St. Martin d'Hères, 2008-09-10

June 2008, we realized the *in situ* Surface X-Ray Diffraction **experiment number 02 02-716** on the French CRG beamline D2AM. This experience is the following of experiment number 02 02-697 (July 2007).

Working at grazing incidence, we could measure the diffraction intensities for various rods on the electrochemical Pd deposition onto Pt(111). We followed the hydrogen insertion/desorption, recording our data before, during and after H insertion for different equivalent thicknesses of deposited palladium (2 - 15 layers).

Equivalent thickness: 2 ML

- **i)** We pointed out the role of chlorides in the deposition solution to favour 2D film growth. The structural description of 2ML equivalent thickness deposit only needs 3 layers, with a very low occupation rate of the third layer (~20%).
- **ii)** After hydrogen insertion at a potential where the deposit should be totally hydrided, the evolution of interlayer distances suggests a resistance to hydriding for the two first atomic palladium layers. A substrate effect is clearly shown.
- **iii)** We observed the lowering of the hydrogen stochiometry between the second and the third Pd layers, compared to bulk Pd.
- **iv)** Measurements after total desorption of hydrogen show that the film structure gets back its initial state. It traduces a good reversibility of the structure towards one hydrogen insertion – desorption cycle, contrarily to bulk Pd.

Equivalent thickness: 15 ML

i) The signature of the Pd hydride formation during insertion, shown in figure 1a, is confirmed.

The comparison between Kiessig fringes (frequency and amplitude) in specular (0,0,3) CTR and non specular CTRs before, after insertion and after desorption o hydrogen gives clear indication that

ii) Hydrogen insertion destroys the pseudomorphic character of Pd deposition

iii) Irreversible morphological modification occur after only 1 insertion/desorption cycle.

Our results, even if quantitative analysis is not yet finished, give original information about the behaviour of hydrogen insertion/desorption in nanosized Pd systems as a function of the thickness and point out the effect of the Pt substrate.

These results have already been presented at an international conference:
“H electroinsertion in Pd nanofilms: in situ SXRD”, Chrystelle Lebouin, Y. Soldo-Olivier, E. Sibert, F. Maillard and M. De Santis, International Society of Electrochemicstry (ISE) 2008, 7-12 september 2008, Seville (Spain), oral presentation

One paper concerning the results on the deposit with equivalent thickness of 2 monolayers will be rapidly submitted. Preliminary quantitative analysis on the data concerning other thicknesses confirms the high quality of measurements and two other papers are planned.

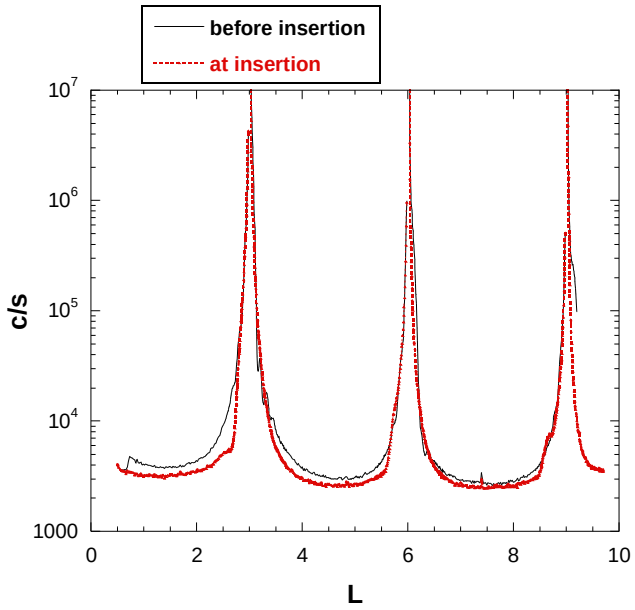

Figure 1: 15 monolayers of palladium electrodeposited on Pt(111). *In situ* recorded diffraction intensities, (11) rod, at -100 mV/ECS (before hydrogen insertion) and at -320 mV/ECS (at hydrogen insertion).