



**Titre de l'expérience:**

**Etude par diffusion centrale de rayons X de l'évolution morphologique des nanoparticules Au/TiO<sub>2</sub> sous pressions élevées de O<sub>2</sub>, de CO et de mélange réactif CO+O<sub>2</sub>**

**Experiment**

**number:**  
32-3-648

**Beamline:**  
BM32

**Date of experiment:**

from: 23/01/2007 to : 29/01/2007

**Date of report:**  
10.10.2007

**Shifts: 24**

**Local contact(s):** Odile ROBACH

*Received at ESRF:*

**Names and affiliations of applicants :**

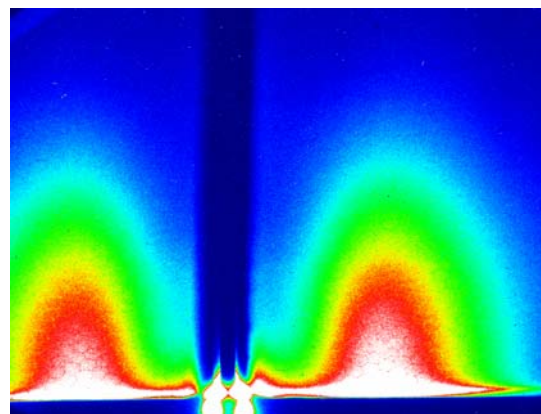
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The beamtime allocated by the CRG committee was followed by the one allocated by the ESRF committee; we report here only on a part of the whole results, the other part being the object of the Experimental Report SI 1459.

First our aim was to validate the set-up adapted to combine GISAXS-GIXS and reactivity measurements on supported nanoparticles. It was already used for in situ GISAX measurements [1]. For this experiment it was necessary to elaborate the gold nanoparticles supported on TiO<sub>2</sub>(110) in the UHV preparation chamber and then to transfer the sample in the x-ray reactor chamber. Guard slits on the incident beam and a beam stop for the direct one were adapted on the reactor for GISAXS (cf Fig.1).

Several equivalent gold thicknesses from 0,5 to 7 Å were explored. As shown in Figure 1, the level of noise was enough low to detect the signal from gold nanoparticles signal on GISAXS patterns. The gold nanoparticles were grown at room temperature and for example, the morphological parameters as deduced for 3.5 Å, are 3.2 nm for the particles diameter, 2 nm for their height and 5 nm for the spacing. These values are similar to those obtained for the same nominal deposit in experiment performed at the SUV-BM32 station [2].



**Figure 1 :** GISAXS image for a gold deposit of 1 Å thick

GISAXS, as well as GIXS, were performed under several conditions: under oxygen, CO pressures between 1 to 100 mbar, as well as under CO + O<sub>2</sub> reactive mixture (total pressure 10 to 20 mbar) with the ratio CO:O<sub>2</sub> between 1:2 and 1:100. In all cases the scattering signal due to the gas in the reactor stayed negligible except when the pressure reached 100 mbar, where the level of noise on GISAXS pattern increased significantly.

From GIXS we observed two epitaxies (fig.2):

(112)Au//(110)TiO<sub>2</sub> and (111)Au//(110)TiO<sub>2</sub>, both have the common direction [110]Au//[001]TiO<sub>2</sub>.

The crystallography was followed by several scans.

For thicknesses of 1 Å and 2 Å, spectra exhibit significant changes illustrated on fig. 3. Since at the beginning of the experiments, we had no idea of what will occurred, we did not systematically explore the more relevant scans.

**Figure 2 :** Cross-sectional representation of Au/TiO<sub>2</sub>(110) interfaces viewed along [001]TiO<sub>2</sub> direction with in (a) (111)/(110)TiO<sub>2</sub>, and (b) (112)/(110)TiO<sub>2</sub> orientations. The Au atoms are marked by circles, while O and Ti are represented by large and small squares respectively (from [3]).

The lattice parameter of fcc gold is  $A=4.08\text{Å}$ . The lattice parameters of TiO<sub>2</sub>(110) are:

$$a=2.96\text{Å}, b=c=6.94\text{Å}$$

With the same axes, the lattice of Au(111)/(110)TiO<sub>2</sub> are:

$$a_1=A/\sqrt{2}, b_1=3A/\sqrt{6} \text{ and } c_1=A\sqrt{3}$$

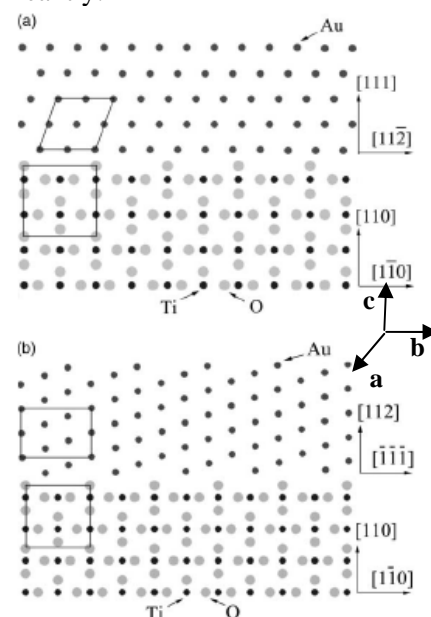
and in the reciprocal unit of TiO<sub>2</sub>(110):

$$a_1^*=1.027a^*, b_1^*=1.3b^*, c_1^*=0.919c^*$$

for Au(112)/(110)TiO<sub>2</sub>:

$$a_2=A/\sqrt{2}, b_2=A\sqrt{3} \text{ and } c_2=3A/\sqrt{6}$$

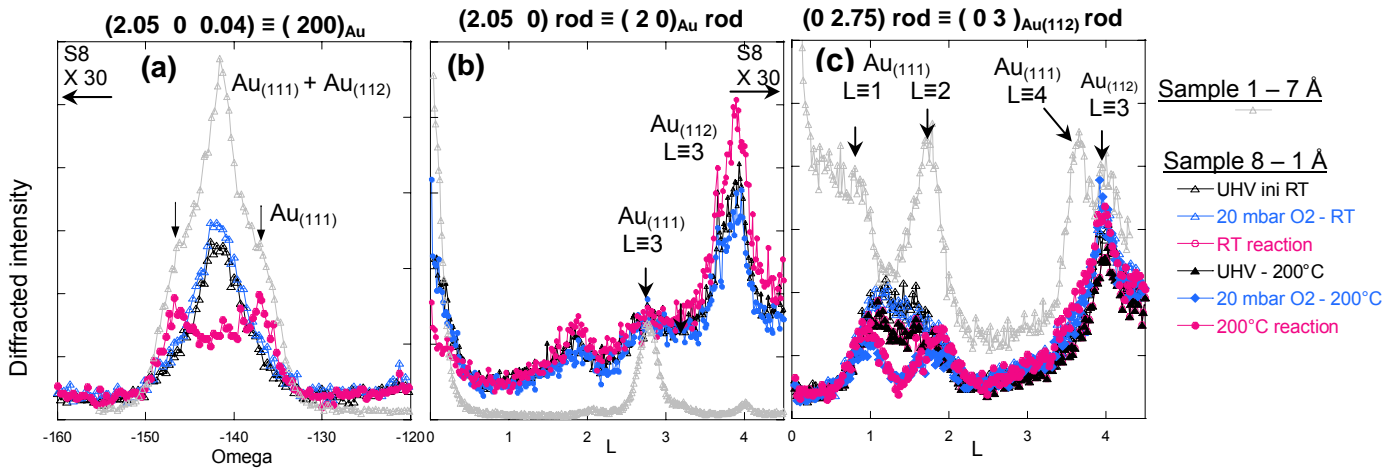
$$a_2^*=1.027a^*, b_2^*=0.919b^*, c_2^*=1.3c^*$$



Anyway, the first conclusions that can be drawn are:

- After gold deposition, the (111)Au//(110)TiO<sub>2</sub> and (111)Au//(110)TiO<sub>2</sub> epitaxies are observed, but the (111)Au//(110)TiO<sub>2</sub> one is predominant for thick deposits in contrast to thinner deposits where the more intense peaks correspond to the (112)Au//(110)TiO<sub>2</sub> epitaxy for the gold nanoparticles.
- No change were detected for the thicker samples under pressure of reactive gas.
- In contrast the GIXS scans of the thin 1 and 2 Å deposits, show that
  - For (111)Au//(110)TiO<sub>2</sub>, the inherent stacking faults due to growth process are healed by gaz exposure. Moreover, the preferential direction of expitaxy rotates with a small angle (4.9°) and the the Au[1-10] direction is no longer parallel to the [001]TiO<sub>2</sub> one.
  - The peak intensities of the (111)Au//(110)TiO<sub>2</sub> epitaxy are increased

However, this was only observed in a few cases and not always in the better conditions, especially for the (111)Au//(110)TiO<sub>2</sub> epitaxy where the scan along the rod were not performed for the good value of h and k. A systematic study with O<sub>2</sub>, CO, CO + O<sub>2</sub> for different Au particle sizes is required and it is the object of new proposals.



**Figure 3 :** GIXS scans along typical reciprocal space directions for sample 1, 7 Å thick, and for sample 8, 1 Å thick. For the thicker sample, there is only one curve since not significant change was seen for different conditions of reactive gas pressure.

- (a) Azimuth scan around the (2.05 0 0) peak, this correspond to (200) reflexion gold unit for the both epitaxial planes (111)//(110)TiO<sub>2</sub> and (112)//(110)TiO<sub>2</sub>. In UHV and for both thicknesses, we observe a main maximum at (200)Au including the contributions of the two orientations. It presents shoulders on both sides, indicated by arrows, which corresponds to islands with the (111) epitaxy rotated by 4.9°<sup>[2]</sup>. For the thin 1 Å deposit, under reactive conditions (20 mbar O<sub>2</sub> + 0,1 mbar CO) and at 200°C, the main peak decreases, when the two satellites become predominant, indicating that most of the (111) Au island has rotated.
- (b) Lscan along the ( 2.05 0 )<sub>TiO<sub>2</sub></sub> rod, equivalent to (2 0)<sub>Au</sub>. For the 7 Å sample, the main peaks correspond to L=0 and 3 of the (111) epitaxy. For the 1 Å sample and in UHV, the main peak correspond to L=0 and L=3 of the (112) epitaxy, this L=3 reflexion being forbidden for bulk Au fcc. Moreover this peak is vanished for the thicker sample, while it is little enhanced for the thin 1 Å sample under the reactive (O<sub>2</sub> + CO) mixture at 200°C.
- (c) Lscan along the (0 2.75 )<sub>TiO<sub>2</sub></sub> rod. This rod corresponds to the (0 3) one for the (112) epitaxy but it does not fit to one direction of the (111) epitaxy, the closer is the (0 2) rod, i. e. (0 2.6 )<sub>TiO<sub>2</sub></sub>. The observed peaks for the 7 Å sample around the corresponding L=1,2 and 4 comes from the cut of the edge of the peaks due to the two 60° fcc twinned domains of the (111) epitaxy (ABC and ACB stacking). For the 1 Å sample and in UHV, the main peak correspond to L=0 and L=3 of the (112) epitaxy. Let us stress that this “forbidden” peak is vanished for the thick sample, while it is little enhanced for the thin 1 Å sample under the reactive (O<sub>2</sub> + CO) mixture at 200°C. We also observe for this sample that the two peaks at L=1 and L=2 of the (111) epitaxy merge around L=1.5, significant of ABC stacking with many faults. These are removed under pressure of oxygen at 200°C.

In conclusion this indicates that the reactive molecules, even oxygen, strongly interact with the Au nanoparticles in contrast to the bulk Au surface. For both epitaxies, the Au nanoparticles structure is fcc but the facet planes and probably the corner an step density at surface are not the same. This would strongly modify the electronic density and thus influence the catalytic activity. More experiments are needed to interpret the observed crystallographic modifications of the gold nanoparticles on TiO<sub>2</sub> under pressure and understand their role on their remarkable activity for CO oxidation.

<sup>1</sup> M.C. Saint-Lager *et al* Rev. Sci. Inst. 78, (2007) 083902

<sup>2</sup> R. Lazzari, G. Renaud, J. Jupille, F. Leroy, Phys. Rev. B 76 (2007) 125412

<sup>3</sup> Cosandey *et al*, Surf. Sci. 474 (2001)1