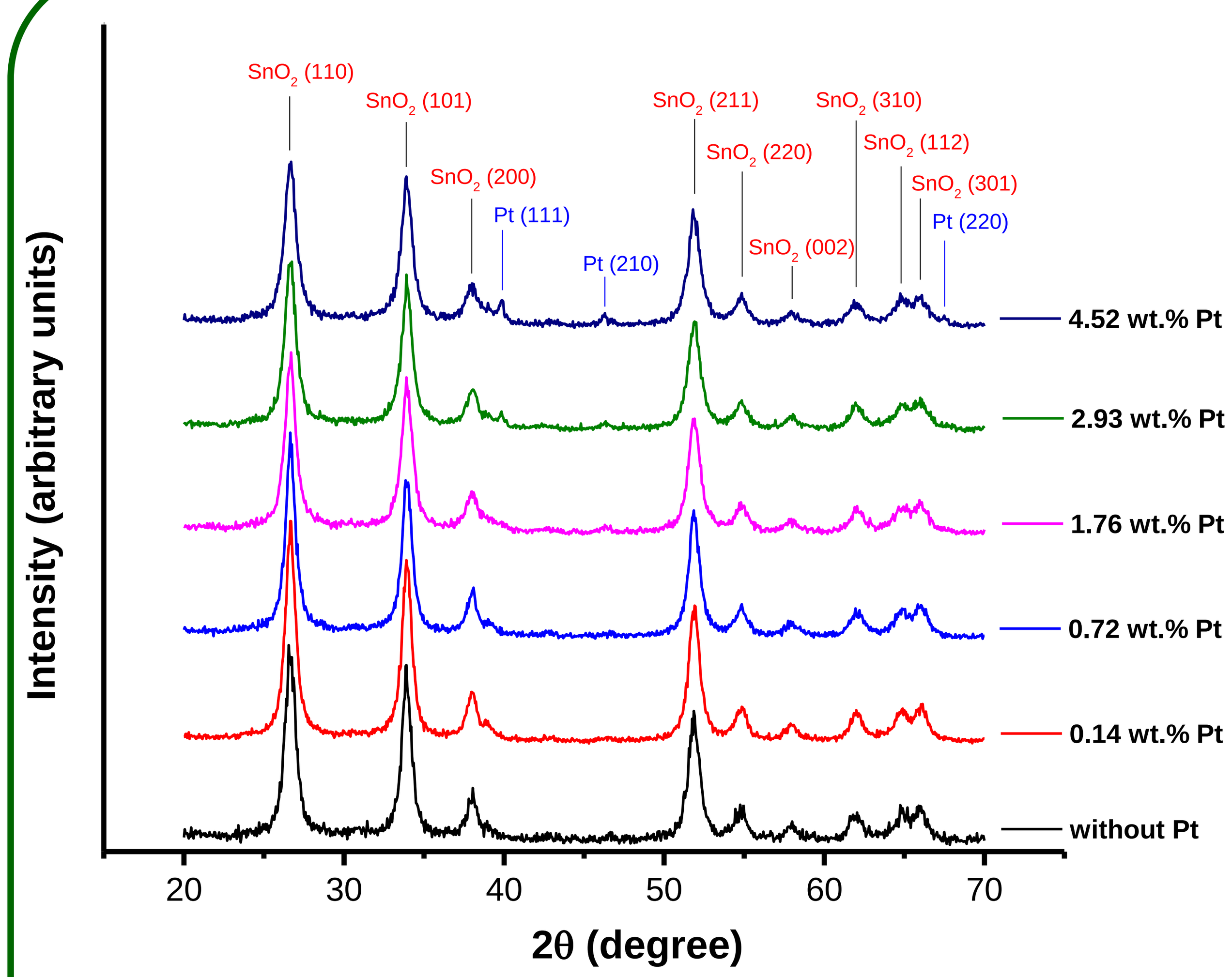
Adsorption semiconductor sensor



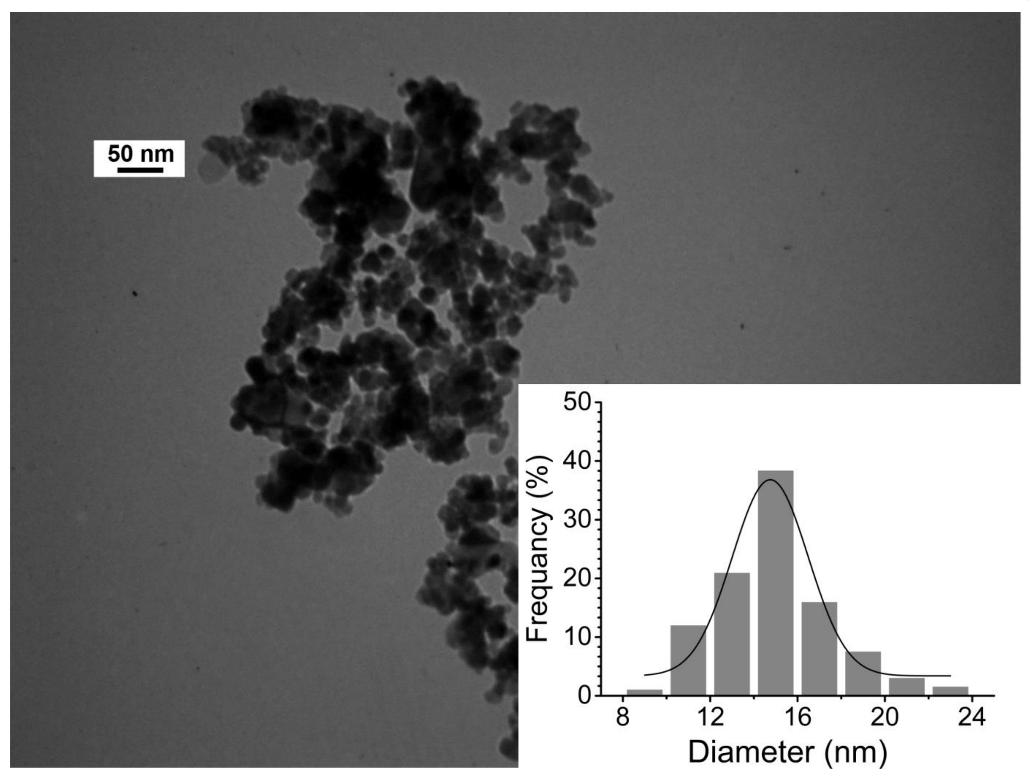
The ceramic plate of the sensor with measuring electric contacts (a) and sensor's heater (b).

The gas sensitive layer of the sensors was created from a paste obtained by mixing nanosized SnO_2 with carboxymethylcellulose (CMC) solution. Platinum was added into the gas sensing materials by impregnation with solutions of $H_2[PtCL_6]$. The concentrations of $H_2[PtCL_6]$ were varied from 2×10^{-2} to 35×10^{-2} mol/L. Loading amount of Pt was controlled by the X-ray fluorescence spectroscopy (ElvaX). To create the sensors, the plates with the deposited layers were sintered in air up to 620 ^oC. A measure of the **sensor response** was taken as a ratio R_0/R_{CH4}, where $\mathbf{R_0}$ is a value of electric resistance of the sensor in air and $\mathbf{R_{CH4}}$ is a value of electric resistance in the presence of 930 ppm CH_4.

Nanosized Pt/SnO_2 sensor materials



Presence of SnO_2 (cassiterite phase) and Pt (in metal form) was confirmed for the materials with high Pt loading. For other samples only cassiterite was found.

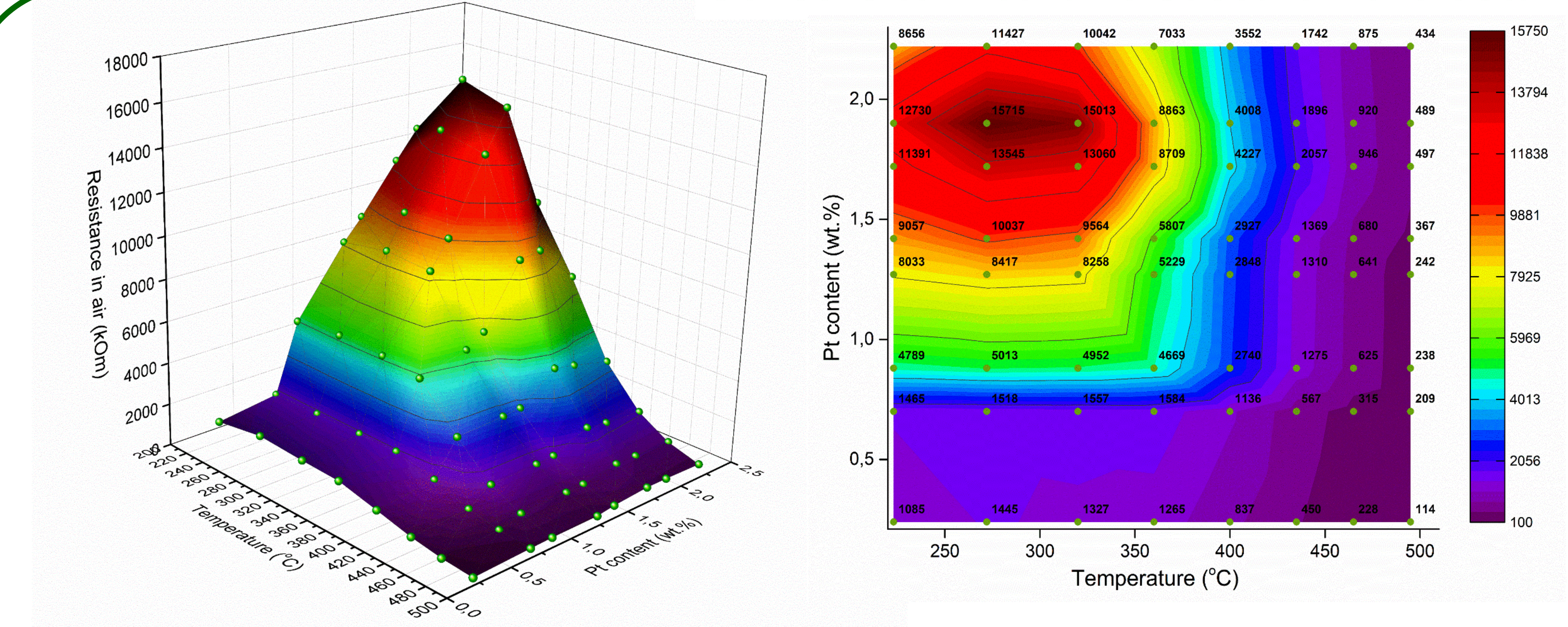


TEM image of the optimal gas sensing material containing 1.76 wt.% of Pt. The histogram of particle size distribution is shown on the insert.

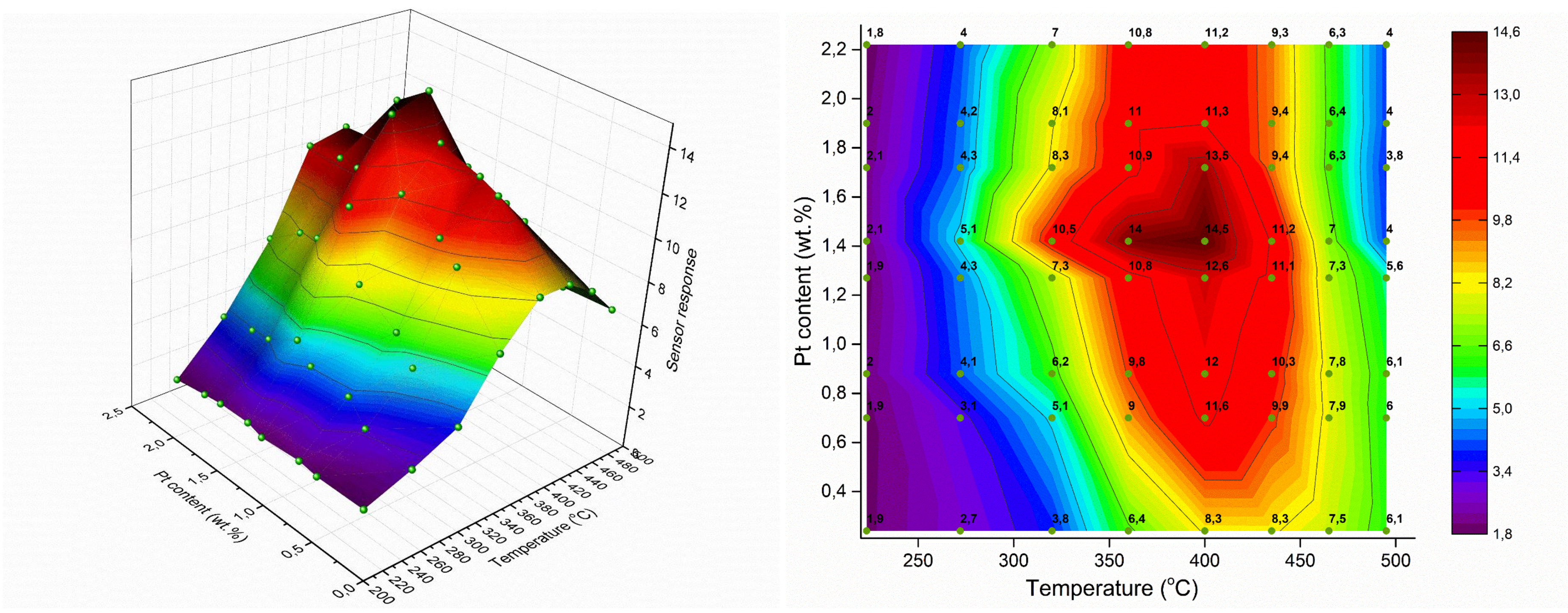
Equality of the particle size of tin dioxide calculated by TEM and by XRD (using Scherrer equation) for sensor material with different Pt loading indicates high crystallinity rate for all studied samples.

Sample	TEM size, nm	XRD size, nm	Sample	TEM size, nm	XRD size, nm
without Pt	19 – 20	20.1	1.76% Pt/SnO_2	14.5	14.1
0.14% Pt/SnO_2	14 – 15	14.2	2.93% Pt/SnO_2	14 – 15	14.3
0.72% Pt/SnO_2	14 – 15	14.6	4.52% Pt/SnO_2	14 – 15	14.1

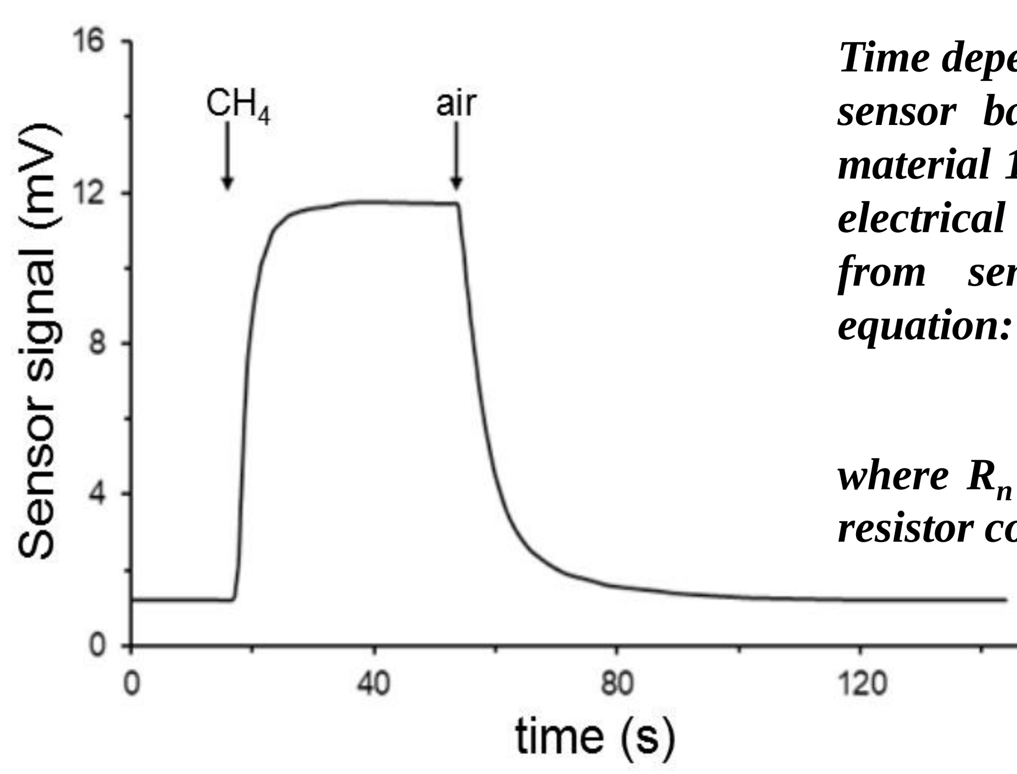
Sensors to methane based on the obtained nanosized Pt/SnO_2 materials



Resistance in air of the sensors based on Pt/SnO_2 and it's projection on "Temperature – Pt content" plot. Balls and circuits represent experimental data.



Sensor response to 930 ppm CH_4 of the sensors based on Pt/SnO_2 and it's projection on "Temperature – Pt content" plot. The sensitivity of the sensors without Pt is around 1.5 (at high temperature). Balls and circuits represent experimental data.



Time dependence of the sensor signal for the sensor based on the optimal gas sensing material 1.76% Pt/SnO_2 at 350 ^oC. Values of electrical resistances (R) were calculated from sensor signals (U) by the next equation:

$$R=R_n\times(4000-U)/U,$$

where R_n is value of electrical resistance of resistor connected sequential to the sensor.

Extreme character of the electrical resistance in air can be explained by combination of two factors. The first one is temperature dependence of oxygen chemisorption-desorption on the surface of gas sensitive layer. Desorption of oxygen prevails in a high temperature region. The second one is changing in the length of the interface between palladium clusters and tin dioxide. The maxima of the response to methane (930 ppm) are shifted towards maxima of the resistance in air in the high temperature region probably due to thermal activation of the methane oxidation reaction.

Summary

Our study of the adsorption semiconductor sensors based on the nanosized tin dioxide doped with platinum has shown their high response to methane and good dynamic properties. This make them useful in methane sensing devices.