	Experiment title : <i>In-situ</i> EXAFS analysis of the local environment of metallic elements incorporated in thin films of semi-	Experiment number:
	conductor oxide used as gas-sensors	HS 53
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Report:

Advances in solid material synthesis and new possibilities offered by microtechnologies have contributed widely to the development of devices for detecting polluting gases in air, particularly reducing gases such as carbon monoxide and methane.

By submicronic aerosol pyrolysis (Pyrosol process) our group is able to synthesize thin films, of doped tin oxide on oxidized silicon substrates (SiO_2 thickness: ≈ 1 micron, SnO_2 thickness ≈ 1 micron, sample area $\approx 15x10$ mm2). A very fine and homogeneous dispersion of metallic aggregates (3-5 nm) within the film is obtained by co-deposition of the two species (tin oxide and metal). This method provides metallic particles whose size increases with the amount of metal in the co-deposition. In the case of 6% Pt doped tin oxide thin films, this particular structure leads to electrical transport properties highly sensitive to carbon monoxide just above $100^{\circ}C$ (fig. 1).

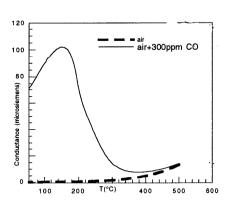


Figure 1: SnO₂ film conductance as a funtion of temperature under air and under air+300 ppm CO

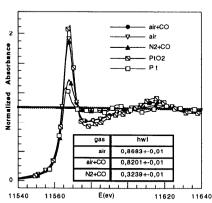
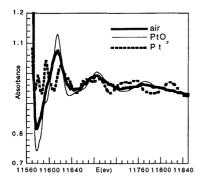


Figure 2: oxidation state of Pt under various working conditions: air in absence of CO, in presence of CO and under N2 in presence of CO

hwl: heigh of the white line

The interaction phenomena between CO and the composite [Sn02 + Pt or Pd (or PdO) clusters] are not completely understood. They are potentially described by a simple model where the adsorption of reducing species leads to a modification of local environment of the metallic element and of its oxidation state as well. This is associated with an electronic charge transfert between the clusters and the SnO_2 support however. This model nevertheless needs to be verified and refined to allow accurate manipulation of the sensitivities to various gases and temperatures.

As EXAFS is the only technique which allows the detection and analysis of the surroundings of metallic elements under controlled atmosphere we have used X-ray absorption to study the local environment and the oxidation state (XANES) of the metallic elements added into the films. To confirm that the method could be used we decided to analyse at first a favourable case: films with platinum as metallic additive. An EXAFSin-situ experiment has been carried out as the material (SnO₂ films with various amounts of Pt particles - 12%, 6%, 3% - deposited on an oxidised $2x2cm^2$ silicon substrate) was inserted in a specific reaction cell, heated to maximum temperatures of 400° C and put in contact with air or with a polluting gaseous mixture containing small amounts of reducing gas (Air + 300ppm CO, N₂ + 900ppm CO). The thickness of the films was in the range of a few μ m. The X-ray absorption has been measured in fluorescence mode within an energy range close to Pt L_{III} edge.



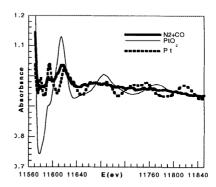


Figure 3: observation of the reduction process of SnO2+6%Pt and comparison with references.

As the experiment has been performed in December 1997, the data processing has not been fully completed but a substantial amount of results has already been obtained:

The evolution of the white line shows that the platinum particles exhibit two states: either oxidised or reduced, depending on the reducing ability of the gas (see fig. 2). Qualitatively, the XANES analysis and the distances to the first neighbours detected in the Fourier transforms of the normalised patterns can be correlated with an oxidized state characterized by Pt-O bondings (PtO₂ type) and a reduced state characterized by Pt-X bondings (CO or Pt) (see fig. 3). An important metallic particle size effect has also been detected: the change in the white line is particularly pronounced (see fig. 4) for the smallest particle concentrations. They correspond to the finest particles. In the case of 12% Pt film a very weak evolution has still be observed.

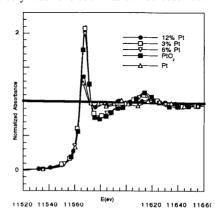


Figure 4: oxidation state of platinium under air gas, in the abscence of CO.

With decreasing the concentration in Pt