

Surface nano-defect and crystal growth of electrochemical deposits

Electrochemical deposition of metals plays a key role in several fields like microchip interconnections protective coating. In the aim of optimizing the deposit quality, we want to understand the underlying mechanism at the atomic scale and link it to macroscopic parameters like electrical potential, temperature, active species and add-ons concentration.

Last years, we did fundamental studies on metal nanofilms electrochemically deposited on single crystal surfaces [1-5]. The use of single crystal allows having surfaces well ordered at the atomic scale with uniform active sites. Up to now, we characterized deposits ranging from 1 to 20 atomic layers, after completion, using electrochemical signature in acid solution, *ex situ* atomic force microscopy (AFM) [1] and *in situ* surface X-ray diffraction (SXRD) done at the European Synchrotron Radiation Source (ESRF, in Grenoble) [2-4].

Now, we are focusing on the growth mechanism of such deposits. For instance, for the deposition of the first atomic layer of Pd on Au(111), transient currents analysis showed three elementary steps including a Langmuir adsorption and a 2D nucleation & growth [5]. Indeed, up to now, we did not determine the corresponding mechanisms at the atomic scale. We also observed a strong variability between from one experiment to the other. We suspect residual nano-defects on the substrate surface.

In the present project, we want to join surface science approach and electrochemistry to really identify key parameters in growth mechanisms. Ultra High Vacuum (UHV) techniques will be used to prepare well-defined surfaces but also to add and quantified nano-defected on it. This part of the work will be done under the supervision of Dr. Bruno Gilles (SIMAP lab) [6]. Electrochemical kinetic studies will be done using classical method like potential step measurements, under the supervision of Dr. Eric Sibert (LEPMI Lab). Deposits, once completed or interrupted during deposition, will be first characterized electrochemically, back in UHV or with scanning tunneling microscopy (STM). In a second stage, we want to perform physical characterization *in situ* during the deposition. We also want to measure the electrochemical deposition current at the same time, to avoid experimental bias related to nano-defects variability. The first method will be SXRD. A specific cell is under development. Measurements will be done at the ESRF in collaboration with Dr. Maurizio de Santis (Néel Institute). The second *in situ* method will be STM. We already host a STM equipment in our lab but some experimental developments need to be done for *in situ* measurements. This will be part of the PhD work.

The candidate can ever have a background in physic or chemistry. The experimental aspect represents a large part of the work.

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1. Lebouin, C., et al., *Electrochemically elaborated palladium nanofilms on Pt(1 1 1): Characterization and hydrogen insertion study*. Journal of Electroanalytical Chemistry, 2009. **626**: p. 59-65.
2. Lebouin, C., et al., *Evidence of the Substrate Effect in Hydrogen Electroinsertion into Palladium Atomic Layers by Means of in Situ Surface X-ray Diffraction*. Langmuir, 2009. **25**: p. 4251-4255.
3. Soldo-Olivier, Y., et al., *Hydrogen Electro-Insertion into Pd/Pt(111) Nanofilms: An in Situ Surface X-ray Diffraction Study*. Journal of Physical Chemistry C, 2011. **115**(24): p. 12041-12047.
4. Soldo-Olivier, Y., et al., *H electro-insertion into Pd/Pt(111) nanofilms: an original method for isotherm measurement coupled to in situ surface X-ray diffraction structural study*. Electrochimica Acta, 2013. **112**(0): p. 905-912.
5. Sibert, E., et al., *Mechanisms of the initial steps in the Pd electro-deposition onto Au(111)*. Electrochimica Acta, 2014. **135**(0): p. 594-603.
6. El-Jawad, M., et al., *A portable transfer chamber for electrochemical measurements on electrodes prepared in ultra-high vacuum*. Review of Scientific Instruments, 2013. **84**(6): p. 064101.