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Gold nanoparticles on TiO₂(110): size and structure evolution under plasmonic excitation

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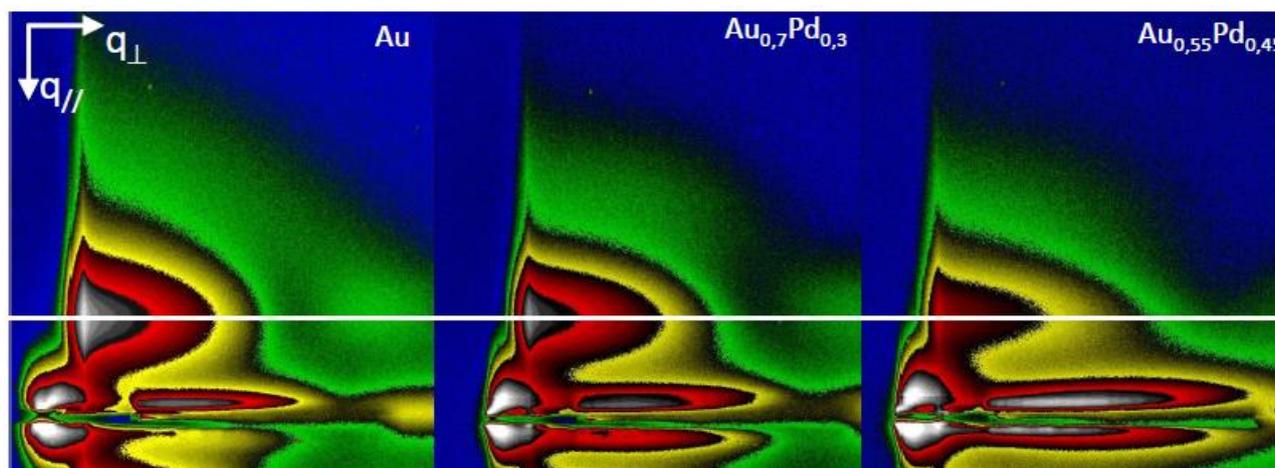
This experiment was performed on the SUV station of the BM32 CRG beamline from 5 to 11 november 2014

The aim of this experiment was the *in situ* study of TiO₂(110)-supported gold nanoparticles (NPs) prepared by molecular beam epitaxy in UHV and followed by GISAXS, surface x-ray diffraction and SDRS (Surface Differential Reflectivity Spectroscopy) under UV-visible illumination. These three techniques would allow us to determine the size, the structure and the Surface Plasmon Resonances (SPRs) of the gold nanoparticles, respectively, and their evolution as a function of the UV-visible light intensity. It was the first step of a larger program dedicated to catalysis assisted by SPRs of Au-Pd nanoparticles on TiO₂(110), which is the subject of the thesis of Antoine Abisset.

It was not possible to *in situ* couple SDRS measurements with X-ray data acquisition because of a mistake in the UHV chamber plans giving a wrong position of the viewports (they must be symmetric relatively to the normal to the sample). Anyway we could put to profit the beamtime studying the growth of Au-Pd nanoparticles on TiO₂(110) by GISAXS and GIXRD in order to correlate these X-ray measurements with our first SDRS laboratory results.

Three Au-Pd compositions were explored: pure Au, Au_{0,55}Pd_{0,45} and Au_{0,7}Pd_{0,3}. The photon energy was set to 18 keV. The GISAXS patterns were collected during the NPs growth done by codeposition of Pd and Au at room temperature, up to an equivalent deposit thickness of 1 nm (~4.4 monoatomic planes). The diffraction spectra were recorded at the end of the deposits.

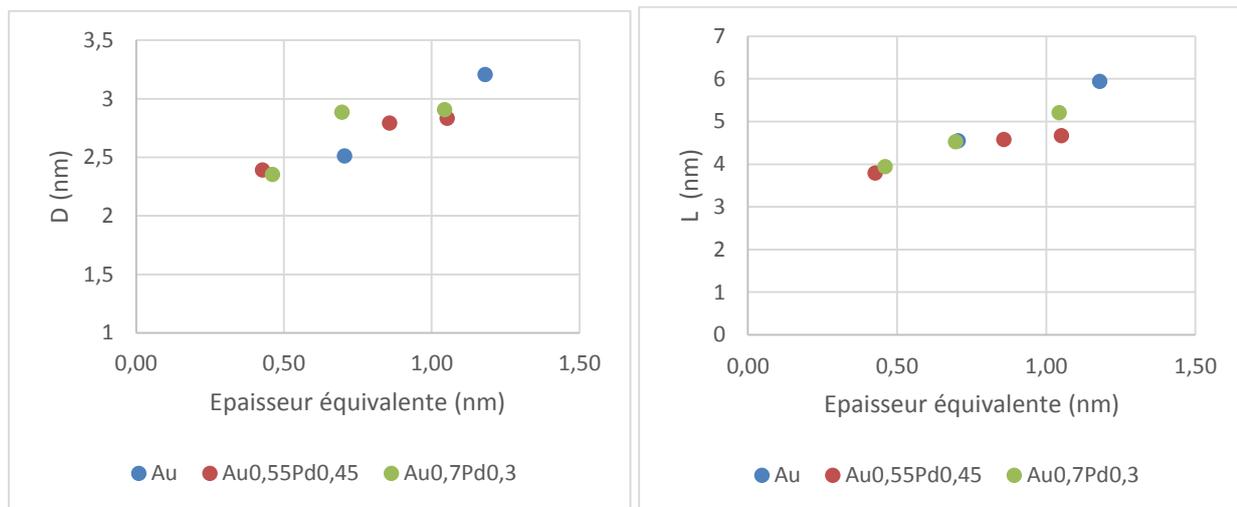
The figures below represent the GISAXS patterns for a total thickness of 1 nm obtained for the three samples. The position of the lobe, representing the correlation peak, is about the same whatever the sample composition. When the palladium concentration increases (i) the lobes are higher in the q_z direction, corresponding to the direction perpendicular to the TiO₂ surface, which means that the NPs are flattened and (ii) the lobe intensity decreases. This last effect results on the much lower scattering power of palladium compared to gold, since close to the reciprocal space origin it is proportional to the atomic number squared, i. e. $(46/79)^2$.



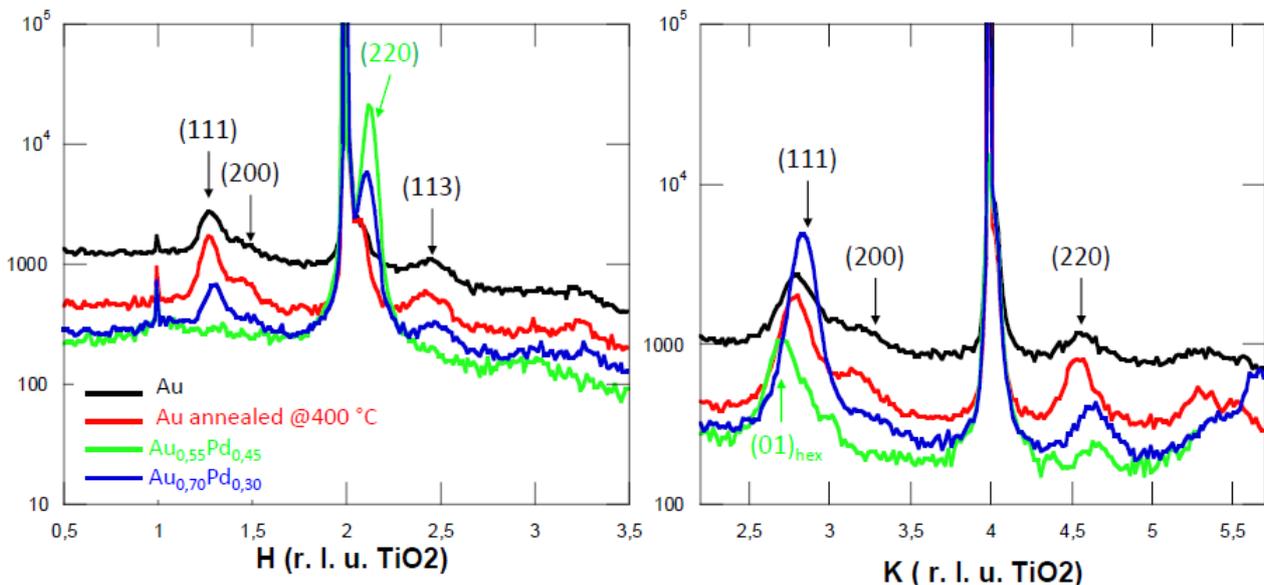
The NPs mean geometrical parameters were calculated with the IsGISAXS software ¹. The quantitative analysis performed on the basis of the GISAXS patterns concluded that the NPs morphology was best accounted for by using a cylindrical shape.

¹ R. Lazzari, J. Appl. Crystallogr. 2002, 35, 406–421. <http://www.insp.upmc.fr/axe2/Oxydes/IsGISAXS/isgisaxs.htm>.

The next figures show that the mean diameter D and the mean distance interparticles L are proportional to the total amount of Au+Pd atoms given by the equivalent thickness, independently on the composition.



From the GIXRD data analysis for 1 nm deposits, we can conclude that in any case the NPs structure is face-centered cubic (fcc). The spectra obtained for pure Au revealed several epitaxies as indexed on the figure below, for the two main directions of the in-plane surface. When the Pd concentration increases, an ordering of the structure occurs with only the (111) epitaxy for Au₅₀Pd₅₀.



Diffracted intensity along the direction H and K (at $L=0$) given in the unit of the TiO₂ reciprocal space. The peaks are indexed in the cubic unit cell of gold, except for the (01)_{hex} rod which is a direction of the (111) epitaxy. The (200) reflection belongs to the (200) epitaxy and the (111) peak can belong to the (112) one.

Concerning the lattice parameter for the three samples, it decreases between the bulk gold value (4.08 Å) and the Pd one (3.89 Å) when the Pd concentration increases, but not proportionally. Indeed the parameter is found larger in the direction perpendicular to the sample surface than in the in-plane directions. The reason of this behavior is not yet understood. Let us mention that the NPs size, as deduced from the diffraction peaks, is consistent with the one obtained from the GISAXS patterns.

A deeper analysis of the X-ray results and laboratory measurements is in progress to correlate the structural properties and the SPR on these samples.