

Al-doped TiO₂ semiconductor gas sensor for NO₂-detection at elevated temperatures

A. Yüce and B. Saruhan

Institute of Materials Research, German Aerospace Center (DLR), Linder Hoehe 51147 Cologne, Germany

E-Mail: bilge.saruhan@dlr.de

Abstract:

Al-doped TiO₂ semiconductor layers were investigated as gas sensor for NO_x detection at temperatures up to 800°C. Thin sensor layers were deposited by reactive magnetron sputtering technique from the metallic targets of Ti and Al under addition of oxygen onto the alumina substrates which consisted of screen-printed interdigitated Pt-electrodes on the front and no heater at the backside. Al-content was adjusted to 6 atm. % in TiO₂. The layers were characterized by XRD and SEM for phase and microstructural constituents. The phase content is consisted of anatase phase on deposition and was converted to rutile at temperatures exceeding 600°C. After annealing at 800°C for 3 hours in air, the sensor response is measured towards NO₂ concentrations up to 200 ppm under dry and humid conditions (5 % H₂O) in argon as the carrier gas. The sensors sensitivity and cross-sensitivity towards CO was also investigated. Al-doped TiO₂ sensor layers exhibited very promising results for sensing NO₂ selectively at temperatures exceeding 500°C.

Key words: Al-doped TiO₂, NO₂-sensor, Magnetron-sputtering, high-temperature sensing

Introduction

One of the challenges in developing gas sensors for harsh environments is the total hold of sensitivity at operation temperatures greater than 500°C. NO₂ is a common air pollutant that is associated even at the ppb level with poor air quality. Its emission is mostly related to combustion processes where gas temperatures exceeding far beyond 500°C. Combustion and exhaust gases contains next to NO/NO₂ also CO and unburned hydrocarbons, requiring higher NO₂-selectivity and less cross-sensitivity to reducing gases by detection of NO₂ relatively high temperatures.

TiO₂ is employed as a high-temperature gas sensor material and its application range can be extended by adding dopants (Nb, Sn, Pt, Zn, La, Y, Cr, Al, etc.) to detect CO, H₂ and NO₂ [1-4]. The addition of dopants to metal oxide semiconductors is the most common route of obtaining selective gas sensors [1]. TiO₂ has three modifications: brookite, anatase and rutile phases. The structural differences at these phases introduce also differences in the gas sensing properties of titania based devices [5]. Anatase phase of TiO₂ is a high resistive n-type semiconductor with rather poor conductivity to be adopted for sensing oxidative gases [6]. Anatase to rutile phase transformation occurs irreversibly at temperatures above 600°C. Addition of additives or dopants to titania may

affect the phase transformation conditions, inhibit the grain growth and increase conductivity [6-7]. Addition of chromium affects the electronic structure of TiO₂. It is reported that the addition of Cr exerts p-type semiconductor properties to TiO₂. Cr-doped TiO₂ sensors may exhibit a certain CO-cross-sensitivity [2]. Moreover, the highest test temperature for the Cr-doped titania based sensors is given in the literature as 500°C. Al-doping inhibits the grain growth and retards phase transformation from anatase to rutile by stabilizing the surface state of TiO₂-particles. It is reported that the conductivity of Al-doped TiO₂ is higher than that of pure TiO₂ in a temperature range of 600-900°C. Substitution of Ti by Al in cationic positions results in a charge imbalance, creating oxygen vacancies [7]. While heat-treatments above 1000°C yield transformation to rutile phase, the amount of Al-dopant (up to 7.5 wt. %) change the concentration of oxygen vacancies and increase the disorder. Choi et al. observed the influence of Al-dopant on CO-sensing and reported that the calcination temperature affects the sensing behavior [7].

In this work, the results obtained with a NO₂ gas sensor which is manufactured using Al-doped TiO₂ as sensing layer and employing a simple sensor design without involving a Pt-heater.

Experimental Methods

Al-doped TiO₂ thin layers were fabricated via reactive magnetron radio frequency (rf) sputtering technique from metallic targets using oxygen as a reactive gas. A sputtering equipment (LA 250 S from von Ardenne GmbH) with two sputter sources was used to deposit the coatings in an argon + oxygen gas mixture. Al-doped TiO₂ thin layers were deposited on the Al₂O₃ sensor platforms, onto which the interdigitated Pt-circuits were previously deposited by screen-printing. During the coating process, the substrate holder was rotated at 13 rpm. This rotational movement enables the homogenous distribution of aluminum in titania-matrix. By applying different power levels on each target, the concentration of aluminum in TiO₂ is adjusted. The employed sensor design requires no heater at the back-side of the sensor platform. Simultaneously, thin layers were deposited onto the sapphire single crystal substrates for enabling interference-free XRD measurements. Microstructure and morphology analysis of the sensing electrodes in terms of porosity, grain size and surface condition were done by means of FE-SEM (Carl Zeiss NTS Ultra 55). The phase analysis of the sensing electrodes was carried out by x-ray diffraction, using a SIEMENS D5000 X-ray Diffractometer equipped with a secondary graphite monochromator using Cu K α -radiation and an acceleration voltage of 40 kV in the 2 θ range of 20° and 80°, at a step size of 0.020° and with a step rate of 3s/step). Gas sensing characterizations were carried out in a specially constructed apparatus. The gas flow rate was adjusted to 400 ml/min and the NOx concentration was varied between 0 and 200 ppm. Mostly argon was used as carrier gas. In some of our experiments, synthetic air (80 % N₂ + 20 % O₂) was employed as the carrier gas indicated relevantly. DC measurements were carried out by using a Sourcemeter Keithley2635A. All measurements were controlled by a PC. A constant current of 1E-6 A was applied during all sensor measurements. Steady-state gas response measurements were started under constant carrier gas flow. After a stable baseline was reached, the target gas was introduced into the chamber, continuously flowing with a constant for 40 min, until it was stopped. Afterwards, the gas flow was changed to only carrier gas. These two steps were repeated for 50, 100 and 200 ppm NO₂ and/or CO gas concentrations.

Results and Discussion

Upon annealing at 800°C for 3 h in static air, the columns start to sinter slightly yielding a granulated morphology containing small pores

having diameters of 10-50 nm between the granulates (Fig. 1b). Each column consists of many grains which are finer in the as-coated state (Fig. 1c) and become coarser and more hexagonal after annealing at 800°C (Fig. 1d). Due to sintering and the growth of the grains after annealing at 800°C, a finer porosity develops between the grains (Fig. 1d). The size of the hexagonal grains was measured to be between 100-250 nm.

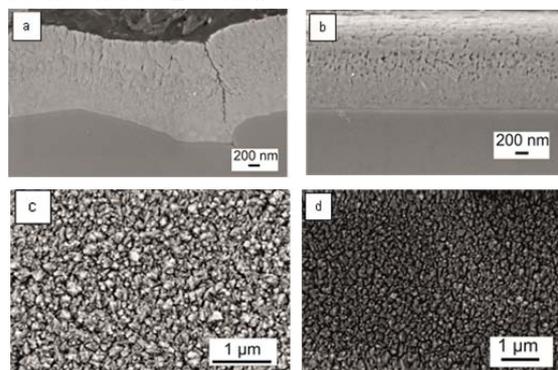


Figure 1: Cross-sectional SEM images of Al-doped TiO₂ layers in as-coated state (a) and after annealing at 800°C for 3 h in air (b). Top-view SEM images of the Al-doped TiO₂ layers in as-coated state (c) and after annealing at 800°C for 3 h in air (d).

Cross-sectional scanning electron microscopy (SEM) images of the Al-doped TiO₂ layer in the as-coated state and after annealing for 3 h at 800°C are shown in Fig. 1. As-coated Al-doped TiO₂ layer displays a dense and columnar microstructure (Fig.1a).

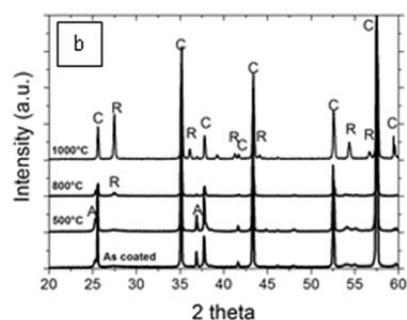
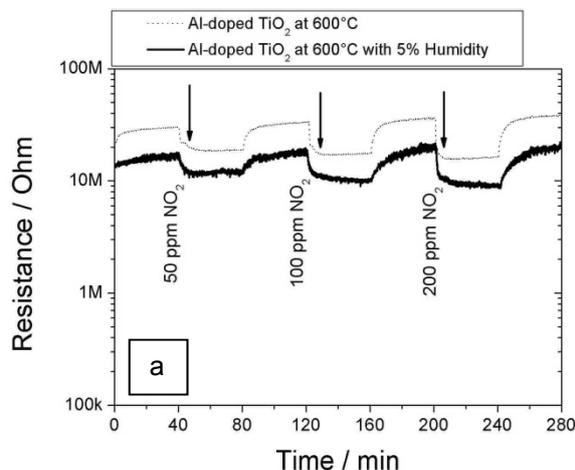


Fig. 2 XRD spectra of Al-doped TiO₂ sensor electrode in the as-coated state and after annealing for 3 h at 500°C, 800°C and 1000°C in static air. A: Anatase, R: Rutile and C: Corundum from the substrate.

The phase constituents of the magnetron-sputtered Al-doped TiO₂ layers were investigated by XRD analysis in the as-coated state and after annealing for 3 h in air at temperatures of 500°C, 800°C and 1000°C. XRD spectra of the as-coated and annealed magnetron sputtered Al-doped TiO₂ layers are given in Fig. 2. Al-doped TiO₂ layer consists of anatase phase in the as-coated state, which

continues to crystallize as the annealing temperature increases to 500°C. The anatase to rutile phase transformation occurs at temperatures above 500°C. A detectable phase transformation to rutile can be measured at the



Al-doped TiO₂ layers after 3 h annealing at 800°C, and a full conversion to rutile phase occurs after annealing for 3 h at 1000°C.

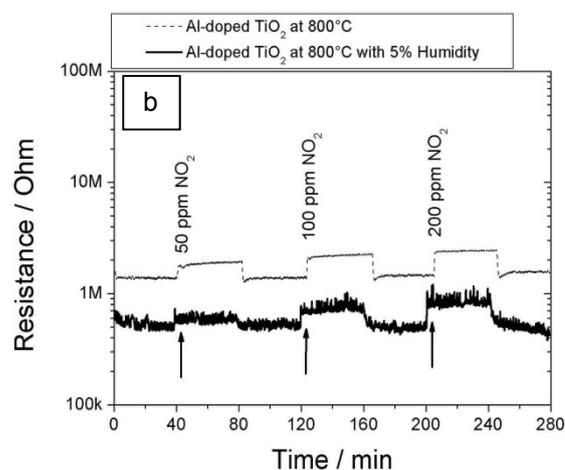


Fig. 3 Response transients of Al-doped TiO₂ layers to 50, 100, 200 ppm NO₂ at 600°C (a) and at 800°C (b) with and without 5 % humidity.

Characterization of the Al-doped TiO₂-sensor layers was carried out at temperatures of 600°C and 800°C by exposing towards NO₂, NO and CO under various concentrations. Fig. 6 shows the response curves of the sensors at the operating temperatures of 600°C and 800°C, yielding the changes in the resistivity values upon exposing to NO₂ in argon carrier gas with and without 5 % humidity. For comparison purposes, the pure TiO₂ layers were obtained by magnetron sputtering and the resistivity changes of these sensors towards NO₂ were measured. These measurements demonstrated that magnetron sputtered pure TiO₂ is not sensitive to NO₂ at higher temperatures. The base-line as well as the reaction and recovery times obtained with the un-doped pure TiO₂ sensor was extremely high. The magnitude of the gas response of this sensor was smaller, and the sensing signal was not stable. Therefore, they were not considered further in this study. At 600°C the resistivity of the Al-doped TiO₂ layers decreases as NO₂ is introduced to the system, whereas at 800°C it increases by addition of NO₂ (Fig. 3). Under an oxidizing gas exposure (i.e. NO₂), this sensor acts as a p-type semiconductor at 600°C, while it acts as an n-type semiconductor at 800°C. This type of alteration in the sensing behavior may be related either to the phase sequences and electronic structure of the sensing layer or to the constituents of the test gas.

The response and recovery times (t_{90}) of the Al-doped TiO₂ layers which were calculated from

the response curves given in Fig. 3, are listed in Table 1.

Tab. 1: Response and recovery time of the measurements at 600°C and 800°C with and without 5 % humidity

Conc. [ppm]	Response time [min]			
	600°C		800°C	
	Dry	Hum.	Dry	Hum.
50	6.82	5.12	5.8	0.4
100	3.19	5.9	2.5	0.2
200	1.93	4.9	0.38	0.23

Conc. [ppm]	Recovery time [min]			
	600°C		800°C	
	Dry	Hum.	Dry	Hum.
50	11.2	21.23	0.52	7.82
100	12.03	28.93	0.73	5.31
200	14.79	25.33	0.85	5.5

Generally the response time decreases and the recovery time increases as NO₂-concentration increases. This tendency alters solely when humidity is present at 800°C. By increasing the operating temperature, relatively shorter response and recovery times were observed. The effect of the operating temperature on recovery times appears to be more visible compared to that on response times. At 800°C, the sensor recovers within a very short time

period of 30-50 s, after ceasing the NO₂ flow. Nevertheless the addition of 5 % humidity, leads to the disappearance of this quick recovery. In the presence of humidity, moderate recovery times (5-7 min) were observed. As far as the response times are concerned, the introduction of humidity resulted in very rapid response as short as 12 to 25 s at 800°C.

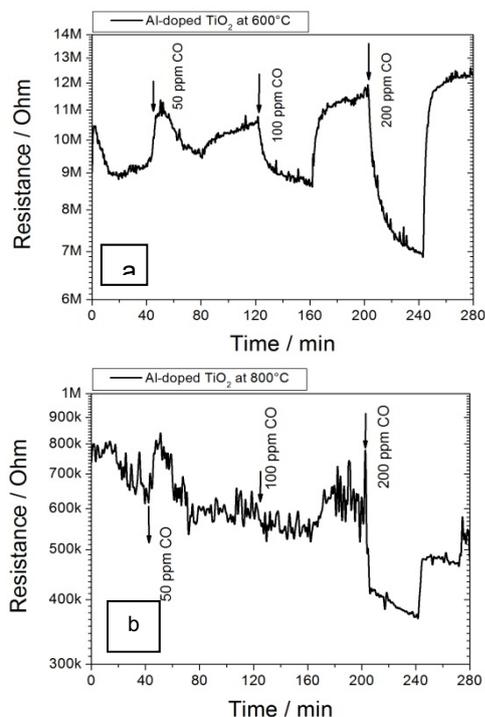


Fig. 4 Response transients of the Al-doped TiO₂ sensor to 50, 100, 200 ppm CO at 600°C (a) and at 800°C (b).

Upon exposure to the reducing gas, CO, at 600°C and 800°C, the Al-doped TiO₂ layers exhibit a decrease in resistivity in the range of 50 to 200 ppm (see Fig. 4). The response to CO is low and instable at both temperatures. The response at lower CO concentrations (e.g. 50 ppm) varies during the exposure to the test gas, yielding a slight increase followed by a decrease. Under exposure to higher CO-concentrations, only a slight increase in response was observed at both test temperatures (e.g. ≥ 100 ppm at 600°C and 200 ppm at 800°C). The level of the base-line resistivity obtained with the Al-doped TiO₂ layers under pure argon gas is higher at 600°C than that at 800°C, indicating a temperature dependent resistivity change probably due to the high negative Temperature Coefficient of Resistivity (TCR) of titania.

Conclusions

In this work, Al-doped TiO₂ was deposited by rf magnetron sputtering, and the sensing film was annealed successfully at elevated temperatures

without any warping and cracking. The layers were of a single oxide phase, no separation of Al₂O₃ has been observed. Al-doping retards anatase to rutile transformation temperature and grain growth. At 1000°C, the un-doped TiO₂ shows full transformation to rutile, while Al-doped TiO₂ display a partial phase transformation. At 800°C, Al-doped TiO₂ contains 35 % rutile. With the addition of Al into the titania lattice, the electronic and ionic conductivity of TiO₂ and oxygen vacancies increase allowing the use of these sensing layer as NO₂ sensor at 600°C and 800°C. Introduction of 5% humidity increases recovery times and decreases the sensitivity at higher test temperature (e.g. 800°C). Additionally, the response time towards NO₂ reduces significantly in presence of humidity at higher test temperatures. At high temperatures, the Debye length tends to decrease while the charge carrier concentration and the conductivity tend to increase [8]. This is another potential reason for the decreased response times in doped materials at higher test temperatures i.e. at 800°C.

References

- [1] Savage N., Chwieroth B., Ginwalla A., Patton B.R, Akbar S.A., Dutta P.K., "Composite n-p semiconducting titanium oxides as gas sensors", *Sens. and Actuators B: Chem.*, 79, 17-27 (2001).
- [2] Y. Shimizu, N. Nakashima, T. Hyodo, M. Egashira, NO_x Sensing Properties of Varistor-Type Gas Sensors Consisting of Micro p-n Junctions, *Journal of Electroceramics*, 6, 209-217 (2001).
- [3] I. Alessandri, E. Comini, E. Bontempi, G. Faglia, L.E. Depero, G. Sberveglieri, Cr-inserted TiO₂ thin films for chemical gas sensors, *Sens. and Actuators B: Chem.*, 128, 312-319 (2007).
- [4] Y. Li, W. Wlodarski, K. Galatsis, S. H. Moslih, J. Cole, S. Russo, N. Rockelmann, Gas sensing of p-type semiconducting Cr-doped TiO₂ thin films, *Sens. and Actuators B: Chem.*, 83, 160-163 (2002).
- [5] Ruiz A. M., Sakai G., Cornet A., Shimano K., Morante J. R. and Yamazoe N., "Cr-doped TiO₂ gas sensor for exhaust NO₂ monitoring", *Sens. and Actuators B: Chem.*, 93, 509-518 (2003).
- [6] D. Qin, W. Chang, J. Zhou, Y. Chen, An investigation of the preparation of TiO₂-based catalysts using methods of thermal analysis, *Thermochimica Acta*, 236, 205-216 (1994).
- [7] Choi Y.J., Seeley Z., Bandyopadhyay A., Bose S., Akbar S.A., "Aluminum-doped TiO₂ nano powders for gas sensors", *Sens. and Actuators B: Chem.*, 124, 111-117 (2007).
- [8] J. Mizsei, How can sensitive and selective semiconductor gas sensors be made?, *Sens. and Actuators B: Chem.*, 23 173-176 (1995).