

Noise enhanced gas sensors based on anodic tungsten oxide nanoparticles

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1 Introduction

Tungsten oxide (WO_3) has been utilized for decades as gas sensing material due to its high sensitivity towards nitric oxides, which is one of the most common pollutants [1] being potentially dangerous for health (e.g. suspected of reducing lung function in school children [2]).

Our research group has a possibility to synthesize and integrate a large variety of nanomaterials (including WO_3) to accomplish novel electrical devices, e.g. gas sensors. The constructed devices can be studied with a large variety of analyzing techniques, including scanning and transmission electron microscopy imaging (SEM/TEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The electrical transport behaviour and sensing performance of the devices can be tested with computer controlled (LabVIEW environment) high-precision measurement units (Keithley sourcemeters).

Nanostructured porous tungsten oxide has been synthesized by electrochemical etching (anodization) of tungsten metal in aqueous NaF electrolytes [3]. The as obtained anodic WO_3 templates have been used for fluctuation-enhanced sensing (FES) measurements by simply sputtering Pt electrodes on the top of the surface. The measurements were carried out in H_2 and NO analytes in synthetic air buffer.

2 Objectives of the research

In this work, we demonstrate fluctuation-enhanced sensing (FES) [4] with anodic nanostructured semi-conducting WO_3 sensing material. FES is a novel method for improving selectivity of gas sensors. In this method, the power density spectrum (PSD) of the fluctuation of the sensor resistance carries the chemical information. In principal, the DC and AC parts of the sensor resistance are separated and the AC part is then analyzed in detail using statistical analysis and pattern recognition. In our case, after separating the DC and AC components, we calculate the PSD for preamplified AC signal. For pattern recognition we use principal component analysis (PCA), which is an optimizing mathematical transformation (projection) of a large data set into a new coordinate system, thus giving more understandable and practical representation of measured data.

3 Results

Tungsten metal was anodized in 0.15 M NaF solution in water to obtain porous anodic tungsten oxide. Platinum electrodes with thickness of ~ 15 nm were sputtered over the synthesized anodic oxide plate (Figure 1.c) to make a W-WO_x-Pt stack for fluctuation-enhanced sensing measurements (FES) using our own noise measurement unit (Figure 1.e). After deposition, the sensors were annealed in ambient conditions at 500 °C for 2 hours using 5 °C/min heating/cooling rates (Figure 1.b). With this annealing process we obtained monoclinic phase of WO_3 , which is reported as an efficient gas sensing structure of WO_3 [5].

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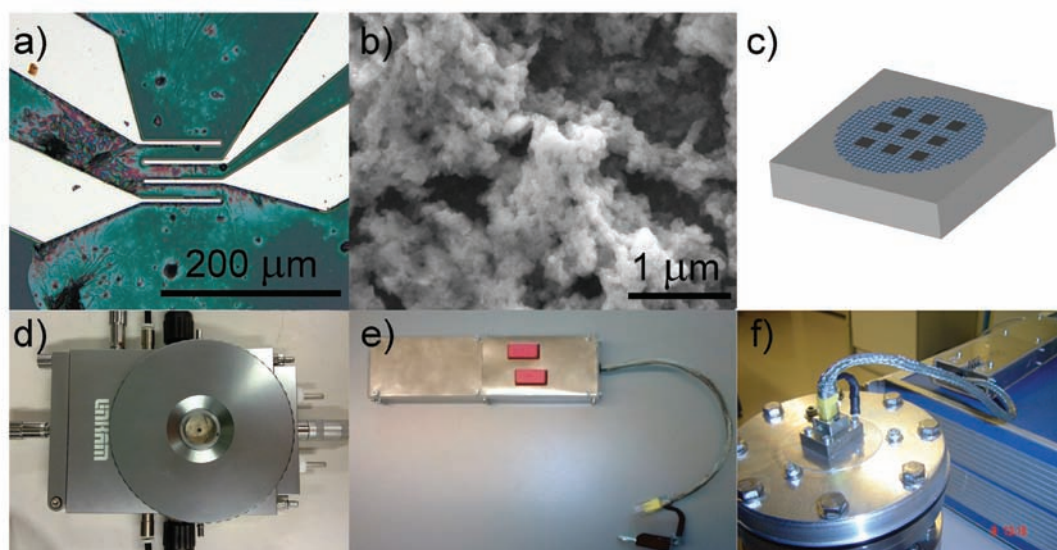


Figure 1 a) Deposited anodic WO_3 over Si/SiO_2 substrate between Pt electrodes, b) FESEM image of deposited and calcined WO_3 , c) schematic of sputtered Pt electrodes over anodic WO_3 on tungsten metal, c) Linkam THMS600 heating and freezing stage, e) noise measurement unit and f) in-house manufactured gas chamber.

The device performance was tested for H_2 (5000 ppm) and NO (90 ppm) gases in synthetic air buffer in a gas chamber of 500 ml volume (Figure 1.f). Alternatively the sensor can be tested in Linkam THMS600 Heating and Freezing Stage (Figure 1.d). The measurement devices as well as premixing gas blender were controlled in LabVIEW using custom self-made applications.

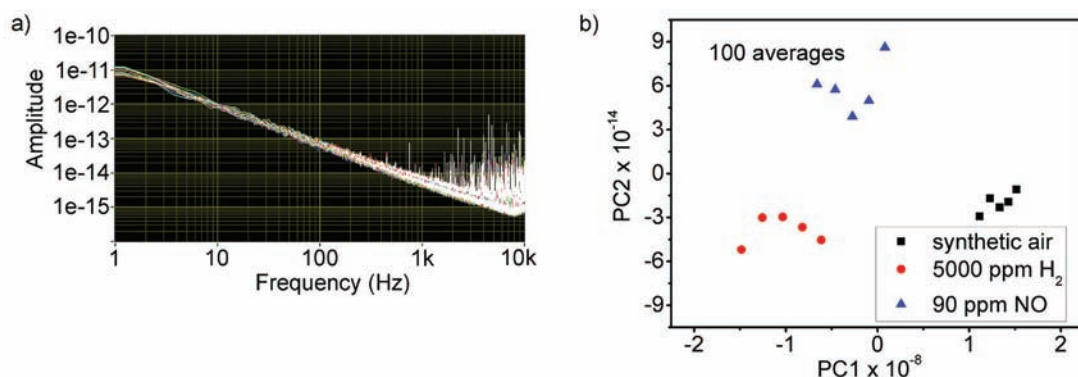


Figure 2 a) typical power spectral density (PSD) curves in noise measurements and b) PCA score plot of measurements performed with H_2 (5000 ppm) and NO (90 ppm) gases in synthetic air.

The score plot of noise measurements (Figure 2.e) shows a clear separation between loadings of synthetic air (black squares), H_2 (red circles) and NO (blue triangles). This is very promising result, as different analytes can be discriminated well. In ideal case, examining more analytes, they would make their own data groups into different locations of the PCA map; however in the practice, the groups are somewhat overlapping each other.

4 Relevance of the research

Traditional gas sensors often suffer from low selectivity to different gases. Fluctuation-enhanced gas sensitivity measurements with the manufactured WO_3 gas sensor prove to be selective method for measuring a few tested analyte gases. Health concerns about nitric oxides demand new kinds of devices to observe and reduce production of these pollutants caused by industries and transportation. Increased selectivity of gas sensors could make testing of pollution sources much more efficient.

References

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