Experimental Report (15/10/2015) Proposal 20130970

"ORGANIZATION OF PREFORMED COPT NANOPARTICLES ON PRE-PATTERNED GOLD SURFACES"

Beamline: IF-INS BM32 Date: 25-30 june 2014
Number of shifts: 18 Local contact: Gilles Renaud

Objective and expected results:

Arrays of size selected bimetallic nanoparticles are extremely promising from a magnetic point of view, but still remain difficult to achieve by conventional physical techniques (atomic deposition). In this domain, we aim at studying the organization and determining the surface pinning sites (steps, kinks..) of preformed size selected CoPt nanoparticles soft-landed on both Au (111) and Au (677) surfaces. The evolution of the system (organization, cluster coalescence...) with post annealing processes (required to obtain chemically ordered CoPt nanomagnets) will also be studied. According to previous results based on cluster deposition on surfaces (CoPt on graphite, Pt on graphene and Pd on gold) that reveal the extreme sensitivity of preformed clusters to atomic defects or super-structures, we should be able to obtain organized networks of size selected CoPt alloy clusters.

Results and preliminary conclusions:

Five samples of nanoparticles deposited on a gold monocrystal surface have been prepared and studied at ESRF (after UHV transfer from the PLYRA platform in Lyon, where the size-selected clusters are deposited, to the BM32 beamline UHV chamber). Two different surfaces have been used: Au(111) with the well-known herringbone reconstruction displaying a rectangular array of specific sites and a vicinal Au(677) surface where regularly spaced steps are present in addition to the reconstruction (note that due to the miscut of this surface, kinks are also present on the steps). We have considered CoPt clusters of two different sizes (2.3 nm and 3.5 nm diameter, corresponding respectively to a 150 V and 450 V deviation voltage in the MS-LECBD setup), with surface densities of a few thousands of clusters per μm^2. In addition, a sample of pure Co particles (4.9 nm diameter, 450 V deviation voltage) deposited on Au(111) has been studied at the end of the beam-time.

Interesting results have been obtained from XRD and GISAXS measurements, which have been performed as a function of the annealing temperature (from room temperature to around 700°C). Although the precise analysis of the data is still ongoing, the main conclusions are the following:

- No 2D spatial organization of the nanoparticles has been detected (no extra correlation peak in GISAXS patterns);
- The largest particles (CoPt and Co) are found to be in epitaxy with the Au surface;
- The surface reconstruction is perturbed by the cluster deposition, but is still present (especially the steps of the Au vicinal surface);
- Annealing has a strong influence, with a more visible epitaxy and disturbance of the surface structure, eventually resulting in an over-layer formation (particles disappear at high temperature);
- For the Au(677) surface covered by CoPt nanoparticles, the steps periodicity, as seen from XRD, is irreversibly modified upon annealing, while it is unmodified on the GISAXS patterns: this surprising result may be related to some step bunching or what is called an "adsorbate induced faceting" phenomenon (unprecedented feature with clusters deposited on a surface!).

In the end, the deposited particles have not diffused on the surface to self-organize on the pre-existing pattern, but instead a **strong interaction between CoPt (and Co) clusters and the Au surface** has been put into evidence, with **original results** (particle epitaxy, impact on the steps for the vicinal surface) that should motivate further experimental and theoretical investigations.

These results and conclusions are illustrated by a selection of experimental data shown in the following figures.

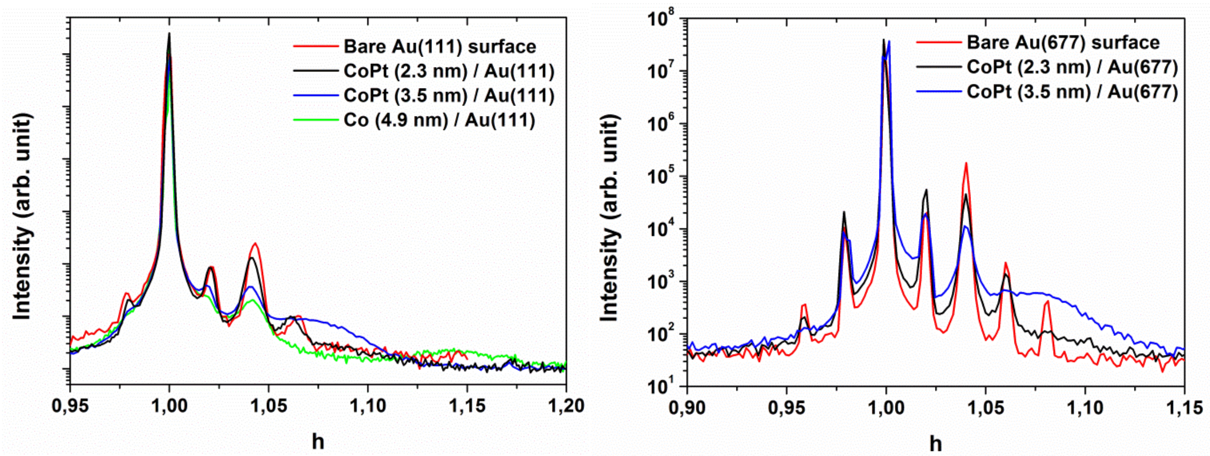


Figure 1: grazing incidence XRD (GIXRD) spectra along the (h00) direction where additional peaks due to the gold surface reconstruction are visible. Left: comparison of the bare Au(111) spectrum with the one measured (at room temperature) after cluster deposition. Right: comparison of the bare Au(677) spectrum with the one measured (at room temperature) after cluster deposition.

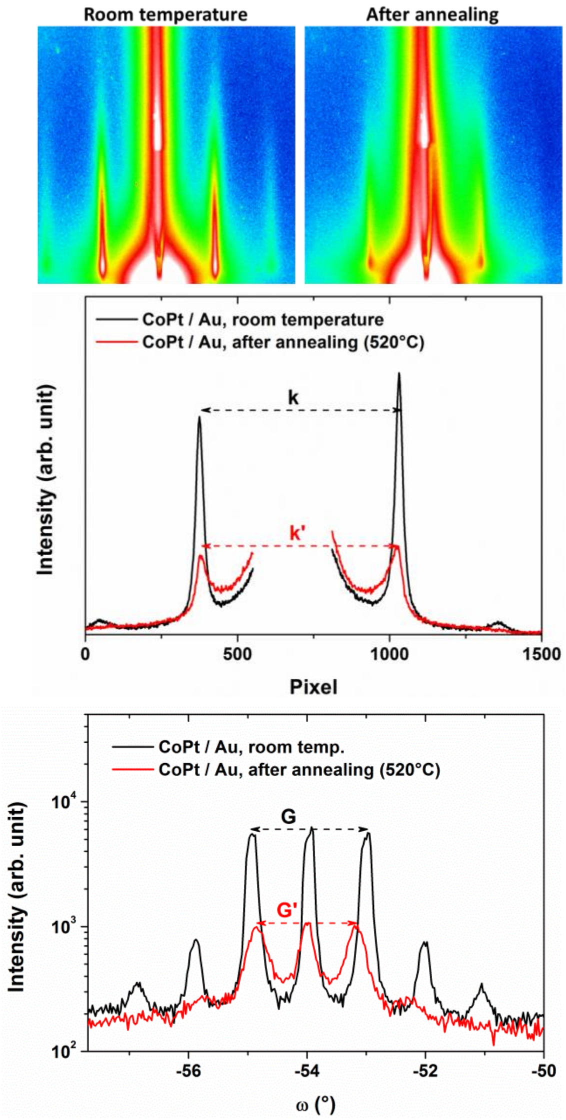


Figure 2: Irreversible change observed after annealing at 520°C, for the CoPt (2.3 nm diameter) / Au(677) sample, on the steps periodicity as measured by GISAXS (patterns on top, and corresponding line profiles in the middle panel) or by GIXRD (bottom). We find that k ~ k' (GISAXS) while $\Delta G/G$ = 13% (XRD, with $\Delta G = G - G'$).

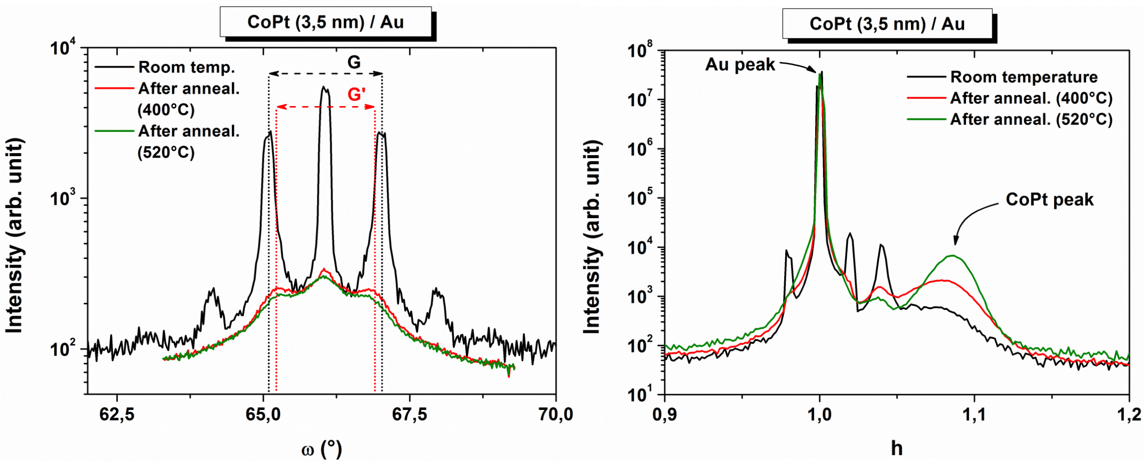
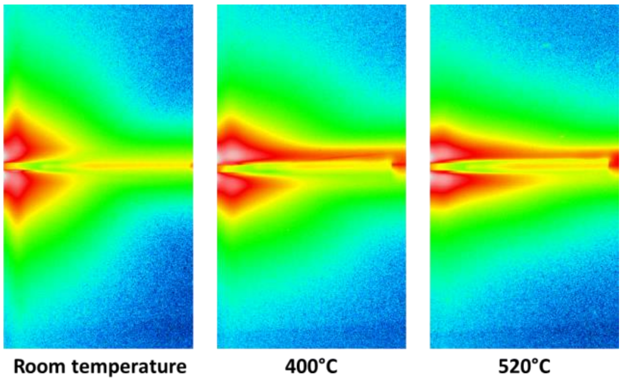


Figure 3: Evolution of the GIXRD spectra upon annealing, for the CoPt (3.5 nm diameter) / Au (677) sample, where the irreversible modifications of the steps periodicity (left) and the surface reconstruction (right) are visible. As for the smaller CoPt particles (2.3 nm diameter), a large ΔG/G value of 13% is measured (left). A clear peak, increasing with annealing, corresponding to a CoPt crystal in epitaxy with the gold surface is also visible (right), while the reconstruction is strongly disturbed.

Figure 4: Evolution of the GISAXS pattern (i.e. of the particle shape, these are out-of-azimuth measurements) upon annealing, for the CoPt (3.5 nm diameter) / Au(677) sample. Qualitatively, a flattening of the particles is detected.



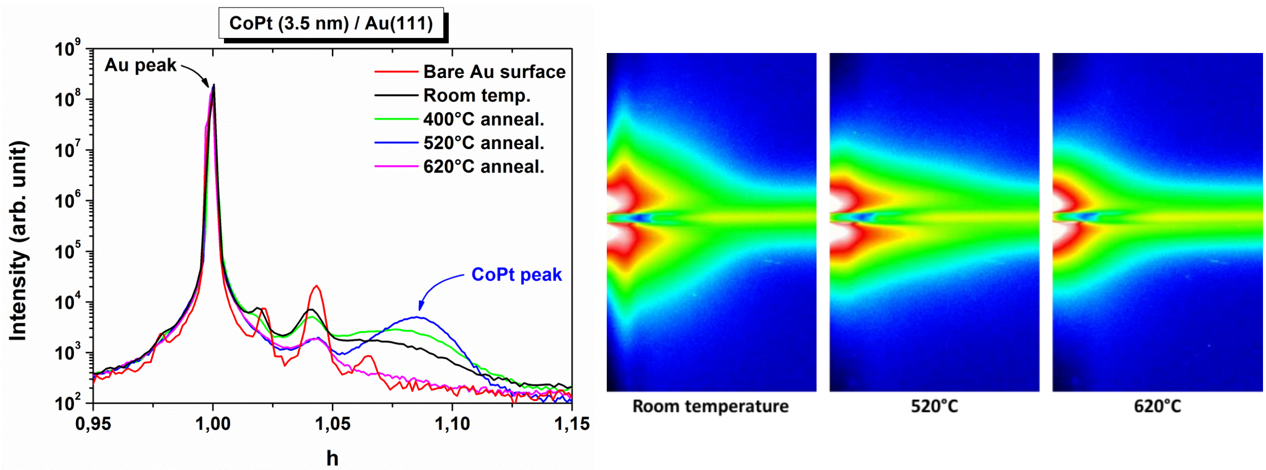


Figure 5: Effect of annealing, as seen on GIXRD spectra (left) and GIXAS patterns (right), for the CoPt (3.5 nm diameter) / Au(111) sample. As for the same particles on the Au(677) surface, the reconstruction is more and more disturbed with increasing temperature, while a peak corresponding to a CoPt crystal in epitaxy with the gold surface is getting more and more visible, before disappearing for the highest temperature (left). From the GISAXS patterns, we can qualitatively observe a concomitant flattening of the particles, which eventually disappear at 620°C (right).

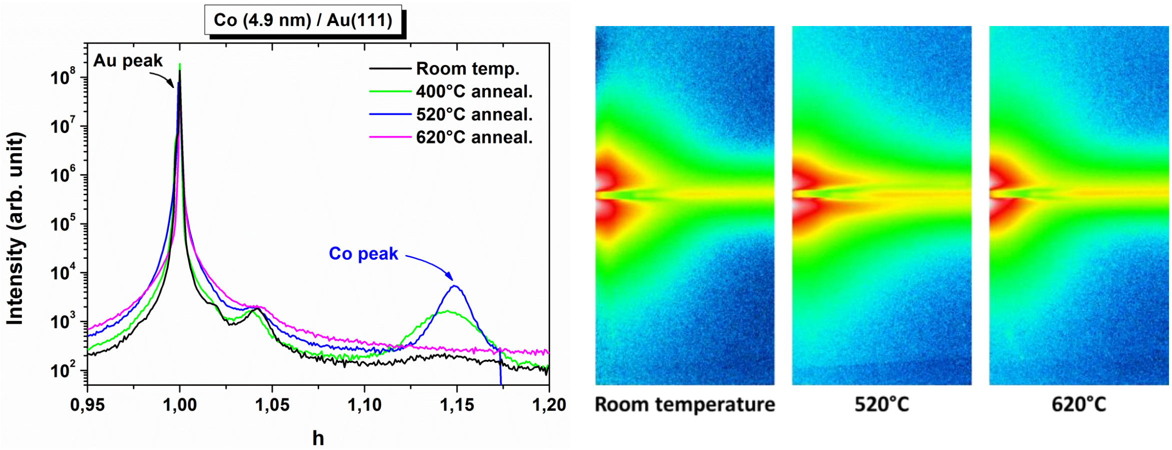


Figure 6: Effect of annealing, as seen on GIXRD spectra (left) and GIXAS patterns (right), for the Co (4.9 nm diameter) / Au(111) sample. The reconstruction is highly disturbed and almost disappears with annealing, while a peak corresponding to a Co crystal in epitaxy with the gold surface is getting more and more visible, before disappearing for the highest temperature (left). From the GISAXS patterns, we can qualitatively observe a concomitant flattening of the particles, which eventually disappear at 620°C (right). This behavior is similar to the one observed for CoPt (3.5 nm diameter) particles.