

Layered thin film nanostructures of Pd/WO_{3-x} as resistance gas sensors

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Abstract. Layered nanostructures of tungsten trioxide WO_{3-x} about 62 nm thick, with a very thin film of palladium (about 3.3 nm) on the top, have been studied for gas-sensing application at temperatures 50°C and 120–130°C and low NO₂ and NH₃ concentrations in 6%, 30% or 45% relative humidity in the air. Thin film WO_{3-x} nanostructures were obtained by vacuum deposition on a common Si-SiO₂ substrate at room temperature and 120°C. The palladium was coated by vacuum evaporation at room temperature and $4 \cdot 10^{-6}$ mbar on WO_{3-x} layers obtained at two different substrate temperatures. The average rate of growth of the films, controlled by a QCM, was 0.1–0.2 nm/s. A multi-channel (four-channel interdigital gold electrodes) planar resistance gas sensor structure was used in the experiments. The surface of the nanostructures was characterized by means of the AFM method. Good sensor results have been observed at these layered nanostructures with an increasing resistance for NO₂ molecules and decreasing resistance for NH₃ molecules in a humid air atmosphere. The interaction and recovery speed were higher in the case of the nanostructure obtained at room temperature.

Key words: tungsten trioxide, palladium, layered nanostructure, resistance sensor, nitrogen dioxide, ammonia.

1. Introduction

Recently, multilayer structures, especially layered nanostructures, have been used extensively to improve the sensitivity and reliability of conventional chemical and biological sensors [1–12]. For instance, thin single films of Pd and WO₃ do not ensure a sufficient sensitivity towards hydrogen molecules [5, 13].

In one of the latest papers [5] a layered nanostructure with 50 nm of WO₃ and 18 nm of Pd on the top was successfully tested with regard to a medium concentration of hydrogen in dry air by means of a Surface Acoustic Wave and electrical resistance planar methods. Placing a thin metal film on the surface of the thin semiconductor film always decreases the entire resistance of the sensor structure. Consequently, measurements for such a structure are much easier than in the case of single films, where the resistance often exceeds the range of the apparatus. In the case of two different exemplary layered nanostructures, like cobalt phthalocyanine 200 nm and Pd 20 nm and tungsten oxide 50 nm with 18 nm of Pd, the relative increase of electrical conductivity between the single and layered nanostructures is about two and three orders of magnitude higher, respectively [5, 13–15]. A layered nanostructure of the semiconductor and metal on the top always increases its electrical surface conductivity, permitting easy investigations of the sensor properties by means of the resistance method.

In the sensor technology, tungsten trioxide (WO₃) is one of the most widely used materials due to its fast response with a high sensitivity to different gases. It has been shown that the addition of an appropriate amount of metal additives promotes chemical reactions by reducing the activation en-

ergy between the film surface and the specific gas. It also increases the response and decreases the maximum operating temperature of the sensor. In the case of sensing H₂ and NO₂, the modification of metal oxides [8–10] (especially WO₃) by metal additives such as Pt, Pd, or Au by applying different techniques intensive investigations are under way. It is known that the sensitivity of gas depends on the large surface area and porosity, both of which are affected by the preparation method. We made a series of samples with a different morphology in order to introduce a catalyst by means of PVD.

The main aim of the present paper is to investigate the sensor properties at low concentrations of NO₂ (100–2000 ppm) and NH₃ (5–25 ppm) in dry and wet air of the layered sensor nanostructures with tungsten trioxide (WO_{3-x}) films and a palladium (Pd) film on the top. The WO₃ films were obtained at two different substrate temperatures – room temperature and 120°C, whereas the catalytic nanofilms of Pd were prepared only at room temperature. These two different technological configurations allow to compare their sensor properties (sensitivity, response and regeneration ability) at the selected interaction temperatures, which are lower (50°C), equal (120°C) and slightly exceeding (130°C) the higher technological substrate temperature.

2. Experiments

2.1. Resistance planar sensor details. The sensing structure of the resistance gas sensor used in the experiments is a four-channel thin tungsten trioxide (WO_{3-x}) film covered by a thin palladium film in two channels. The sensor consists of four interdigital electrodes (period 100 μm), covered by a WO_{3-x} or Pd/WO_{3-x} layered sensor structure.

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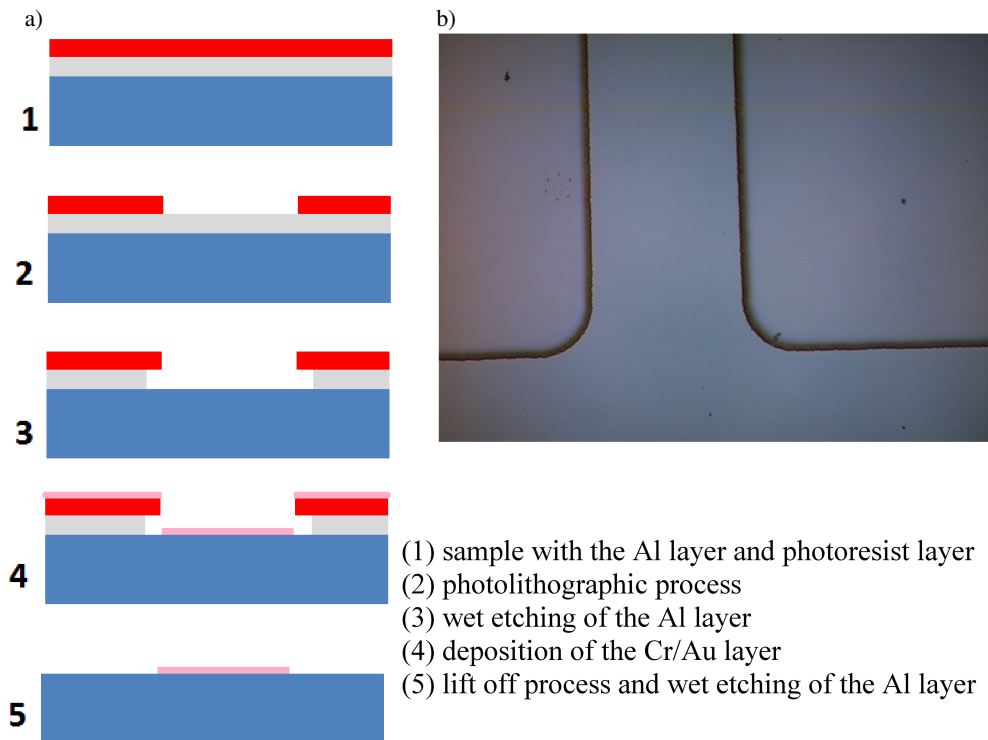


Fig. 1. a) Steps of lift-off process with sacrificial layer, b) shape a fragment of the electrode after the lift-off process (AFM image)

The basic structure is produced by means of the lift-off process. The substrate materials, silicon wafers, were covered by a $2\ \mu\text{m}$ silicon oxide film which was attained by thermal oxidation. The interdigital electrodes and heater (optionally) are achieved in a two-step process, which is described further on. In order to get a sharp edge of the electrodes and a smooth growth of the sensitive material, the lift-off method is used. It consists of an aluminium layer about $200\ \text{nm}$ thick. The deposition of the aluminium layer onto the substrate was performed by means of DC magnetron sputtering an aluminium target under argon gas at a chamber pressure of $5 \cdot 10^{-3}$ mbar. Subsequently, the photoresist is spin-coated onto the substrate and structured by means of a photolithography process. Afterwards the exposed aluminium is chemically etched. A strong undercut of the photoresist warrants a trapezoidal shape of the final structure. The subsequent metallization of the electrode is performed by e-beam evaporation. In order to obtain a good adhesion of the gold film, a $30\ \text{nm}$ chromium adhesion layer is deposited onto the substrate. Then a $90\text{--}100\ \text{nm}$ gold layer is deposited on top of the chromium. The lift-off process is applied on the photoresist and the sacrificial layer is removed by chemical etching. Schematically this process is shown in Fig. 1.

2.2. Details of the layered nanostructure. In order to get a gas sensing structure consisting of a metal oxide layer and

a palladium layer on the electrodes no extra layer or photolithographic process need be used. The gas sensitive WO_{3-x} layer is deposited on top of the interdigital electrodes using a mechanical mask with apertures, about few millimetres in diameter, through which the desired pattern is evaporated. The active thin films of amorphous tungsten trioxide (WO_{3-x}) were prepared by thermal evaporation of WO_3 powders of 99.99% purity (*Fluka*) from a molybdenum boat onto the electrodes. The substrate was specially, optionally, heated up to 120°C during the evaporation process. The evaporation chamber was pumped out to a vacuum of $2 \cdot 10^{-6}$ mbar. The sublimation temperature was about 900°C to 1000°C when WO_3 powder was used. The average rate of the growth of the film, controlled by a quartz monitor, was $0.1\text{--}0.2\ \text{nm/s}$. The film thickness of WO_3 amounted to about $50\text{--}100\ \text{nm}$. The WO_3 layer may also be covered with Pd clusters due to the evaporation process. The Pd clusters also act as a catalyst in the surface reaction of various target gases. The palladium was coated by vacuum evaporation at $4 \cdot 10^{-6}$ mbar on an previously obtained WO_{3-x} layer. The thickness of the Pd film was about several nanometers (estimated to $3.3\ \text{nm}$). The four-channel resistance sensors are summarized in Table 1. Figure 2a shows a schematic view of the sensor, and in Fig. 2b the details of the single channel are presented.

Table 1
Four-channel resistance sensor

CH 1	62 nmWO ₃ (RT) + 3.3 nm Pd (RT)	
CH 2 – overload (R too high)	62 nm WO ₃ (RT)	
CH 3	63 nm WO ₃ (120°C) + 3.3 nm Pd (RT)	
CH 4 – overload (R too high)	63 nm WO ₃ (120°C)	
RT – at room temperature process PVD		

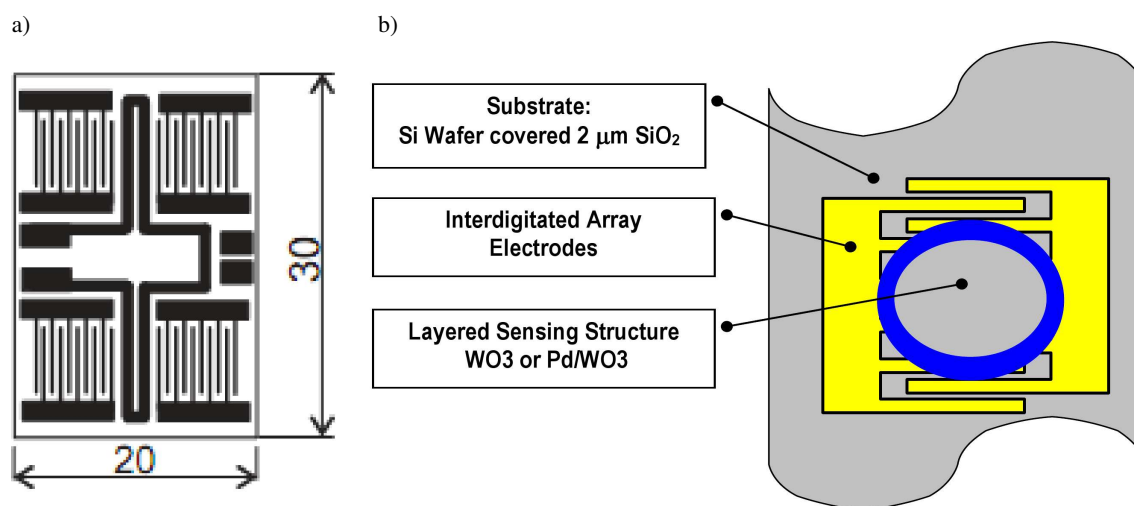


Fig. 2. a) The shape of the channels (dimensions in mm), b) a schematic image of the interdigital Cr/Au electrodes upon which the layered sensing structures are deposited (one section)

Atomic force microscopy (AFM) was used to obtain information about the surface topography of the films. Surface morphology and the roughness of the sensing structures were examined using Atomic Force Microscopy (AFM, NT-MDT model NTEGRA PRIMA). The images were taken in the semi-contact mode in ambient air (RH 50(10)% and 23(2)°C) with a silicon cantilever (HA_NC with a resonant frequency of about 240 kHz). The root-mean-square (RMS) roughness was calculated with the manufacturer's AFM software on images of $5 \mu\text{m} \times 5 \mu\text{m}$ scan size. The AFM pictures of the obtained layered nanostructures of WO_{3-x} and Pd/WO_{3-x} are shown in Fig. 3. The morphology of two-layered structures is quite different.

The nucleation and growth of Pd clusters on the surfaces of the films by thermal evaporation deposition of an ultrathin film of 3.3 nm Pd were investigated and visualized by means of the AFM method. The microstructure changes in WO₃ films due to covering Pd films and the deposition of WO₃ onto the substrate at different temperatures were studied using AFM. Figure 3 shows the surface microstructure over a $1 \mu\text{m} \times 1 \mu\text{m}$ area concerning a 62(1) nm thick WO₃ film

before and after the deposition of 3.3 nm Pd. In these images, the z-direction is highly magnified with respect to the lateral dimensions. The effect of the substrate temperature on the growth of WO₃ and the film morphology during the film deposition were characterized concerning two double channels grown at RT (25°C) and 120°C substrate temperatures (see Table 1). The results (CH2 @ RT and CH4@120°C) indicated that the film grown at 120°C substrate temperature showed larger and more compact surface grains, which could be attributed to a higher granular growth rate at elevated temperature. The AFM images of the sensing structures onto the electrodes and between the electrodes are shown. From CH1 and CH2 (WO₃ deposited at room temperature), a flat surface with small clusters, with RMS below 2nm, can be observed. AFM images of the sensing structure with WO₃ deposited at 120°C are shown in Fig. 3 – CH3 and CH4. It can be seen that the surface shows a large quantity of islands with different diameters dispersed over the whole scanned area (CH4). In CH3 and CH4 the root mean square (RMS) roughness is at least two times higher than in CH1 and CH2.

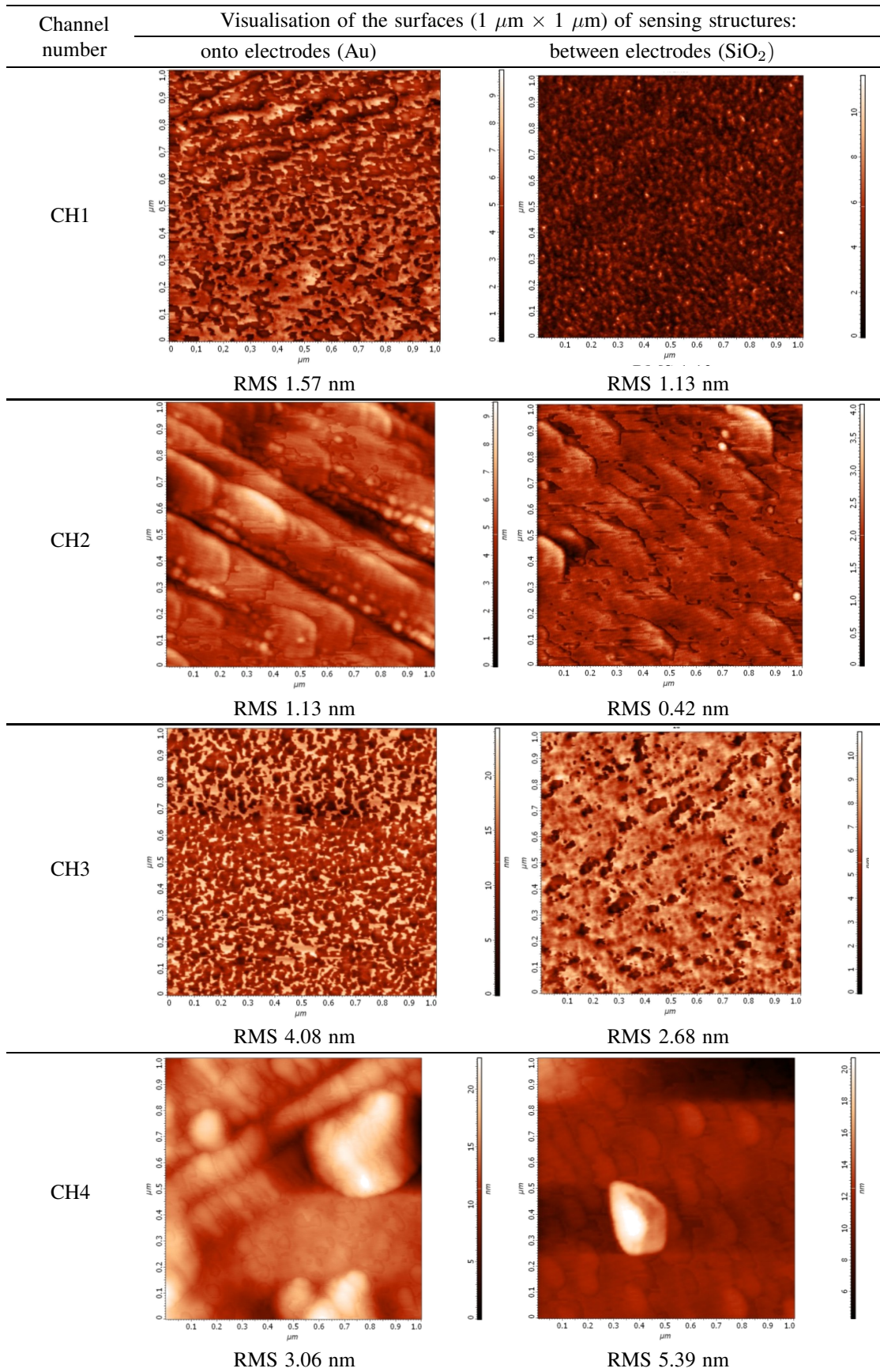


Fig. 3. AFM images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) comparing the surface morphology of an uncovered WO_3 and a covered WO_3 film by Pd film. The RMS roughness concerns different channels over a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area (calculated with the manufacturer's AFM software)

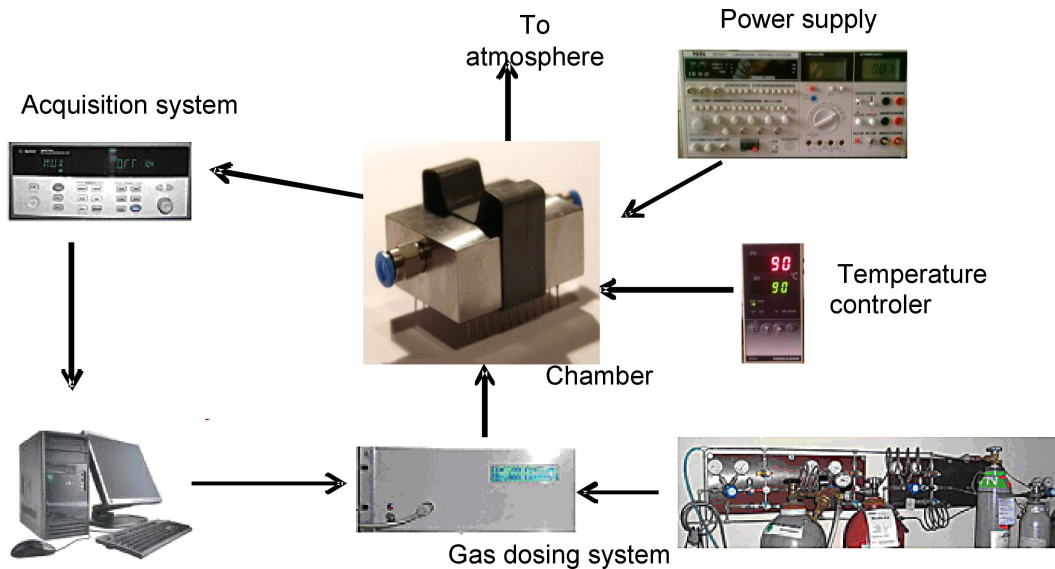


Fig. 4. The experimental set-up

3. The experimental set-up

The experimental set-up is based on electrical planar resistance changes in a 4-channel sensor system. This set-up is schematically shown in Fig. 4. The total flow rate of the gas mixture 500 ml/min was used in all the measurements. The volume of the measuring chamber was about 5 cm³. The sensor sample was tested in a computer-controlled system. Gases of 100–500 ppm NO₂ in dry air and 5–25 ppm NH₃ in synthetic wet air (30 and 45% RH) were mixed using mass flow controllers (Bronkhorst Hi-Tech). The temperature was measured and controlled using a Pt 100 thermoresistor sensor adjacent to the tested structure.

4. Results

The obtained results for the 4-channel sample with different layered nanostructures, in the case of nitrogen dioxide and ammonia detection are shown in Figs. 5–10. Unfortunately, the channels with single WO_{3-x} films (sensors 2 and 4 in Table 1) were not measurable, because of too high resistances (above 100 MΩ), so we show, the results for the CH1 and CH3 channels only. Maximum resistances of these sensors are about 10 Ω to 57 Ω. In every figure the symbols mean: R1 – nanostructure of 62 nm WO_{3-x} and 3.3 nm of Pd, both prepared at room temperature (RT) of the substrate, R3 – nanostructure of 62 nm WO_{3-x} prepared at 120°C of the substrate and 3.3 nm of Pd – at room temperature (RT).

Relative changes of the resistances, R/R_{max}, versus the investigated NO₂ concentration in dry air (RH 6%) at 50°C are shown in Fig. 5. The sample resistance decreases inconsiderably versus the NO₂ concentration. We can see that this interaction is changed after thermal aging. The samples are burnt-in at 150°C for 24 hours in ambient atmosphere. After this stabilization process the character of the resistance changes differ – now the resistance increases under the influence of NO₂ (Fig. 6).

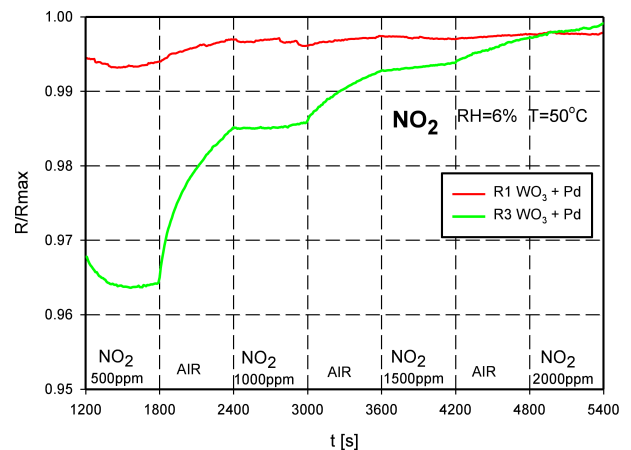


Fig. 5. Interaction of two nanostructures of Pd/WO_{3-x} with NO₂ at 50°C, R1 – nanostructure of 62 nm WO_{3-x} and 3.3 nm of Pd, both prepared at room temperature (RT) of the substrate, R3 – nanostructure of 62 nm WO_{3-x} prepared at 120°C of the substrate and 3.3 nm of Pd – at RT. R1_{max}=23Ω, R3_{max}=57Ω

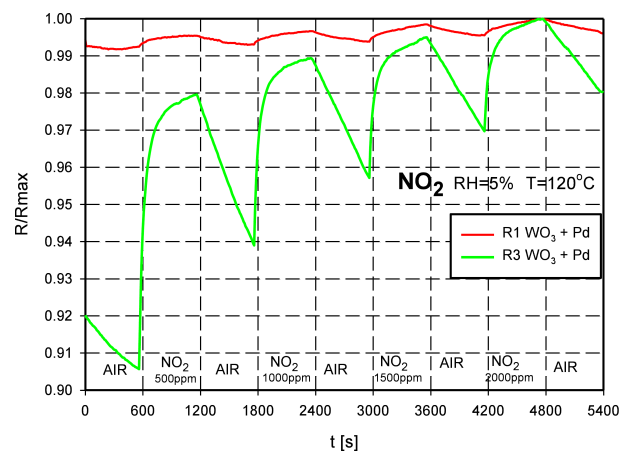


Fig. 6. Interaction of two nanostructures of Pd/WO_{3-x} with NO₂ at 120°C. R1_{max}=18Ω, R3_{max}=36Ω (after thermal aging)

The interaction of two nanostructures WO_{3-x} and Pd with NO_2 at a temperature increased to $120^\circ C$ is shown in Fig. 7. At this temperature the steady-state resistance (R1) of the structure with the WO_{3-x} film prepared at RT can be observed. For R1 response times t_{90} (90% level) are about 80 sec at 100 ppm NO_2 and 50 sec at 200 ppm NO_2 concentration in dry air and in the case of R3 they are 950 sec and 400 sec, respectively. The recovery times t_5 (5% level) for R1 are 130 sec at 100 ppm and 300 sec at 200 ppm NO_2 concentration in dry air and in the case of R3 they are 100 sec and 300 sec, respectively. At this higher interaction temperature, the resistance of the sample increases.

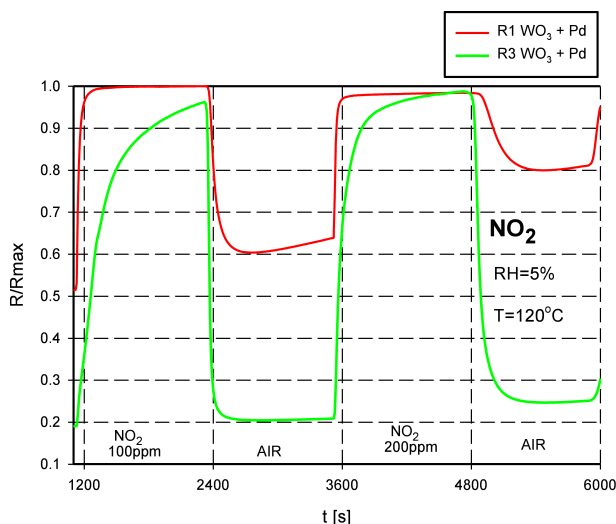


Fig. 7. Interaction of two nanostructures of Pd/ WO_{3-x} on the Si-SiO₂ substrate with NO_2 at $120^\circ C$, $R1_{max}=18\Omega$, $R3_{max}=36\Omega$

The interaction of two nanostructures of WO_{3-x} and Pd with NH_3 at the temperature $130^\circ C$ and RH of the air about 45% is shown in Fig. 8. At this temperature the steady-state in both samples (R1 and R3) at NH_3 concentrations of 5–25 ppm can be observed. The response and recovery times concerning R1 are presented in Table 2. However, the regeneration process is much faster in the nanostructure with the WO_{3-x} film prepared at room temperature (R1). At this higher interaction temperature, the resistance of the sample decreases.

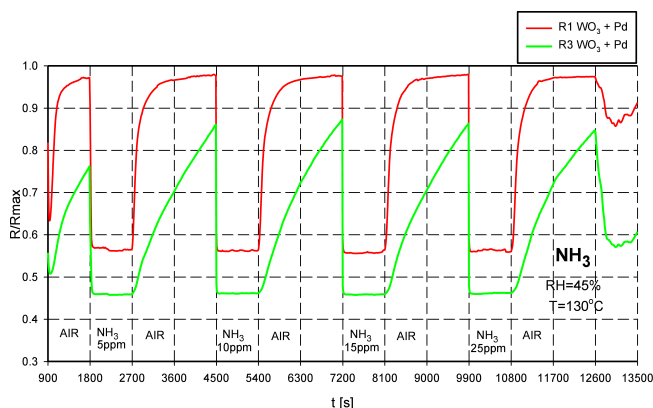


Fig. 8. Interaction of two nanostructures of Pd/ WO_{3-x} with NH_3 at $130^\circ C$, and RH of 45% $R1_{max}=13\Omega$, $R3_{max}=12\Omega$

Table 2

The response time t_{90} and recovery time t_5 of CH1 sensor for different concentrations of ammonia gas in synthetic air (R1 sensor signal)

	Concentrations of NH_3 in wet air RH 45%, in ppm			
	5	10	15	25
Response time t_{90} in sec	40	20	8	5
Recovery time t_5 in sec	390	410	380	410

In Fig. 9 we can see, that no influence of the relative humidity (RH) of the mixture of air and NH_3 on the resistance of the sensors is to be observed. In the case of RH 30% and 45% the changes in the resistances and speed responses are essentially the same, but recovery time is longer in lower humidity of the air.

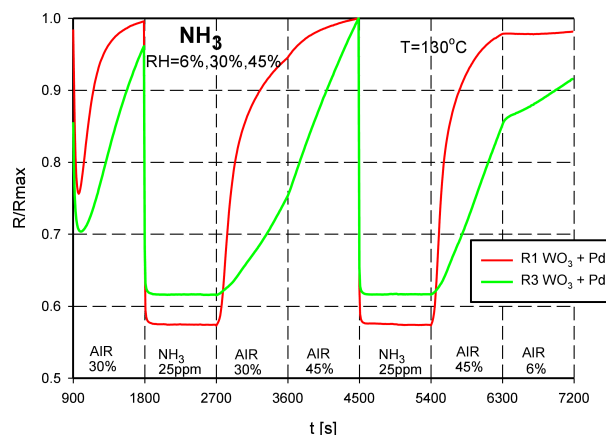


Fig. 9. Interaction of two nanostructures of Pd/ WO_{3-x} with NH_3 at $130^\circ C$, and RH of 30%, 45% and 6%. $R1_{max}=13\Omega$, $R3_{max}=11\Omega$

The response and recovery times for R1 are presented in Table 3.

Table 3

The response time t_{90} and recovery time t_5 of CH1 sensor for the same concentrations (25 ppm) of ammonia gas in synthetic air at different relative humidity of gas mixture (R1 sensor signal)

	Air RH, in %	
	30	45
Response time t_{90} in sec	15	18
Recovery time t_5 in sec	950	600

The interaction of the two nanostructures of WO_{3-x} and Pd with 25 ppm of NH_3 and 40 ppm of NO_2 at the temperature $120^\circ C$ and RH of the air 6% is shown in Fig. 10. Again the steady-state in both samples (R1 and R3) in the presence of NH_3 molecules can be observed. Besides, the repeatability is generally quite good.

In this paper we have focused our attention on the sensing properties of thin evaporated metal oxide films (WO_{3-x}) covered with palladium. We have shown that thin metal oxide films presented here, prepared by thermal evaporation, may be employed as toxic gas (NH_3 and NO_2) sensing material. The sensors exhibit a relatively good sensitivity, especially to ammonia concentrations, and generally also good dynamical properties, as well as stable parameters at relatively low temperature (below $150^\circ C$). Traditional MOS sensors operate

with surface temperatures of 250–600°C and require a heated substrate which is often fragile. The sensors require high power (0.5–2 W) to operate the on-chip heaters, limiting their mobility. Thus, our sensor provides potentially a low power consumption by toxic gas sensors. Moreover, the sensor response does not obtain an ideally constant level at higher concentrations of toxic gasses, and more work is still required to improve the sensing properties of our sensors. The development of a resistance toxic gas detector has been partially successful, but further investigations are required to optimize sensor coatings which would be more sensitive to low concentrations of toxic gasses and achieve a long-term stability at low temperatures.

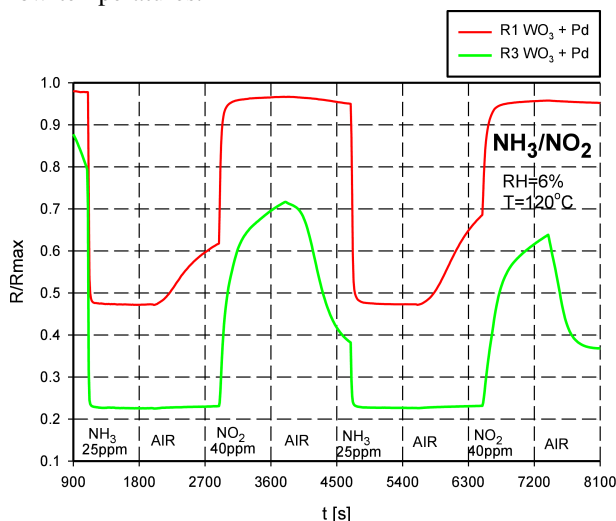


Fig. 10. Sensor repeatability in NH₃/NO₂ gas. R1max=16Ω, R3max=20Ω

5. Summary

The gas sensing properties of the thin WO_{3-x} film covered with an ultra-thin film of Pd sensors indicate that these sensors exhibit a quite high sensitivity, an excellent selectivity and a quick response to NO₂ and NH₃ gas. The nanostructures of WO_{3-x} and Pd have been prepared and tested in a 4-channel resistance sensor system. However, only structures with palladium on the top were measurable in the applied apparatus. At higher interaction temperatures in the layered nanostructures the resistance increases in the presence of oxidizing NO₂ gas molecules and their resistance decreases in the case of reducing NH₃ gas molecules. In the case of NO₂ molecules the steady-state depends on the surface morphology and is much faster in the case of tungsten trioxide prepared at room temperature. The regeneration cycle is also faster in the same structure in the case of strong reducing NH₃ molecules. Both investigated nanostructures show a good repeatability in the presence of NH₃/NO₂ dosing cycles, which is very important from the practical point of view. Investigations of the WO₃/Pd sensor structure show, that at 5 ppm NH₃ and 100 ppm NO₂ the responses reach the saturation level. A relative humidity of the air does not affect the responses of the sensors. We can also conclude that the temperature of the substrate in technological processes influences the microstructures of the sensors layers.

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