Resistance noise in TiO$_2$-based thin film gas sensors under ultraviolet irradiation

Z. Topalian$^a$, J.M. Smulko$^b$, G.A. Niklasson$^a$, C.G. Granqvist$^a$

$^a$ Department of Engineering Sciences, The Ångstrom Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden

$^b$ Gdansk University of Technology, WETiI, ul. G. Narutowicza 11/12, 80-952 Gdansk, Poland

E-mail: Zareh.Topalian@angstrom.uu.se

Abstract. Resistance fluctuations in thin crystalline TiO$_2$ films were investigated for gas sensing applications. The measurements were carried out as the films were irradiated by ultraviolet (UV) light with a wavelength of 370 nm in the presence of H$_2$S. The films were prepared by reactive DC magnetron sputtering. They had a crystalline phase of anatase and a mean grain size of 17.8 nm, as found by X-ray diffraction. A prominent change in resistance noise level was discovered as the irradiated film was exposed to a gas containing 1.5 ppm of H$_2$S, while no change was observed in the absence of UV. This effect is possibly due to decomposition of the adsorbed gas, via photocatalysis induced by TiO$_2$, or to a decrease of the potential barrier between the charged grains.

1. Introduction
Gas sensing with semiconductor metal oxide thin films has been intensively studied during the last decades [1]. Such films are prominent candidates for developing reliable and inexpensive gas sensors. Among the most studied metal oxide gas sensing materials are SnO$_2$ [2,3], WO$_3$ [4], and ZnO [5]. Recently TiO$_2$ has also been considered, and in particular the effect of UV irradiation on the resistance response was investigated [6]. It is important to note that TiO$_2$ is a well-known photocatalytic material, which has been the subject of extensive research during the last decades [7]. Since photocatalytic reactions are induced by UV irradiation it is very probable that this will also affect the gas sensing properties of TiO$_2$, as further explored in the present investigation.

In this paper we report on noise spectroscopy [8] to study the effect of exposure to H$_2$S and UV irradiation for TiO$_2$ thin films. An increase of the noise level in the presence of H$_2$S was observed only under UV irradiation.

2. Film preparation and characterization
Titanium dioxide films were prepared using reactive DC magnetron sputtering in a thin film deposition system based on a Balzers UTT 400 unit [9]. Two magnetron sources were used for sputtering Ti from 99.99% pure metallic targets. The targets were 51 mm in diameter and 5.6 mm thick. The chamber was evacuated to ~10$^{-7}$ Torr by turbo molecular pumping. The Ti targets were first pre-sputtered in argon for 10 minutes to remove oxides and other possible contaminants. Argon
(99.998%) and oxygen (99.998%) were then introduced into the chamber via separate mass-flow controlled inlets. The O2/Ar gas flow ratio was kept constant at a value of 0.072. The sputter plasma was generated at a constant current of 750 mA, and the total gas pressure during sputtering was maintained at ~40 mTorr. The films were deposited onto unheated alumina and glass substrates. The alumina substrates had preprinted gold electrodes separated by a 0.2-mm wide gap, and a platinum heating resistor was printed on the reverse side. Film thickness was determined by surface profilometry using a Tencor Alpha-Step instrument. The work reported below used 2.7 µm thick films. The films were first annealed in air at 450 °C for 4.5 h and then at 500 °C for 1 h, using an oven with a temperature stabilization of ±5 °C.

Structural studies were made by X-ray diffraction (XRD) using a Siemens D5000 diffractometer operating with CuKα radiation at grazing incidence. Standard data [10] were used to identify the diffraction peaks for TiO2. The mean grain size D was estimated from Scherrer’s formula, i.e.,

\[ D = \frac{K \lambda}{\beta \cos \theta}, \]

where K is a dimensionless constant, usually 0.9, 2θ is the diffraction angle, λ is the X-ray wavelength, and β is the full width at half maximum of the diffraction peak.

Figure 1 shows grazing incidence X-ray diffractograms for TiO2 films sputter deposited onto glass substrates kept at different annealing temperatures. No diffraction peaks due to titanium oxide were found for un-annealed samples. However annealing at 450 °C led to diffraction peaks corresponding to pure anatase, and further heat treatment at 500 °C made the diffraction peaks grow in intensity with the (004) reflection being strongest. Applying Scherrer’s formula to the anatase (101) peak, it was found that \( D \approx 15.8 \) nm after annealing at 450 °C and \( D \approx 17.8 \) nm after annealing at 500 °C.

![Figure 1. X-ray diffractograms for TiO2 films sputtered onto glass and annealed at the temperatures \( \tau_a \). The anatase structure is denoted A.](image-url)
3. Noise measurements
Resistance fluctuations $R(t)$ in the TiO$_2$ film were observed as voltage fluctuations at the output of a current-voltage converter as shown in Fig. 2. The output voltage is proportional to $R(t)$ and the DC current $U_{\text{ref}}/R_1$ flowing through both resistors $R_1$ and $R$. The measurement set-up used a low-noise operational amplifier (OPA 129). The circuit converts current into voltage for $R(t)$ values as high as a few GΩ. Electromagnetic shielding was provided by placing the circuit with the gas sensor inside a metal chamber. A stable source for the reference voltage $U_{\text{ref}}$ and a battery supply for the circuit were employed to ensure dominance of the gas sensor resistance fluctuations in the observed voltage noise.

![Figure 2](image-url)

**Figure 2.** Current-voltage converter to observe resistance fluctuations in TiO$_2$ films. The symbols are explained in the main text.

The output voltage fluctuations of the current-voltage converter were amplified by a low-noise voltage preamplifier (Stanford SR 560) and were registered by a precise data acquisition board (National Instrument NI 4474). The measurement set-up comprised two gas bottles with synthetic air and nitrogen mixed with 200 ppm H$_2$S, respectively. Each gas was controlled by a separate mass flow meter. The gases were mixed in a blender before reaching the gas chamber. A UV diode, with a wavelength of 370 nm, was placed inside the gas chamber approximately 1 cm from the sensor. The gas-sensitive layer was irradiated uniformly by the UV diode.

The sensor was preheated for one hour at 500 °C and then the temperature was decreased to 275 °C. Synthetic air (SA) was introduced into the chamber, and after stabilization of the system, the DC voltage and voltage fluctuations of the sensor were measured with and without UV irradiation of various intensities. The same measurements were carried out for the gas mixture of SA and H$_2$S with H$_2$S concentrations from 1.5 to 9 ppm. The flow of the gas mixture was kept below 0.3 ml/min to avoid turbulence that otherwise could have influenced the intensity of the observed resistance noise.

Voltage noise measurements were performed at a sampling frequency of 50 kHz. A total number of $10 \times 2^{16}$ data points was used to estimate the power spectrum each time. The random error of the estimated power spectrum was then below 5% at a frequency resolution of 25 Hz.

4. Results and discussions
Figures 3-5 illustrate some results of the noise measurements. Figure 3 shows normalized resistance power spectra multiplied by frequency as observed in SA with and without UV irradiation. The power spectrum depends on frequency as $f^{-1.5}$ in the low-frequency range, which suggests that the origin of the observed data is diffusion noise [12]. Figure 3 shows clearly that UV radiation does not affect the observed noise when the gas sensor is exposed to air only. This conclusion is essential for the following measurement results because it proves that the UV irradiation do not influence the measurement system. The DC resistance of the sensor remained at 574 MΩ for both of these measurements.
Putting the sensor into a gas with 1.5 ppm of H$_2$S, Fig. 4 shows that there was an easily detectable change of the noise intensity—by about 35 %—upon UV irradiation. At the same time the DC resistance dropped slightly to 522 M$\Omega$ at a diode current of 12 mA. The other measurement conditions were not altered and hence we conclude that the sensitivity for gas detection is unambiguously increased by UV radiation. The change in the resistance noise is expected to be larger with a more optimal design of UV radiator and sensor film.

![Figure 3](image1.png)

**Figure 3.** Normalized resistance power spectrum multiplied by frequency $f$ for a TiO$_2$ sensor exposed to synthetic air only at different UV diode currents $I_D$. The sensor was kept at 275 °C.

![Figure 4](image2.png)

**Figure 4.** Normalized resistance power spectrum multiplied by frequency $f$ for a TiO$_2$ sensor exposed to synthetic air with 1.5 ppm of H$_2$S at different UV diode currents $I_D$. The sensor was kept at 275 °C.
Figure 5. Normalized resistance power spectrum multiplied by frequency \( f \) for a TiO\(_2\) sensor exposed to synthetic air with 3 ppm of H\(_2\)S at different UV diode currents \( I_0 \). The sensor was kept at 275 °C.

Figure 5 shows that an increase of the H\(_2\)S content to 3 ppm intensified the noise detected upon UV irradiation. At the same time the shape of the power spectrum changed and became different from the one observed in SA only (cf. Fig. 3). An analogous behavior of the spectra was detected when the sensor temperature was increased.

5. Conclusions
We made explorative studies of gas sensing with anatase TiO\(_2\) thin films. It was shown that low concentrations of H\(_2\)S can be detected by noise spectroscopy provided that the gas sensor is irradiated by UV light. We surmise that this effect is associated to the well known photocatalytic activity of TiO\(_2\) but the details have not yet been clarified. Combining gas adsorption and photocatalysis appears to be a promising new approach for enhancing gas sensor sensitivity.

References
[1] N. Yamazoe, G. Sakai, and K. Shimanoe, Catal. Surveys Asia 7, 63 (2003).
[2] V. Lantto, in: G. Sberveglieri, editor, Gas Sensors (Kluwer, Dordrecht, The Netherlands, 1992).
[3] L. Xiangdong P. Chuanyun, W. Xiaobing, and C. Wenfei, Vacuum 81, 883 (2007).
[4] L.F. Reyes, A. Hoel, S. Saukko, P. Heszler, V. Lantto, and C.G. Granqvist, C.G., Sensors Actuators B: Chem. 117, 128-134 (2006).
[5] P. Mitra, A.P. Chatterjee, and H.S. Maiti, Mater. Lett. 35, 33 (1998).
[6] T.-Y. Yang, H.-M. Lin, B.-Y. Wei, C.-Y. Wu, and C.-K. Lin, Rev. Adv. Mater. Sci. 4, 48 (2003).
[7] A. Fujishima, K. Hashimoto, and T. Watanabe, TiO\(_2\) Photocatalysis, Fundamentals and Applications (Bks, Tokyo, Japan,1999).
[8] L.B. Kish, R. Vajtai, and C.G. Granqvist, Sensors Actuators B: Chem. 71, 55 (2000).
[9] D. Le Bellac, G.A. Niklasson, and C.G. Granqvist, J. Appl. Phys. 77, 6145 (1995).
[10] Powder Diffraction Files (Int. Center for Diffraction Data); file 00-021-1272.
[11] J.S. Bendat and A.G. Piersol, Random Data Analysis and Measurement Procedures (Wiley, New York, USA, 1999).
[12] R.F. Voss and J. Clarke, J. Physics A: Math. 9, 561 (1976).