Layered thin film nanostructures of Pd/\text{WO}_3-x \\
\text{as resistance gas sensors}

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Abstract. Layered nanostructures of tungsten trioxide \text{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 \text{NO}_2 and \text{NH}_3 concentrations in 6%, 30% or 45% relative humidity in the air. Thin film \text{WO}_{3-x} nanostructures were obtained by vacuum deposition on a common Si-SiO$_2$ substrate at room temperature and 120°C. The palladium was coated by vacuum evaporation at room temperature and 4 \cdot 10^{-6} \text{ mbar} on \text{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 \text{NO}_2 molecules and decreasing resistance for \text{NH}_3 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 \text{WO}_3 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 \text{WO}_3 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 (\text{WO}_3) 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 energy 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 \text{H}_2 and \text{NO}_2, the modification of metal oxides [8–10] (especially \text{WO}_3) 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 \text{NO}_2 (100–2000 ppm) and \text{NH}_3 (5–25 ppm) in dry and wet air of the layered sensor nanostructures with tungsten trioxide (\text{WO}_{3-x}) films and a palladium (Pd) film on the top. The \text{WO}_3 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 (\text{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 \text{WO}_{3-x} or Pd/\text{WO}_{3-x} layered sensor structure.
The basic structure is produced by means of the lift-off process. The substrate materials, silicon wafers, were covered by a 2 µm 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 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 nm chromium adhesion layer is deposited onto the substrate. Then a 90–100 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$_3$) 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 0.1–0.2 nm/s. The film thickness of WO$_3$ amounted to about 50–100 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 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.
Layered thin film nanostructures of Pd/WO3-x as resistance gas sensors

Table 1
Four-channel resistance sensor

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<tbody>
<tr>
<td>CH 1</td>
<td>62 nmWO3 (RT) + 3.3 nm Pd (RT)</td>
<td></td>
</tr>
<tr>
<td>CH 2 – overload (R too high)</td>
<td>62 nm WO3 (RT)</td>
<td></td>
</tr>
<tr>
<td>CH 3</td>
<td>63 nm WO3 (120°C) + 3.3 nm Pd (RT)</td>
<td></td>
</tr>
<tr>
<td>CH 4 – overload (R too high)</td>
<td>63 nm WO3 (120°C)</td>
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RT – at room temperature process PVD

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 µm × 5 µm scan size. The AFM pictures of the obtained layered nanostructures of WO3-x and Pd/WO3-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 µm × 1 µm 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.
<table>
<thead>
<tr>
<th>Channel number</th>
<th>Visualisation of the surfaces (1 $\mu$m × 1 $\mu$m) of sensing structures: onto electrodes (Au)</th>
<th>between electrodes (SiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH1</td>
<td><img src="image1.png" alt="AFM Image 1" /> RMS 1.57 nm</td>
<td><img src="image2.png" alt="AFM Image 2" />  RMS 1.13 nm</td>
</tr>
<tr>
<td>CH2</td>
<td><img src="image3.png" alt="AFM Image 3" /> RMS 1.13 nm</td>
<td><img src="image4.png" alt="AFM Image 4" />  RMS 0.42 nm</td>
</tr>
<tr>
<td>CH3</td>
<td><img src="image5.png" alt="AFM Image 5" /> RMS 4.08 nm</td>
<td><img src="image6.png" alt="AFM Image 6" />  RMS 2.68 nm</td>
</tr>
<tr>
<td>CH4</td>
<td><img src="image7.png" alt="AFM Image 7" /> RMS 3.06 nm</td>
<td><img src="image8.png" alt="AFM Image 8" />  RMS 5.39 nm</td>
</tr>
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</table>

Fig. 3. AFM images (1 $\mu$m × 1 $\mu$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 $\mu$m × 5 $\mu$m area (calculated with the manufacturer’s AFM software).
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 cm$^3$. The sensor sample was tested in a computer-controlled system. Gases of 100–500 ppm NO$_2$ in dry air and 5–25 ppm NH$_3$ 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 M$\Omega$), so we show, the results for the CH1 and CH3 channels only. Maximum resistances of these sensors are about 10 $\Omega$ to 57 $\Omega$. 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 $^\circ$C of the substrate and 3.3 nm of Pd – at RT. R1max=23 $\Omega$, R3max=57 $\Omega$.

Relative changes of the resistances, R/Rmax, versus the investigated NO$_2$ concentration in dry air (RH 6%) at 50$^\circ$C are shown in Fig. 5. The sample resistance decreases considerably versus the NO$_2$ concentration. We can see that this interaction is changed after thermal aging. The samples are burnt-in at 150$^\circ$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 NO$_2$ (Fig. 6).
The interaction of two nanostructures \( \text{WO}_3-x \) 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 \( \text{WO}_3-x \) 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/\( \text{WO}_3-x \) on the Si-SiO\(_2\) substrate with NO\(_2\) at 120\(^\circ\)C, R1\(_{\text{max}}\)=18\(\Omega\), R3\(_{\text{max}}\)=36\(\Omega\)](image)

The interaction of two nanostructures of \( \text{WO}_3-x \) 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 \( \text{WO}_3-x \) 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/\( \text{WO}_3-x \) with NH\(_3\) at 130\(^\circ\)C, and RH of 45\%, R1\(_{\text{max}}\)=13\(\Omega\), R3\(_{\text{max}}\)=11\(\Omega\)](image)

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/\( \text{WO}_3-x \) with NH\(_3\) at 130\(^\circ\)C, and RH of 30\%, 45\% and 6%. R1\(_{\text{max}}\)=13\(\Omega\), R3\(_{\text{max}}\)=11\(\Omega\)](image)

In this paper we have focused our attention on the sensing properties of thin evaporated metal oxide films (\( \text{WO}_3-x \)) 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 gases, 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.

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