

# Influence of Pd and Pt doping concerning the sensing mechanism

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## Abstract

DRIFTS, MS and DC electrical measurements were simultaneously performed on Pt, Pd and blank SnO<sub>2</sub> thick film sensors with the target gas CO (and D<sub>2</sub>O) @ 300°C in synthetic air. It was found, that the results are very different for the undoped (extremely decreased sensor signal in humid air) and doped materials (increased sensor signal in humid air). In order to understand the electrical effects, additional measurements were performed (exposure to 3% r.h. D<sub>2</sub>O). This experiment showed that water reacts very differently on the three materials and also that the presence of the dopants decreases the surface heterogeneity.

**Key words:** surface reaction Co<sub>3</sub>O<sub>4</sub>, ethanol sensing, DRIFT on Co<sub>3</sub>O<sub>4</sub>

## Introduction

One of the main problems related to the use of SnO<sub>2</sub> based sensors in real life applications is their lack of selectivity and the most encountered cross interference comes from the water vapor. Its effect is twofold: it decreases the sensor resistance, as the target reducing gases do, and its presence in various concentration changes the response magnitude under exposure to identical target gas concentrations [1]. Accordingly, it is very important to understand the exact mechanism in order to devise appropriate counter-measures. It is also known that the addition of small quantities of noble metals, e.g. Au, Pt or Pd, has a considerable impact on the gas sensing with SnO<sub>2</sub> based sensors; among others, it also influences the effect of water vapor on sensing. For the materials presented here, we found that the CO sensor signal of the undoped SnO<sub>2</sub> sensor decreases in humid air whereas for the doped SnO<sub>2</sub> materials (0.2 % wt. Pt and 0.2 % wt. Pd), the sensor signals increase. This fact indicates that, because of the presence of noble metal additives, different reactions paths determine the sensing process. Here, we present the results of our *operando* investigations, which combine simultaneously performed DC resistance, catalytic conversion and Diffuse Reflectance Infrared Spectroscopy DRIFTS measurements.

## Experimental part

All measurements were performed on thick film sensors at 300°C; the layers were obtained by screen printing onto Al<sub>2</sub>O<sub>3</sub> substrates provided with interdigitated electrodes and heaters on the backside. DRIFTS offers the possibility to investigate sensors in real operation conditions and also gives access to the surface species associated to water exposure, namely hydroxyl groups [2]. Because the spectral region where their adsorption bands appear is also extremely affected by the background absorption linked to the free charge carriers [3], we performed H<sub>2</sub>O/D<sub>2</sub>O exchange experiments and also CO exposures in a D<sub>2</sub>O background. Moreover, a concave rubberband correction (Iterations: 5 baseline points: 25, software: OPUS) was applied on the single channel spectra before any further calculation. The absorbance spectra were obtained by

$$\text{Absorbance} = -\log (SC_{\text{Sample}}/SC_{\text{Reference}}) \quad (1)$$

The spectra were recorded with an evacuable Bruker Vertex 80 V at spectral resolution of 4 cm<sup>-1</sup> and 1024 scans. A nitrogen cooled MCT detector and a special homemade chamber were used [4].

A constant monitoring of the humidity level during all measurements showed that the system was contaminated with 7-9 ppm water, in "dry air" conditions. This fact plays an important role in the understanding of the water / OH equilibrium on the surface.

In the catalytic conversion measurements we examined the changes in the composition of the ambient atmosphere by analyzing the exhaust with the help of a residual gas Mass Spectrometer (MS): Hiden Analytical mass spectrometer (HPR-20 QIC). The electrical resistance measurements were performed by using a computer controlled digital multimeter.

## Results and discussion

The impact of the presence of different concentrations of water vapor on the CO sensing is shown in figure 1.

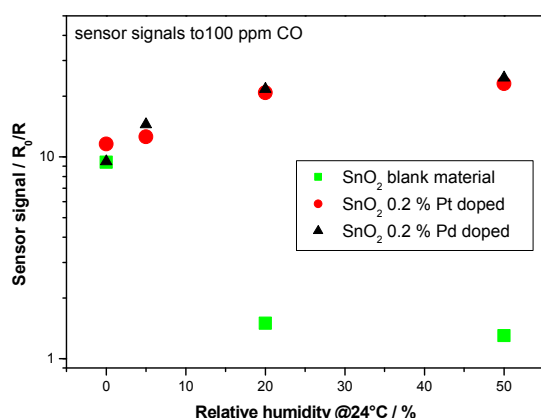
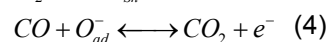
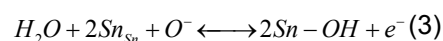
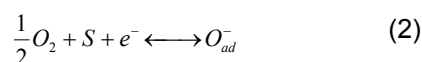


Fig.1 Sensor signal of SnO<sub>2</sub> blank, SnO<sub>2</sub> 0.2% Pt, SnO<sub>2</sub> 0.2 % Pd at different humidity levels, 300°C

As already mentioned, the results are very different for the undoped and doped materials. For the undoped one, the sensor signal is extremely decreased, which can be understood in the light of the previous results that showed a competition between water vapor and reducing gases (Eq. 3 and 4) over the same reaction partners, pre-adsorbed oxygen ions, at the surface of the oxide [5].



In dry air (7-9 ppm humidity level), the reducing gas will react with the adsorbed oxygen and forcing a shift in the H<sub>2</sub>O (7-9 ppm in the ambience)/ OH equilibrium to the left. But, in case of humid air, the concentration of water molecules is increased; the majority of adsorption sites (O<sub>ad</sub><sup>-</sup>) are occupied by the water. Hence, not many reaction sites for CO are available and the impact on the resistance (sensor response) is much lower compared to dry air.

Also the results for the Pd doped materials are not that surprising because we knew, also from DRIFT experiments [2], that in its presence the influence of atmospheric oxygen on the concentration of hydroxyl groups is not significant. In other words: the additive Pd blocks the reaction of water with adsorbed oxygen on the surface. The present (small amount) of OH groups on the surface of the Pd doped sensor may be formed through another reaction path, not including O<sub>ad</sub><sup>-</sup>.

The results for Pt are surprising because our previous results, obtained by using materials with very different grain sizes and doping procedures, indicate that the influence of humidity is similar to the effects recorded on undoped materials [6]. The present study however indicates a similar effect for the noble metal additives Pd and Pt.

These explanations are supported by findings in the DRIFTS. Measurements with 100 ppm CO in dry air were performed.

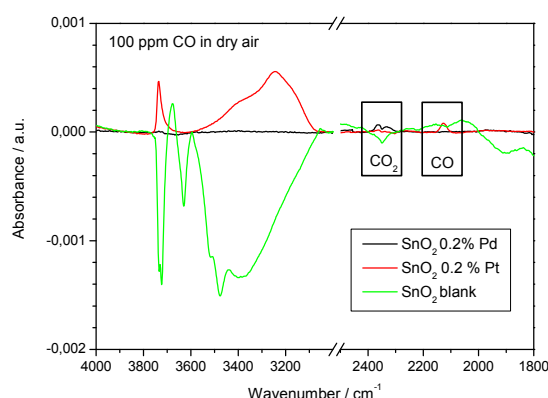


Fig.2: reaction with 100 ppm CO @ 300°C, dry air (7-9 ppm H<sub>2</sub>O contamination)

The undoped material shows a loss of OH groups under CO exposure, due to the co-adsorption of CO and H<sub>2</sub>O. A very weak signal of CO<sub>2</sub> (2346cm<sup>-1</sup>, almost covered by artifacts, introduced by the baseline correction) is visible. The Pd doped material shows a different behavior: the reaction with CO has no impact on the OH / H<sub>2</sub>O species; the only reasonable band in the spectrum is caused by the reaction product CO<sub>2</sub>. However, the most contrary reaction compared to the undoped material is taking place on the Pt doped material: OH groups are crowing upon exposure to CO. Moreover, the reaction product CO<sub>2</sub> cannot be seen in the spectrum, but CO (2130cm<sup>-1</sup>) is visible. The reactions of water on the surface and CO on the surface seem to be complementing each other: humidity increases

the sensitivity to CO and reaction with CO creates new OH groups.

In order to understand the electrical effects, we performed additional measurements: the results of the exposure to 3% r.h. D<sub>2</sub>O are displayed in figure 3.

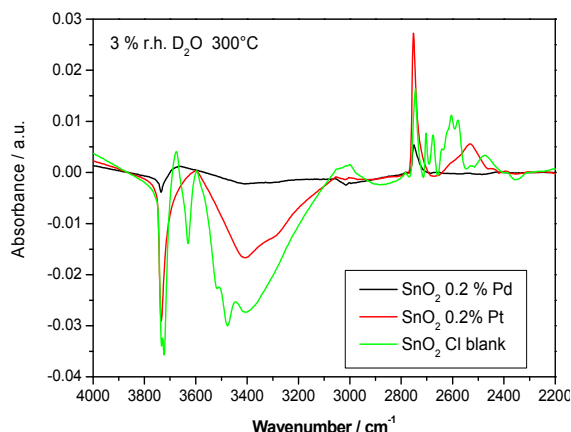
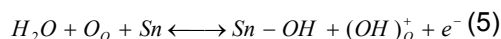


Fig.3: reaction with 3% r.h. D<sub>2</sub>O @ 300°C

Obviously, the reaction with D<sub>2</sub>O forces an exchange of surface OH groups with OD groups, as expected. What is striking in the results is the difference between undoped and the doped materials. In the case of undoped SnO<sub>2</sub> a large amount of surface OH is replaced with OD and also it looks like there are many types of those. In case of the Pt doped material, only one sharp peak (one type of OH group) and a broad band are present and changing due to this exchange reaction. For the Pd doped SnO<sub>2</sub> one single peak, with very low intensity, is present and changes due to the exposure to D<sub>2</sub>O.

Keeping the results from the CO sensing in mind, one explanation could be the creation of so called "rooted" OH groups. Since water and CO are not competing for the same reaction sites on the doped SnO<sub>2</sub> materials, there have to be different adsorption sites for each compound.



If we assume, that CO is reacting with O<sub>ad</sub><sup>-</sup>, one has to look for an alternative for the reaction with water on the surface. One possibility could be the reaction with lattice oxygen to rooted OH. Those compounds are believed to be donor species and release an electron to the conduction band.

Currently we are performing exposures to CO in various backgrounds of H<sub>2</sub>O and D<sub>2</sub>O vapor concentrations in order to better understand the reaction paths.

## References

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