

Optimization of Pt electrode porosity for improved hydrogen gas sensing performance in vertical Pt/TiO₂/Pt chemiresistive gas sensors

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Abstract

The transition of chemiresistive hydrogen gas sensor architecture from in-plane to vertical electrode configuration offers advantages for sensitivity, device integration and manufacturing scalability. The main drawback of the vertical arrangement is the limited analyte access due to the poor permeability of the top electrode, resulting in a sensor response dominated by lateral diffusion beneath this electrode. Previous studies have shown that sensors with the top electrode width of ~100-200 nm or less exhibit significantly enhanced response to H₂ compared to sensors with wider top electrode. Similar or even higher responses have been achieved in sensors utilizing wide but nanoporous top Pt electrodes with very narrow Pt-covered areas. In this work, we optimize the porosity of such nanoporous Pt electrodes prepared via annealing-induced reduction of PtO_x films to maximize the sensor's response to H₂. The porosity and corresponding response to H₂ is evaluated as a function of the precursor PtO_x film thickness and annealing temperature. It is shown that optimizing the Pt porosity can lead to a 100-fold increase in the sensor's response to 10 000 ppm H₂, demonstrating an effective strategy for high-performance vertical chemiresistive gas sensors.

Introduction

Highly sensitive hydrogen gas sensors with a low limit of detection and fast response/recovery times are in ever increasing demand as they are crucial for ensuring safety in the whole chain of the emerging hydrogen economy. Chemiresistive metal oxide semiconductor gas sensors based on TiO₂ have been widely investigated due to their non-toxicity^{[1][2]}, chemical stability^{[3][4]}, cost-efficiency, and high resistive response to hydrogen gas^{[5][6]}. The most common sensor design consists of interdigital comb-like electrodes^{[7][8]}

deposited on top of or under a polycrystalline TiO_2 film, making the gas-sensing material between the electrodes readily accessible to the surrounding atmosphere.

The magnitude of the response depends on the electric field intensity inside the metal oxide^[9] and can be improved by catalytic agents such as platinum or palladium^[10]. Gas sensors in vertical Pt/ TiO_2 /Pt arrangement can be fabricated with the inter-electrode distance down to a few tens of nm, achieving extremely high electric intensity in the TiO_2 film between the electrodes, potentially providing a very high response. Moreover, the vertical arrangement allows for combining a gas sensor and memristor in a single device^[11], which can be exploited in sensors with built-in memristive memory^{[12][13]} or in-sensor computing^{[14][15]}. However, the active TiO_2 region in this arrangement is not directly exposed to the surrounding atmosphere as it is covered by the top electrode (TE). The H_2 gas diffuses laterally under the electrode from the electrode edges. In accord with the lateral diffusion mechanism, it has been shown that a great leap in sensitivity is achieved when the width of the TE narrows to $\sim 100\text{-}200$ nm and less^[16], allowing reactant/product diffusion to and from the whole active TiO_2 region subjected to high electric field intensity. To achieve such a small width of the TE, an e-beam lithography is required. Moreover, the small active area of the gas sensor typically leads to extremely high baseline resistance, potentially limiting observation of response to low H_2 concentrations.

To significantly increase the active area of the gas sensor while maintaining the benefits of the very narrow ($< \sim 100\text{-}200$ nm) top Pt electrode, a nanoporous or otherwise nanopatterned TE is necessary. In this work, we produce such nanoporous Pt electrodes by depositing PtO_x via reactive magnetron sputtering through a shadow mask. The sensor structure is subsequently annealed, which transforms the PtO_x into a porous Pt layer in accord with previous studies^{[17][18]}. We study the resulting porosity of the Pt TE and corresponding response of the sensors to hydrogen as a function of the PtO_x thickness and annealing temperature to find the parameters leading to optimal porosity and sensitivity. We note that the sensors require annealing as the last fabrication step, even if a standard top Pt electrode is used, to achieve sufficient TiO_2 crystallinity and to smear the Pt/ TiO_2 interfaces, which could otherwise form Schottky barriers. Making the TE nanoporous by the method used here thus does not require any additional technological step, which makes the method feasible for large-scale production.

Materials and methods

Two series of sensor samples were used in this study, differing only in the TiO_2 thin film deposition method being either reactive magnetron sputtering or atomic layer deposition (ALD). Such duplication was necessary since our magnetron sputtered TiO_2 films provide superior H_2 gas sensing performance but suffer from limited reproducibility in this regard. On the other hand, the ALD-deposited films exhibit lower sensitivity but excellent reproducibility, which is key for determining the influence of porosity on the gas sensing performance over a set of samples.

All samples were fabricated as follows. First, a 200 μm wide Pt bottom electrode (BE) with a thickness of 30 nm was prepared on a polished (0001) Al_2O_3 substrate by DC magnetron sputtering through a shadow mask. In the next step, a uniform TiO_2 film was deposited on the sample either via reactive DC magnetron sputtering (50 nm thick film, 100 mm Ti target, constant discharge current of 200 mA at bias voltage of 335 V, oxygen partial pressure of 1.6×10^{-2} Pa, total $\text{O}_2 + \text{Ar}$ pressure of 9.6×10^{-1} Pa) or via ALD (30 nm thick film, pressure 2 mTorr, temperature 275°C, 1500 ms pulses of H_2O), excluding the contact pad areas. Finally, the ~ 200 μm wide PtO_x top electrode (TE) was prepared by reactive DC magnetron sputtering through a shadow mask with various thicknesses $d \in \{30; 45; 60; 75\}$ nm, oriented perpendicular to the BE to form a crossbar structure as shown in Fig. 1. The PtO_x deposition parameters for all samples were as follows. The total pressure of $\text{Ar} + \text{O}_2$ mixture during the deposition was 6×10^{-1} Pa, with the partial pressure of oxygen being 3.2×10^{-1} Pa. The voltage applied to the 1-inch Pt target was 470 V, sustaining plasma at 40 mA.

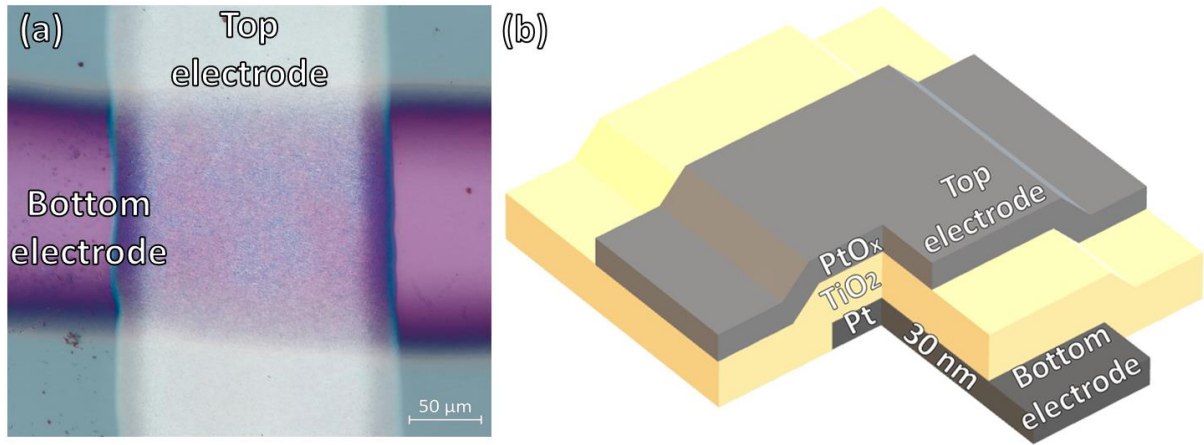


Figure 1: (a) Optical microscopy image and (b) schematic diagram of the BE-TE crossbar structure of the studied gas sensors.

After each sample has been annealed in air for 1 hour (ramp rate 6°/min) at one of the four temperatures (645°C, 660°C, 675°C, 690°C), the porosity of the TE was investigated by AFM topography measurements (NT-MDT Solver P47 Pro) in semi-contact mode using standard silicon probes (HA_NC ETALON, NT-MDT). The electrical transport and gas sensing measurements were performed in 2-contact configuration using Keithley 6487 Picoammeter/Voltage Source connected to the sample via gold wires and silver paste, with the BE grounded and TE voltage-biased. All measurements were performed in an enclosed chamber with controlled temperature, humidity and H_2 concentration in a gas flow regime with a constant flow of 100 sccm. The H_2 concentration was controlled by mixing a pure synthetic air and pre-mixed 10 000 ppm (or 100 ppm) H_2 in synthetic air using two mass flow controllers (Vögtlin Instruments).

To evaluate the composition of the PtO_x layers, reference PtO_x films were prepared in the same way as the top electrodes in studied sensors but without the TE patterning and analyzed by the energy-dispersive X-ray spectroscopy (EDS, JEOL JED-2300T CENTURIO SDD) and X-ray photoelectron spectroscopy (XPS, Omicron multiprobe system). For the EDS analysis a thicker (500 nm) reference PtO_x film was deposited to suppress the influence of the substrate.

Results and discussion

The EDS analysis of the as-deposited 500 nm thick reference PtO_x film showed the O/Pt ratio of 41.45 / 47.41 at. %, with the rest being carbon, corresponding to the chemical formula PtO_{0.87} (Fig. 2(a)). To obtain better insight into the composition of the prepared PtO_x layers, detailed XPS analysis (Fig. 2(b,c)) was performed on three reference samples for comparison – pure Pt film, as-deposited PtO_x film and PtO_x film annealed at 645 °C. The data show that the Pt 4f peak as well as other Pt peaks are present in all three cases, while the O 1s peak is only visible in as-deposited and annealed PtO_x films. Since the O 1s peak can be related not only to the PtO_x film but also to various oxygen-containing species adsorbed at the surface, the Pt 4f peaks (Pt4f7/2 and Pt4f5/2) were selected for detailed analysis. The table in Fig. 2(c) and the inset of Fig. 2(b) show that the as-deposited PtO_x film contains exclusively the peaks at the energy corresponding to Pt-O bonds, indicating pure PtO. On the other hand, the deconvolution of the Pt 4f peaks of the annealed PtO_x layer (Fig. 2(c)) clearly shows that it contains both Pt-Pt and Pt-O bonds with the Pt/PtO ratio of 0.45. Although this result indicates that the reduction of PtO_x to Pt is incomplete, it will be shown later that it is sufficient for our purposes. The pure Pt film, shown for comparison, contains mostly Pt-Pt bonds with only a small fraction (~15%) of Pt-O bonds as expected.

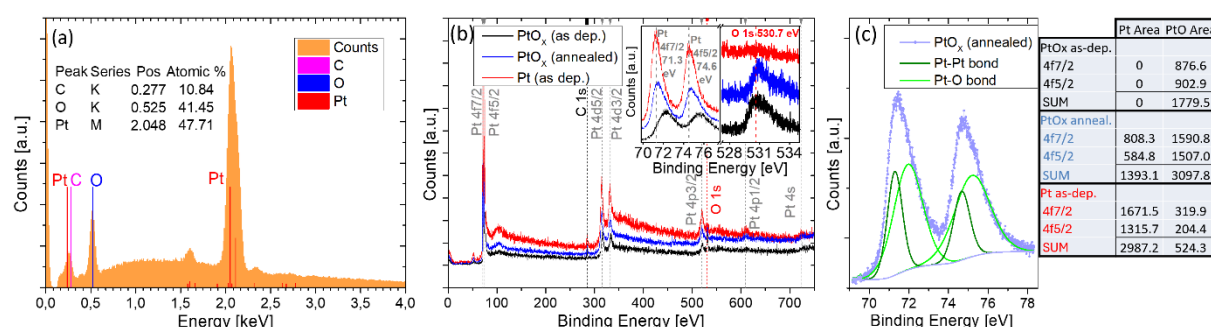


Figure 2: (a) EDS spectra of a reference as-deposited 500 nm thick PtO_x film, (b) XPS spectra of a Pt film (red) and the PtO_x film before (black) and after (blue) annealing at 645 °C. The inset shows detail of Pt 4f peaks (left) and the O 1s peak (right). (c) Deconvolution of Pt 4f peaks of the PtO_x film after annealing showing that the Pt 4f peaks are composed of two sub-peaks corresponding to Pt-Pt and Pt-O bonds. The areas under the Pt-Pt and Pt-O sub-peaks of the Pt 4f peaks for all three samples (Pt, PtO_x as-deposited, PtO_x annealed) are shown in the table.

The transformation of PtO_x to Pt is evident from measurement of the TE resistance, which decreased from several tens of $\text{k}\Omega$ (depending on the PtO_x thickness) to several tens of Ω after annealing (Fig. 3). Despite the incomplete PtO_x reduction indicated by the XPS analysis, we thus consider this transformation to be sufficient for our purposes since TE with the resistance of several tens of Ω is perfectly suitable for gas sensors of this type.

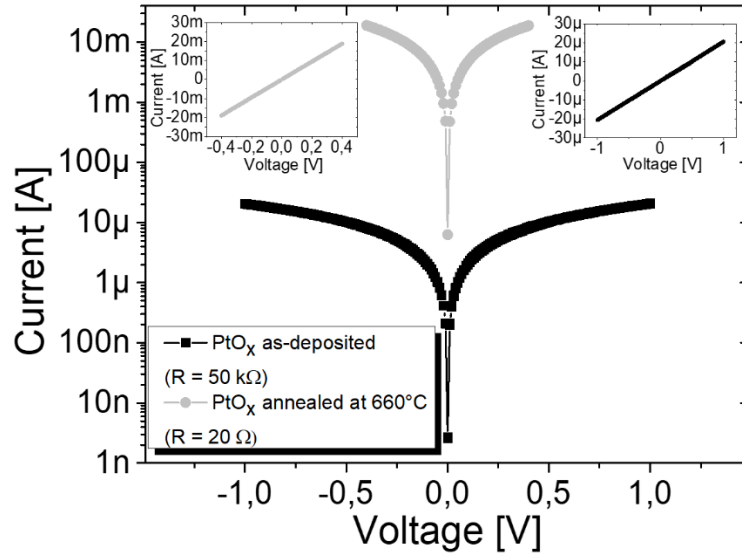


Figure 3: Typical current vs. voltage characteristics of the top PtO_x (as-deposited, black squares) and Pt (after annealing at 660 °C, gray circles) top electrode in logarithmic scale. Insets show the same data on a linear scale.

In the AFM topography scans the temperature-induced reduction of the PtO_x film is revealed as an increase of the surface roughness and formation of pores. Panels (a) and (d) of Fig. 4 show a matrix of $5 \times 5 \mu\text{m}$ AFM topography images of the studied samples with magnetron-deposited (panel(a)) and ALD-deposited (panel(d)) TiO_2 thin films, in which the thickness d of the precursor PtO_x film was varied between 30 – 75 nm and the annealing temperature T_A ranged from 645 to 690 °C. The AFM topography images clearly show that the porosity significantly depends on both varied parameters. Samples with higher thickness d annealed at lower temperatures show only a scarce number of small pores. With increasing T_A , the size of the pores increases. With decreasing d , we observe an increasing number of pores of small to mediocre size. Since neither the size, shape, nor density of the pores can be directly associated with the resulting gas sensing performance, a numerical approach is taken.

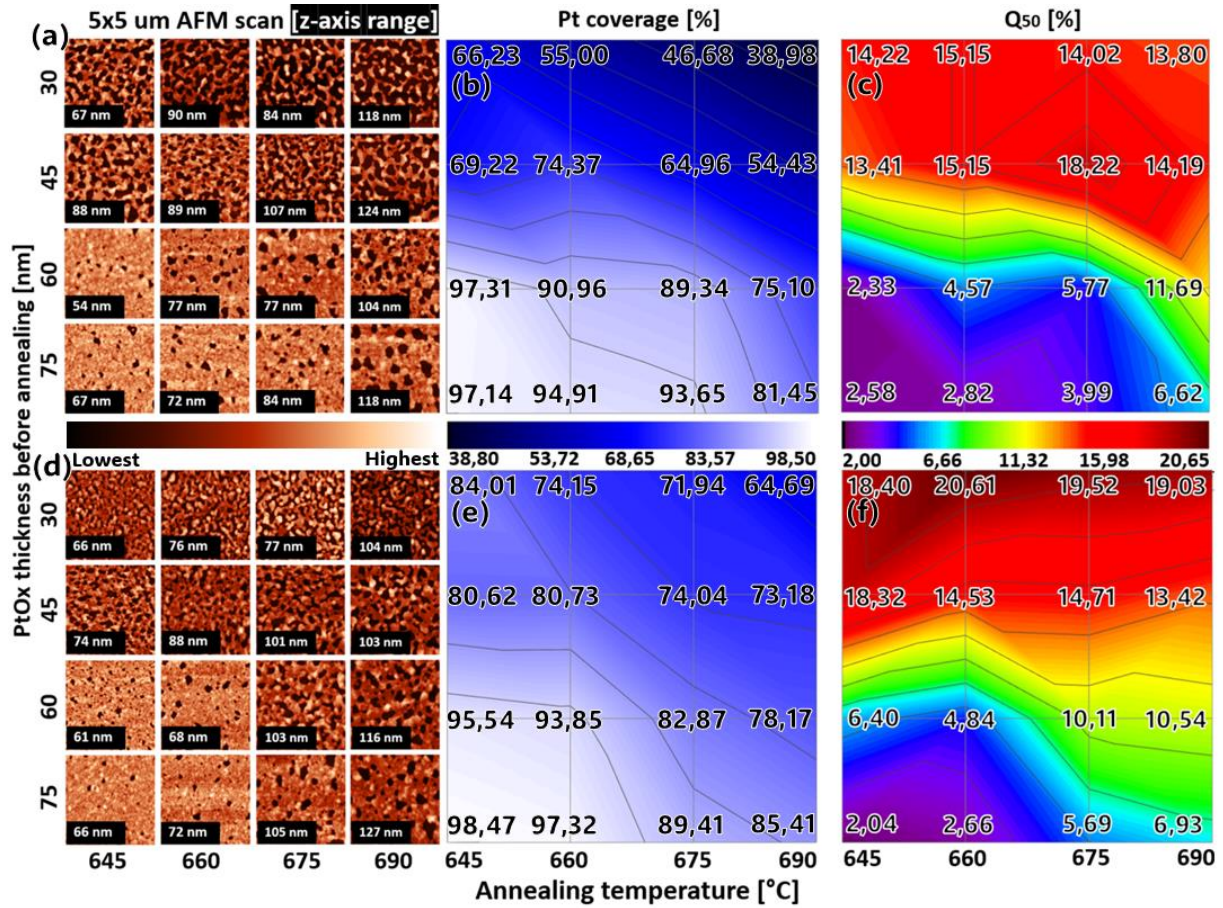


Figure 4: Porosity analysis of two sets of 16 samples with various thickness of the precursor PtO_x layer (30 – 75 nm), annealed at one of four temperatures in the range of 645 – 690 °C. The top row (panels (a)-(c)) shows results from samples with magnetron-deposited TiO_2 , the bottom row (panels (d)-(f)) shows results from samples with ALD-deposited TiO_2 . The first column (panels (a), (d)) shows a matrix of 5x5 μm AFM topography scans with an embedded number indicating the peak-to-peak height range. The second column (panels (b), (e)) shows the coverage of the samples by Pt. The third column (panels (c), (f)) shows the Q_{50} parameter calculated for each sample from the AFM scans shown in panels (a), (d), respectively (see the Appendix A for details).

According to [16], the response of similar vertically arranged Pt/ TiO_2 /Pt gas sensors to hydrogen increases as the width of the top electrode decreases, with a large leap in response for electrode width of $\lesssim 100$ nm. The same study estimates the diffusion length λ of H_2 molecules in a nanocrystalline TiO_2 layer to be about 30 nm, not far from the value $\lambda \simeq 100$ nm, reported for the SnO_2 films^[19]. Based on the above, we consider the TiO_2 areas under the top Pt electrode distanced within ~ 50 nm from a nearest electrode edge (pore) to be the most active sensing area providing a major contribution to the response. To evaluate the proportion of the active areas in our samples, the AFM topography data of each sample have been processed as described in detail in Appendix A. In summary, the AFM topography images were divided into Pt-covered and non-Pt-covered areas based on topography histograms. The extracted Pt coverage is shown in Fig. 4b,e. Subsequently, individual pores were identified and

mapped. In the next step, the proportion of the total scan area corresponding to the Pt-covered areas distanced within 50 nm from the nearest pore has been calculated. This quantity, further referred to as the porosity quality Q_{50} , has been calculated for each studied sample. The resulting values shown in Fig. 4c,f demonstrate that until certain point, Q_{50} is directly proportional to T_A while indirectly proportional to d . However, from Fig. 4b it can be seen that layers with 30 nm thickness annealed at 675 and 690 °C on magnetron-deposited TiO₂ film have Pt coverage below 50%. Based on percolation threshold on finite square lattice, they are thus at risk of being discontinuous, which was later confirmed by measuring their electrical resistance. Despite high Q_{50} , these samples were thus discarded as inapplicable. Similarly, the layer with 30 nm thickness annealed at 690 °C on ALD-deposited TiO₂ film was proven to be discontinuous by electrical measurements despite the 64.69% Pt coverage and was discarded as well.

The H₂ gas sensing performance of the vertical Pt/TiO₂/Pt gas sensors with nanoporous top Pt electrode has already been studied previously in sensors with magnetron-deposited TiO₂ and the TE prepared using a 45 nm precursor PtO_x layer annealed at 660 °C. Since complex overview of the porosity as a function of the fabrication parameters was not yet available at the time of the study, the used parameters were not optimal yet very close to those corresponding to the highest Q_{50} (PtO_x thickness of 45 nm and annealing temperature of 675 °C). Dynamic responses of two such sensors prepared together on the same substrate, further referred to as Spt#1 and Spt#2, to various H₂ concentrations in the range of 3 – 10 000 ppm obtained at room temperature (24 °C) are shown in Fig. 5. Both sensors exhibit excellent sensitivity across the whole tested H₂ concentration range. The response S , defined as $S = (R_0 - R_g)/R_g$, where R_0 is the baseline resistance at 0 ppm H₂ and R_g is the resistance at the end of the H₂ exposure window, ranged from 1.394 / 0.055 at 3 ppm H₂ for Spt#1 / Spt#2, respectively, up to 9.49×10^9 at 10 000 ppm H₂ for Spt#2. The response of Spt#2 at 10 000 ppm H₂ is over three orders of magnitude higher compared to sensors based on similar TiO₂ layers with standard comb-like electrodes ($< 10^7$)^[20]. However, from Fig. 5 it is also clear that after exposure to H₂ concentrations of 1000 ppm and higher, the sensors are not recovering to the original baseline resistance with the 2-hour window and even within 12-hour period (see Spt#1 in Fig. 5b) when the hydrogen is removed from the atmosphere. The sensor can however be recovered by heating to 150 °C or more. This suggests that the uncomplete recovery at room temperature is likely caused by accumulation of water molecules, produced by the reaction of hydrogen and oxygen, in the volume of the TiO₂ layer due to insufficient diffusion rate.

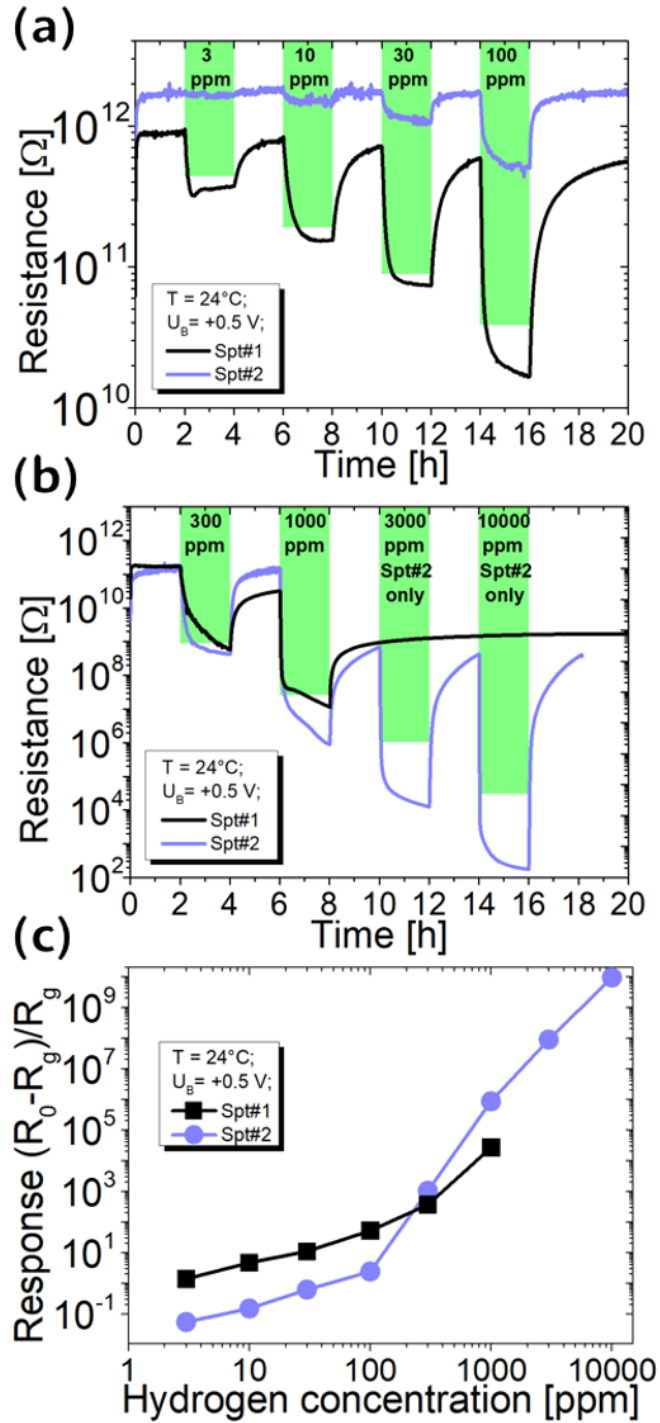


Figure 5: Dynamic response of the gas sensors Spt#1 (black) and Spt#2 (light blue) with magnetron-deposited TiO₂ layer and porous TE fabricated from 45 nm thick PtO_x layer annealed at 660 °C measured at room temperature in dry conditions (relative humidity < 5%) to H₂ concentrations in the range of 3 – 100 ppm (a) and 300 – 10 000 ppm (b). The data shown in panels (a) and (b) are smoothed by a 50-percentile filter with a 20-points window for better visibility of the response. Panel (c) shows corresponding calibration curves obtained from the data in panels (a) and (b). The dynamic response data of Spt#1 are taken from Fig. 7 in Ref. [21] and are shown here for easier comparison with Spt#2. Ref. [21] provides more detailed H₂ gas sensing analysis of Spt#1, only a subset of the data relevant for this study is shown here.

Despite their exceptional response to hydrogen, the magnetron-sputtered TiO₂ thin films exhibited significant variability in H₂ gas-sensing performance, as can be seen from Fig. 5. Notably, the two identically prepared sensors displayed differences exceeding an order of magnitude in response across most tested H₂ concentrations. For this reason, they do not represent a suitable medium to establish a reliable correlation between porosity of the top Pt electrode and sensitivity throughout a set of samples. Another set of samples with ALD-deposited TiO₂ layer, providing excellent reproducibility at the cost of lower response, was thus prepared to evaluate the correlation between the porosity quality Q_{50} and the response of the gas sensors to H₂. The lower sensitivity of ALD-deposited TiO₂ films is anticipated to stem from the morphology^[22]. The difference in crystallinity is clearly visible on AFM topography images shown in Fig. 6 and X-Ray diffractograms shown in Appendix B. As a countermeasure, the thickness of the ALD-TiO₂ film has been decreased to 30 nm, as lower thickness is expected to improve the sensitivity^[23].

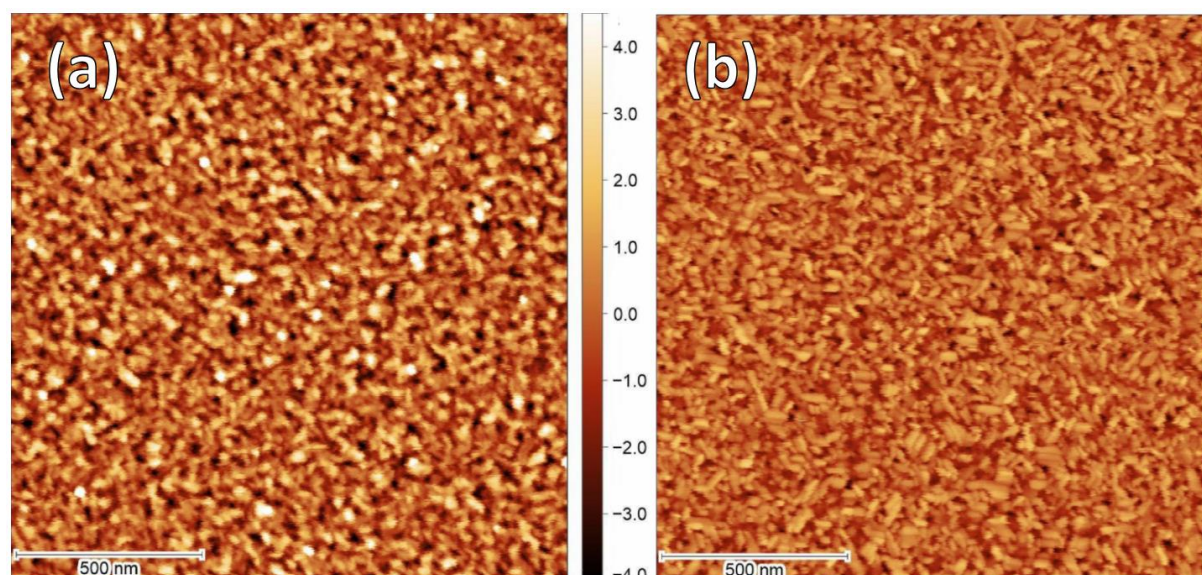


Figure 6: 1.5×1.5 μm AFM topography scans of an (a) magnetron-deposited TiO₂ film after annealing at 675°C, and a (b) ALD-deposited TiO₂ film after annealing at 690°C. The roughness of magnetron-deposited film and ALD-deposited film is 1.056 nm and 0.709 nm, respectively.

From the studied porosity matrix (Fig. 4d-f), the secondary diagonal (from sample ALD#1 with 30 nm PtO_x layer annealed at 690°C to sample ALD#4 with 75 nm PtO_x layer annealed at 645°C) has been chosen for closer examination. Samples ALD#1 to ALD#4 have been fabricated identically, except for the PtO_x layer thickness and annealing temperature. Dynamic responses of the four (ALD#1 – ALD#4) sensors obtained at room temperature along with corresponding calibration curves are shown in Fig. 7a. In all cases, H₂ concentrations below 3000 ppm have not been detected. This can be caused by very high baseline resistance of the sensors, exceeding the measurement limit of our setup (~ 1 TΩ) even in the presence of 1000 ppm H₂. Sensor ALD#1 did not show any response even at 3000 and 10 000 ppm H₂ due to discontinuous top Pt electrode as mentioned above. On the other hand, sensors ALD#2 – ALD#4 exhibited moderate response to 3000 ppm H₂ and high response to 10 000 ppm H₂,

ranging from $S_{ALD\#4}=2.3\times10^6$ to $S_{ALD\#2} = 7.6\times10^8$. As can be seen in Fig. 7b, the response values are directly proportional to the porosity quality Q_{50} of the sensor's TE, in accordance with the expected behavior.

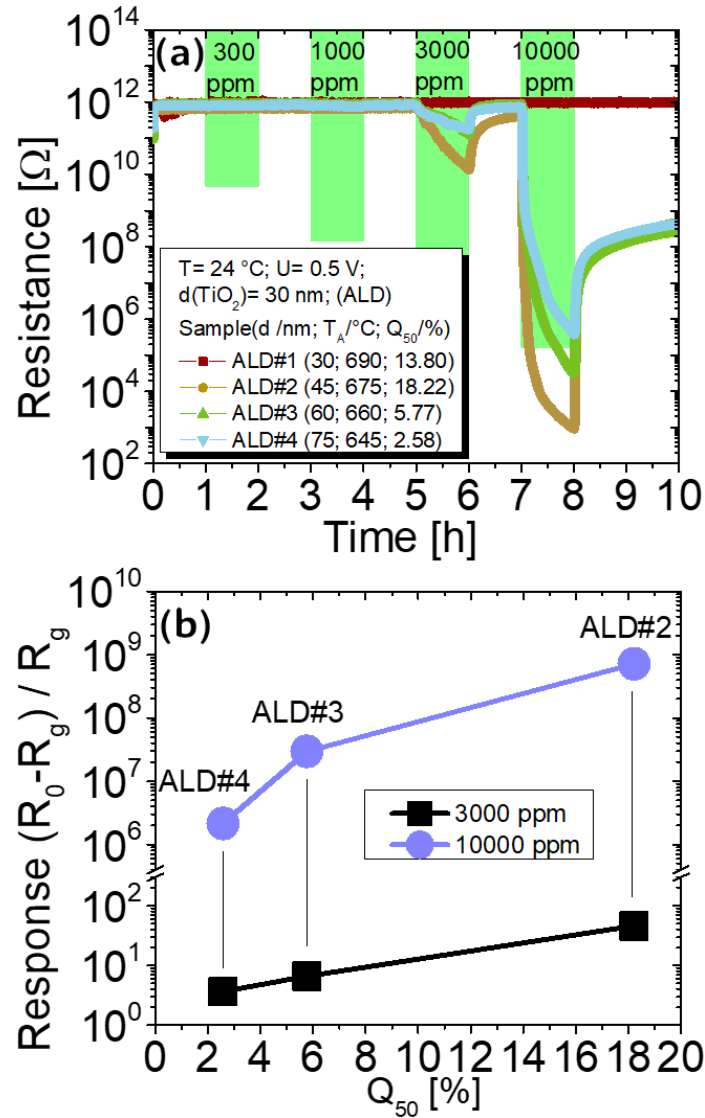


Figure 7: Dynamic responses of sensors ALD#1 – ALD#4 with TE prepared using different PtOx thickness d and annealing temperature T_A to various hydrogen concentrations (a). The data shown in panel (a) are smoothed by a 50-percentile filter with a 20-points window for better visibility of the response. Panel (b) shows the dependence of the resistance response of ALD#2 – ALD#4, calculated from the data in panel (a), on the porosity quality parameter Q_{50} .

Although the correlation between the sensor response and the TE porosity in Fig. 6b is convincing, it should be noted that the different annealing temperatures can influence not only the porosity of the TE, but also the crystalline structure of the TiO_2 film. This aspect needs to be addressed since variations in crystallinity of the sensing layer can also have a non-negligible impact on the sensor's response^[24]. To rule out the influence of different crystallinity, reference ALD-deposited TiO_2 layers annealed at 645 °C and 690 °C were prepared and analyzed by X-Ray diffraction (XRD). The results of the XRD analysis are

described in detail in Appendix B. The main conclusions are that both films are almost identical, contain pure anatase phase with average grain size of about 13 nm and 17 nm for the sample annealed at 645 and 690 °C, respectively. Although such variations in grain size can slightly influence the sensor's response, previous studies^[24] indicate that a difference in grain size ranging from 13 nm to 17 nm is unlikely to account for the orders of magnitude difference in response observed between sensors ALD#2, ALD#3 and ALD#4.

Conclusions

Metal oxide semiconductor gas sensors with vertical Pt/TiO₂/Pt configuration offer exceptional response to hydrogen if the width of the top electrode is very small, typically ~100-200 nm. An affordable way to achieve such narrow electrodes, alternative to electron beam lithography, is the formation of a nanoporous top electrode with very narrow Pt-covered areas. In this work, such nanoporous top Pt electrodes were fabricated by depositing PtO_x film on top of the magnetron-deposited or ALD-deposited TiO₂ layer by reactive magnetron sputtering and subsequent annealing. The porosity of the resulting Pt films has been investigated and evaluated as a function of the precursor PtO_x layer thickness (30 – 75 nm) and annealing temperature (645 – 690 °C). The evaluation criterion was the porosity quality parameter Q_{50} , defined as the ratio of the Pt-covered area distanced ≤ 50 nm from the nearest pore to the total electrode area. This criterion was based on previous studies estimating the H₂ diffusion depth in nanocrystalline TiO₂ films to be about 50 nm. In sensors with magnetron-deposited TiO₂ layer the highest porosity quality ($Q_{50} = 18.22\%$) of the Pt electrode was achieved when a 45 nm thick PtO_x layer was annealed at 675°C for 1 hour. It has been shown that sensors with such top electrode exhibit extremely high response to hydrogen ranging from 1.394 at 3 ppm H₂ up to 9.49×10^9 at 10 000 ppm H₂. To reliably correlate the sensor response with the porosity quality Q_{50} , sensors prepared in the same way but with an ALD-deposited TiO₂ layer were prepared and investigated in terms of porosity and response to H₂ gas. The results clearly show that higher porosity quality Q_{50} results in higher response of the sensors to H₂. The sensor with an ALD-deposited TiO₂ layer and nanoporous top electrode with $Q_{50} = 14.71\%$ exhibited over two orders of magnitude higher response to 1% H₂ compared to a similar sensor with $Q_{50} = 2.04\%$.

Acknowledgement

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Appendix A

Here we describe the process of obtaining the value of the porosity quality Q_{50} from AFM topography images. The AFM topography output is a pixel matrix of height values $z(x,y)$. To separate the pixels corresponding to pores from the pixels representing the Pt-covered areas (the top electrode), a cutoff height value z_{cut} is selected for each topography image by analyzing the corresponding height histogram $N(z)$. The height values of pores closely align across the scan due to low roughness of the underlying TiO_2 layer. The height values corresponding to the Pt TE approximately align as well, but with higher variation due to varying thickness of the Pt and edge effects. The histogram thus consists of two peaks, one sharper corresponding to the underlying TiO_2 layer and one broader corresponding to the Pt-covered areas. The height value of the local minimum in between the two peaks is selected as the z_{cut} . The pixels in the AFM topography matrix can then be divided into two groups: Z_p (pore) with $z < z_{cut}$ and Z_e (electrode) with $z \geq z_{cut}$. The Z_e points distanced no more than 50 nm from the nearest pore are then selected numerically and assigned to group $Z_{e<50}$. The number of points in the group $Z_{e<50}$ divided by the total number of points in whole AFM scan matrix is finally defined as the porosity quality Q_{50} :

$$Q_{50}(x, y) = \frac{\#Z_{e<50}(x, y)}{\#Z_p + \#Z_e} = \frac{\#Z_{e<50}(x, y)}{256 \times 256} \quad (1)$$

where $\#Z_{e<50}$, $\#Z_e$ and $\#Z_p$ are the number of points in groups $Z_{e<50}$, Z_e and Z_p , respectively, x_{max} and y_{max} are the pixel dimensions of the scan matrix, in our case $x_{max} = y_{max} = 256$. The porosity quality Q_{50} describes the coverage of the AFM scan by an area contributing to the gas response and represents the permeability of the top electrode. To ensure that the obtained results are a good representation of the film porosity, three AFM scans from different areas were taken from each sample, two with a scan area of $5 \times 5 \mu\text{m}$ and one with a scan area of $10 \times 10 \mu\text{m}$. The results presented are obtained from the $5 \times 5 \mu\text{m}$ scan which fits best the average value in terms of number of pores per unit area and Pt coverage $\#Z_e/(\#Z_e + \#Z_p)$.

Appendix B

X-ray diffraction (XRD, PANalytical X'Pert PRO MRD) analysis was used to determine the crystal phase composition and preferential orientation of the ALD-deposited thin films grown on c-cut sapphire substrate annealed at 645°C and 690°C . The diffractometer was equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operated at 45 kV and 40 mA.

In both samples, the TiO_2 layer shows pure anatase phase, there is no indication of any other Ti-containing phase. In symmetrical diffraction in Fig. B.1 beside intense and narrow sapphire substrate 0006 diffraction with doublet $\text{CuK}\alpha_{1,2}$ accompanied by $\text{CuK}\beta$ and $\text{WL}\alpha_1$

lines, for TiO₂ thin film only a relatively broad peak around $2\theta \sim 38.5^\circ$ in position of anatase 004 and 112 diffractions is observed. From the shape of this anatase diffraction peak we estimated the size of the average crystalline coherent domain in the direction perpendicular to the surface: 13 nm for 645°C and 17 nm for 690°C.

The absence of other TiO₂ peaks is a sign of strong preferential orientation. Similar biaxial texture, called granular epitaxy, has been analyzed in magnetron-sputtered TiO₂ thin films in our previous study^[25] using pole figures measurements. Here, we have proved the preferential orientations (001) and (112) of anatase by measurements of selected azimuthal Φ -scans. The biaxial texture relationships with respect to the substrate is: $A(001)[110] \parallel \text{sub}(0001)[\bar{1}100]$ and $A(112)[\bar{1}10] \parallel \text{sub}(0001)[\bar{2}110]$. For both samples, the Φ -scans show narrow diffraction lines with average FWHM of around 3°.

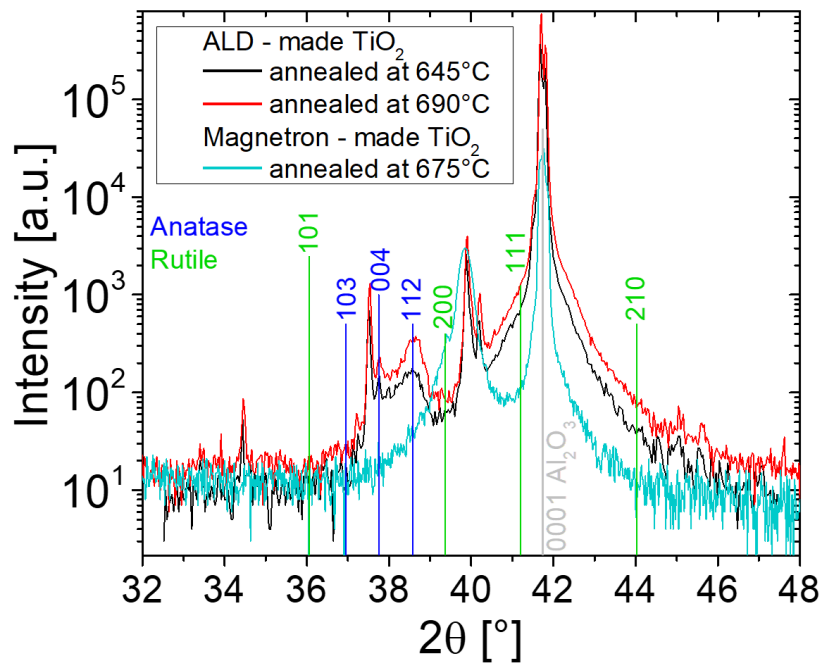


Figure B.1: XRD symmetric scan of an ALD-deposited TiO₂ film on c-cut Al₂O₃ substrate annealed at 645°C (black) and 690°C (red) for 1 hour in ambient air and magnetron-deposited TiO₂ film on c-cut Al₂O₃ substrate annealed at 675°C (cyan). Only anatase 112 and 004 diffraction peaks were observed in both cases of ALD deposited TiO₂, while a weak rutile 200 peak is observed in case of a magnetron-deposited layer (for further analysis see [21]).

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