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To cite this article: Jan-Dierk Grunwaldt *et al* 2013 *J. Phys.: Conf. Ser.* **430** 012078

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The potential of operando XAFS for determining the role and structure of noble metal additives in metal oxide based gas sensors

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Abstract. Noble metal additives significantly improve the performance of SnO₂ based sensors. Recently, it has been found that X-ray absorption spectroscopy is an excellent tool to identify their structure under sensing conditions, despite of the low concentrations and the rather thin (50 μm) and highly porous layers. For this purpose a new in situ approach has been established and here we highlight the potential with an overview on the results of Pd-, Pt-, and Au-additives in SnO₂-based sensors at work. Emphasis was laid on recording the structure (by XANES and EXAFS) and performance at the same time. In contrast to earlier studies, Pd- and Pt-additives were observed to be in oxidized and finely dispersed state under sensing conditions excluding a spillover from metallic noble metal particles. However, Au was mainly present as metallic particles in the sensing SnO₂-layer. For the Pt- and Au-doped SnO₂-layers high energy-resolved fluorescence detected X-ray absorption spectra (HERFD-XAS) were recorded not only to minimize the lifetime-broadening but also to eliminate the Au- and Pt-fluorescence effectively and to record range-extended EXAFS.

1. Introduction

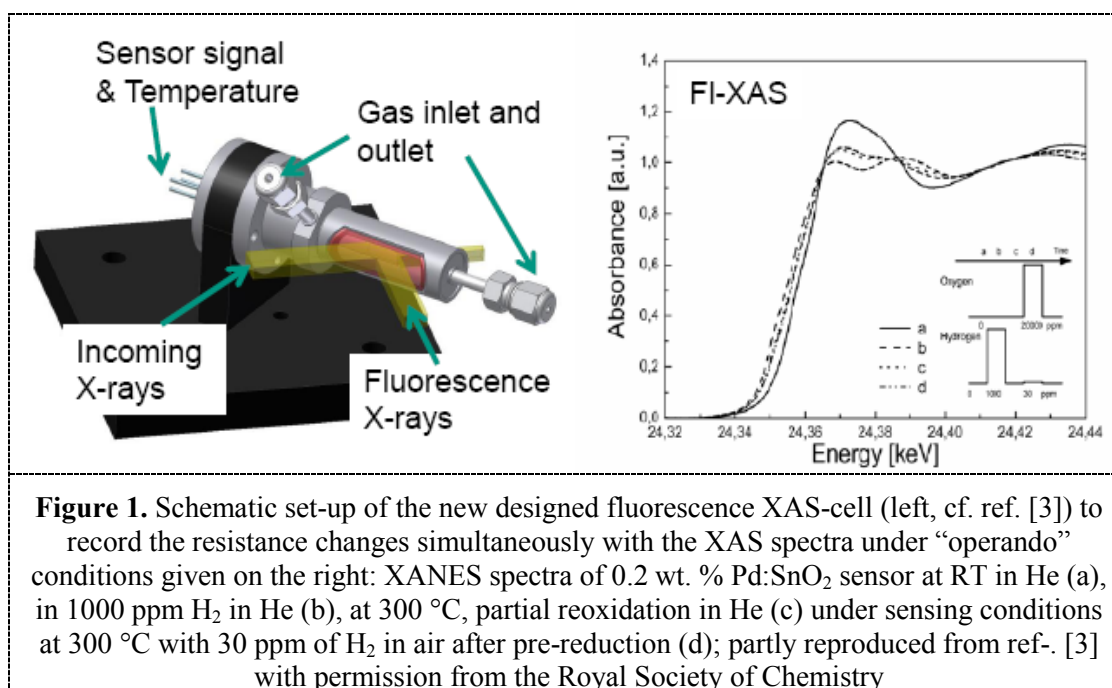
The qualitative and quantitative detection of various gases is essential for areas like process monitoring, environmental control, safety, comfort and health. One of the most promising approaches is the use of gas sensors based on semiconducting metal-oxides due to their high sensitivity, long-term stability, low cost in production and relative low power consumption during operation. State-of-the-art semiconducting metal oxide based gas sensors are mostly using porous, 10 – 50 μm thick film SnO₂ layers deposited via screen printing or drop coating onto a transducer [1]. In order to further improve their sensing performance, especially to diminish the cross sensitivity towards water vapor, small quantities of noble metal additives (Pt, Pd and Au) are generally introduced into the sensing layer [2].

Although these promoters are considered to be the most relevant ones since several decades, the understanding of their role is still under strong discussion. This is mainly due to the lack of spectroscopic measurements on real sensors under relevant operation conditions (“operando”). We were recently able to minimize this gap by applying for the first time X-ray absorption spectroscopy under real “operando” conditions and thereby deriving structure-function relationships helping to

explain the improving effect of these additives [3-5]. The greatest challenge in these studies is the fact, that the noble metals Pt, Pd and Au are present in very low concentration (0.2 wt. %) in a heavily X-ray absorbing, highly porous SnO₂ matrix (50 μm thick films). In addition, the platinum present in the electrodes and the heater of the conventional sensor devices leads to strong Pt-fluorescence hiding the signals of the gold and platinum additives in SnO₂. In the present study, we give an overview how to tackle the structure of the mentioned noble metal additives in SnO₂-sensors and how the challenges in low concentration, sensor and cell-design can be overcome.

2. Results

In a first step, the structure and role of Pd additives in SnO₂ based gas sensors was elucidated by using X-ray absorption spectroscopy in real sensing operation conditions. For this purpose a new cell was designed (Figure 1, ref. [3]) which allows (i) measuring the variation in resistance (corresponding to the sensor signal) as a function of the atmospheric compositions, (ii) operating the sensing layer at well controlled temperatures and (iii) recording at the same time X-ray absorption spectra in the fluorescence mode at the Pd K-edge. The experiments were performed at the undulator beamline ID26 of the European Synchrotron Radiation Facility (ESRF) using a pair of cryogenically cooled Si(311) crystals. The Pd K α fluorescence was recorded using a Si photodiode and copper foil as filter. Both XANES and EXAFS analysis showed that Pd at low concentration (< 1wt%) is present on an atomic level in an oxidized state, well dispersed at the surface and in the bulk of the host SnO₂ material [3,6]. Due to the high dispersion 0.2wt%Pd/SnO₂ is only reduced above 200 °C in 1000 ppm H₂/He (Figure 1). A change in the chemical state of the Pd sites during sensing of CO and H₂ could not be observed although tremendous changes in the resistance were observed with 30 ppm H₂ or 50 ppm CO in air. In addition, these Pd species depict a rather dynamic reduction-re-oxidation behavior [3].



In case of Pt additives two additional challenges came up. Since Pt was also used for the heater/electrodes in the conventional sensor device, a new sensor substrate - showing similar electrical characteristics - had to be designed. Au was used instead of Pt for the electrodes and the Pt heater was replaced by a Pd/Ag alloy resistance heater on the back (see schematics in Figure 2). Nevertheless, the disturbing gold fluorescence from the new electrode material had to be eliminated (Au L α_1 line at 9.442 keV and Pt L α_2 -line at 9.713 keV). This was achieved by recording high energy resolved

fluorescence detection (HERFD) XAS at ID26 at the ESRF with an X-ray emission spectrometer in horizontal plane. Sample, analyzer crystal and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry [7]. The Pt HERFD-XANES spectra at the L_3 -edge were obtained by recording the intensity of the Pt $L\alpha_1$ emission line (9442 eV) as a function of the incident energy (Figure 2). The emission energy was selected using the $\langle 660 \rangle$ reflection of four spherically bent Ge crystal analyzers (with $R = 1\text{ m}$) aligned at 80° Bragg angle. A combined (incident convoluted with emitted) energy resolution of 1.8 eV was obtained as determined by measuring the elastic peak. This approach succeeded and due to the 0.2 wt. % Pt/SnO₂ layer being on top of the Au electrodes no self-absorption effects were found (Figure 2). This also demonstrates that no remarkable diffusion of gold into the sensing layer has occurred. The experiments further uncovered that under operating conditions – temperature of 300°C in dry air - platinum is in a highly oxidized state and does not change upon CO and H₂ exposure [4]. In addition, also no change in the oxidation state of Pt during similar reduction-reoxidation experiments like in the case of Pd could be observed. Finally, EXAFS analysis uncovered that the highly oxidized Pt is dispersed also on an atomic level in the lattice of SnO₂, on the surface as well as incorporated in the bulk.

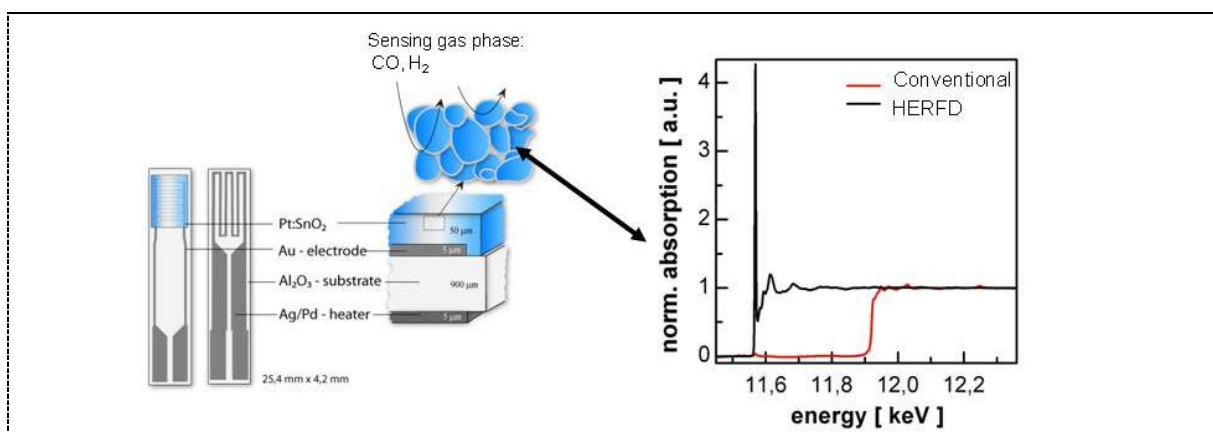
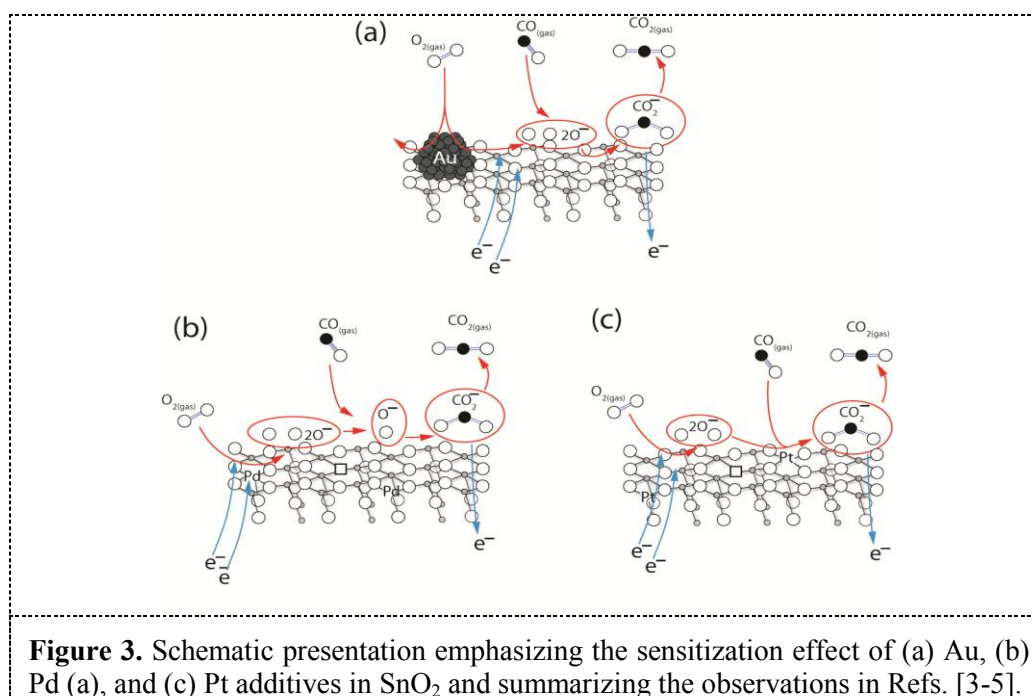


Figure 2. Principal hierarchical structure of the sensor for studying the Pt-doped Pt:SnO₂ based sensor with Au-electrode and PdAu-heater (left, cf. Ref. [4]b) and XANES and EXAFS spectra (right, cf. Ref. [4]): Pt L_3 edge EXAFS spectra of the 0.2 wt. % Pt:SnO₂ sensor with Au electrodes measured by HERFD-XAS (black) and traditional (red, Pt L_3 -edge hardly visible) detection mode.

These results are surprising because in previous studies dealing with model samples (much higher concentrations) or conditions (far away from the operational ones), metallic particles or clusters were found and have been ascribed in some of the models to the improved sensing performance [8,9]. In our samples, Pd and Pt exhibit a quite similar effect, namely on one side a surface effect (surface sensitization) and on the other side a bulk effect (change of the electrical properties of the semiconductor) as illustrated schematically in Figure 3 a and b.

Finally, the focus was on Au promoted SnO₂ based gas sensors, demonstrating an improved sensing and catalytic performance towards CO due to the presence of the additive. Contrary to Pd and Pt - being present in an oxidized state - HERFD-XANES spectra at the Au L_3 -edge revealed that Au is present in a bulk metallic form and that the chemical state is not changing during exposure towards CO and H₂ [5]. The sensitization effect of gold additives in SnO₂ based gas sensors is therefore attributed to small gold metallic particles incorporated in the SnO₂ layer. The high chemical activity of these very small Au particles facilitates the dissociation of oxygen as known from CO-oxidation (spill-over effect; see Figure 3 c) and therefore enriches the surface of the metal-oxide with oxygen ions, which are the source of CO and H₂ sensing. A direct electrical connection with the SnO₂ matrix could not be observed.



3. Conclusions and outlook

This overview on differently doped metal oxides underlines the importance of studying the materials as close as possible to the operating conditions, the strength of novel X-ray absorption spectroscopic techniques and the design of in situ cells/devices that allow both monitoring of the structure and sensor performance as known from catalysis. They provided new insight into the sensing mechanism demonstrating a rather similar sensitization effect for Pt and Pd, but a very different mechanism for the Au additive. In future, it will be interesting to extend this to sensors prepared by different preparation techniques and further dopants as well as sensor materials.

4. Acknowledgements

We thank ESRF (Grenoble, F) for beamtime allocation at the insertion device beamline ID26, financial support and Kristina Kvashnina, Marcin Sikora, and Pieter Glatzel for their help and discussion. Moreover, JDG thanks for financial support and original seed funding by the Karl Winnacker grant.

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