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Experiment Report Form

ESRF	**Experiment title:** Identification of Pt(II) in Pt-SnO_2 gas sensor under real working conditions using High-energy-resolution fluorescence detection (HERFD) XAS	**Experiment number**: MA-319
Beamline: ID26	**Date of experiment**: from: 11/07/2007 to: 25/07/2007 from: 21/08/2007 to: 25/08/2007	**Date of report**: 22/02/2008
Shifts: 38	**Local contact(s)**: Pieter Glatzel, ESRF	*Received at ESRF:*

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Report:

Nanocrystalline SnO_2 is the most promising material for the development of resistive gas sensors, which are used for the detection of toxic and explosive gases in the atmosphere (CO, H_2, NO_x etc). SnO_2 is a wide band gap semiconductor of n-type. The conductivity of this material depends on the atmosphere composition. Adsorption of oxygen on the SnO_2 surface creates so-called ‘trapped charges’. Chemisorption and subsequent redox reactions of a target gas with the adsorbed oxygen species lead to modulations of the quantity of charge on the surface and a variation of conductivity. Deposition of metal nanoparticles (Pt, Pd) on the SnO_2 surface enhances the sensitivity to CO and H_2 and decreases the working temperature. In spite of the wide practical application the role of the nanoparticles is still under discussion.

In the present work we have studied the gas sensors, which were nanocrystalline SnO_2 films of 1 micron thickness containing 0.6 at% of Pt (sensor **A**, Pt nanoparticles of 1.5 nm [2]) and 6.3 at% Pt (sensor **B,** Pt nanoparticles of 2.5 nm [1]), respectively. The idea was to see in which state Pt nanoparticles (size, oxidatation state) improve the sensor properties of SnO_2 thin films towards low concentrations (1000ppm) of

CO and H_2 in low temperature regime (25 and 100°C). To produce Pt nanoparticles having different oxidation states sensors **A** and **B** were treated either in oxidizing (**ox** 20%O_2 in He) or in reducing (**red** 1000 ppm CO in He) atmospheres at 350°C then cooled down and purged with He. Then gas sensor properties of **A_ox**, **B_ox**, **A_red**, and **B_red** were studied at 25 and 100°C in the same reactor. During all the process we measured the evolution of HERFD XAS spectra at Pt L_3 – edge (with 2 min time resolution) and also catalytic properties (CO_2 production from CO) using mass-spectrometer. Exactly the same measurements were repeated using 1000 ppm H_2 in He as a reducing atmosphere.

Figure 1 shows Pt L_3 HERFD XAS spectra in **A_ox**, **B_ox**, **A_red**, and **B_red** gas sensor films together with the spectra of pure PtO_2 , 1nm-Pt nanoparticles on alumina (reduced in H_2), and Pt(II)acac used as the reference samples. One can see that sensor **A** changes significantly its oxidation state depending on the annealing atmosphere and the sensor **B** does not. It may be explained by the fact that nanoparticles in the sensor **A** are smaller and the structure of SnO_2 thin film is more porous [1] compared to the sensor **B**. This is probably why the nanoparticles in the sensor **B** stay metallic after annealing in oxidizing atmosphere.

None of the spectra look like Pt(II)acac. It is also interesting to note that (i) HERFD XAS spectra of Pt in the **B_ox** and **B_red** are very similar to that of metallic platinum, (ii) the spectrum **A_ox** resembles that of PtO_2, (iii) but the spectrum of **A_red** is different. The white line of **A_red** is small like in the reduced state but shifted to higher energies compared to that of metallic Pt. We were considering two possible explanations: (1) absorption of CO on Pt nanoparticles (this structure was discussed in [3]) and (2) formation Pt-Sn alloyed nanoparticles due to reduction of SnO_2 during interaction with reducing atmosphere. Figure 2 shows the Pt L_3 HERFD XAS spectrum of **A_red** plotted together with that of **A_red_H₂** (**A** sensor reduced in 1000 ppm H_2 in He atmosphere at 350°C) and the reference spectra of 1nm Pt nanoparticles on alumina reduced in H_2 and the same Pt particles covered with chemisorbed CO [3]. The spectra of **A_red** and **A_red_H₂** resembles the one of 1nm Pt on alumina covered by CO, however, in our case this explanation is impossible since **A_red_H₂** cannot have chemisorbed CO on its surface. Therefore the second explanation related to formation of Pt-Sn alloyed nanoparticles is more probable. To confirm it we performed FEFF8 calculations using Pt_6 and $PtSn_5$ clusters simulating platinum atoms on the surface surrounded by Pt and Sn, respectively [3]. Figure 3 shows the experimental spectrum of **A_red** compared to theoretical ones of Pt_6 and $PtSn_5$ clusters. One can see that the white line of $PtSn_5$ cluster is shifted to the higher energies compared to the one of Pt_6. Therefore we suppose that Pt **A_red** sensor can be partially surrounded by Sn, partially by Pt, and partially by O atoms

The most important result is that we have found a very clear correlation between the oxidation state of Pt nanoparticles at the sensor properties of corresponding SnO_2-based gas sensors. The sensor properties of four sensors towards low concentration of CO at 25°C are shown in Figure 4. One can see that **A_ox** sensor, which contains mostly oxidized Pt nanoparticles, is the most performing. In the presence of CO the conductivity of sensor **A_ox** changes reversibly by three orders of magnitude. The sensitivity of the other sensors is much smaller. It should be mentioned that changes Pt L_3 HERFD XAS spectra of **A_ox** due to the presence of CO at 25°C are very small, platinum stays oxidized like PtO_2 and not like Pt(II) (Figure 6). Therefore we can conclude that platinum nanoparticles is the performing SnO_2 gas sensors has to be oxidised, however, Pt(II) species do not need to be present. The experiments with 1000 ppm H_2 have shown very similar results both in conductivity response and changes in Pt L_3 HERFD XAS spectra. It means that the role of Pt nanoparticles in the low temperature (25-100°C) sensor response towards CO and H_2 is similar and rather 'chemical' than 'electronic' [2]. The mass-spectrometer data also correlates with proposed mechanism. Figure 5 shows the kinetics of CO_2 production during the sensor response process towards 1000 ppm CO in He. **A_ox** sensor has the highest catalytic activity in CO oxidation reaction with oxygen chemisorbed on SnO_2 surface, which means that oxidised Pt nanoparticles (in oxidised state) are more active than metallic or alloyed, which fully explain their promoting effect on the sensor properties of nanocrystalline SnO_2. Recent surface diffraction studies on platinum single crystal surfaces have indicated a higher rate of oxidation of carbon monoxide at when the surface is oxidized to PtO_2 [4]. There is a clear correlation with our data.

1. I. Matko et al., *Sensors and actuators B*, 59(1999) 210-215
2. O.V. Safonova et al., *J. Phys. Chem B*, 2006, 110, 16162
3. O.V. Safonova et al., *Chemical Communications,* 2005, 5202-5204.
4. M.D. Ackermann et al., *Phys. Rev. Lett.,* 95 (2005) 255505
5.

Figure 1a

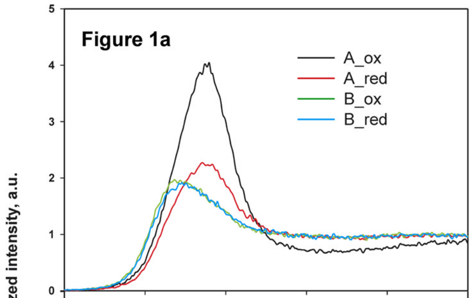

Figure 1b

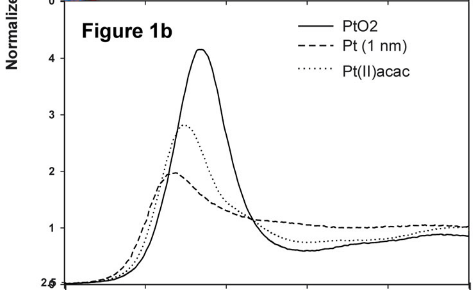

Figure 2

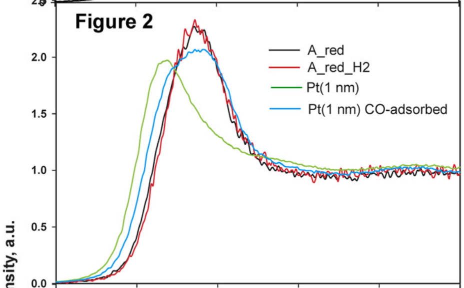

Figure 3

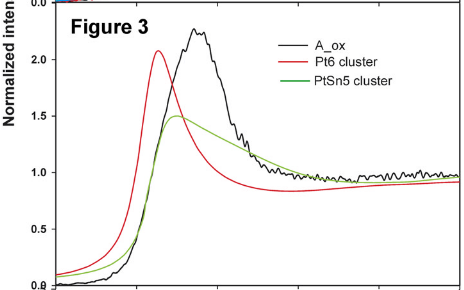

Figure 6

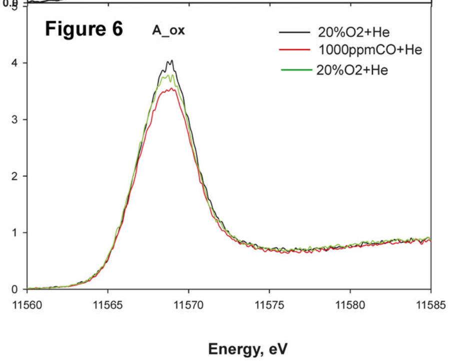

Figure 4

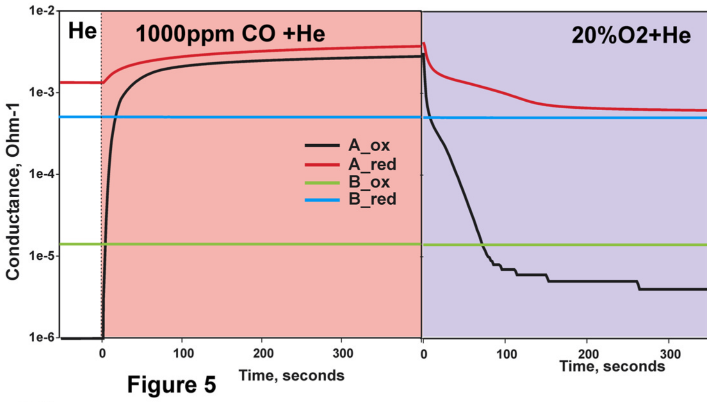

Figure 5