Poster

Atomic structure of metallic nanoparticles from EXAFS: transition from monolayer-thick 2D to 3D strained Ag nano-clusters on α-Al_2O_3(0001)

R. Lazzari[1], J. Goniakowski[1], G. Cabailh[1], R. Cavalotti[1], J. Jupille[1], N. Trcera[2], P. Lagarde[2]

[1]Insitut des NanoSciences de Paris, CNRS/Sorbonne Université, 4 Place Jussieu, 75005 Paris, France, [2]Synchrotron SOLEIL, L'Orme des Merisisers, Départementale 128, 91190 Saint-Aubin, France

remi.lazzari@insp.jussieu.fr

Surface and epitaxial stresses play a paramount role in the atomic structure of supported nanoobjects and thereof in their use, such as in the catalytic properties of metal particles. They are suspected to drive transitions of shape [1], of atomic structure and of epitaxy when size is reduced. Nevertheless, x-ray diffraction intrinsically struggles to faithfully characterize clusters in the nanosized regime.

In this context, this poster will report on the interest of coupling x-ray absorption spectroscopy, nanoplasmonics and atomistic calculations in the crystallographic analysis of supported Ag metallic nanoparticles [1-3]. Clusters were grown *in situ* by evaporation on a α-Al_2O_3(0001) surface under ultra-high vacuum and analysed by EXAFS at the Ag L_3 edge to determine the Ag local environment [average Ag-Ag (d_{Ag-Ag}) and Ag-O (d_{Ag-O}) interatomic distances and Ag coordination number (CN)] as a function of the particle size. The experimental key was the capability of a structural study from clusters involving only a few atoms to large nanoparticle obeying the macroscopic equilibrium shape. For large objects, d_{Ag-Ag} is dominated by surface stress and follows the Laplace rule. At sizes below 5 nm, 3D particles in registry on the substrate O sire are partially strained while above interfacial dislocations allow releasing stress. For cluster of a few tens of atoms or less, a transition of registry site from O-top to Al-top is associated to the formation of buckled 2D clusters (Fig. 1), which fingerprint is the concomitant evolution of d_{Ag-Ag} and CN. This finding is unexpected in the light of the poor adhesion at such interface and questions the usual size-independent picture of metal/oxide epitaxy.

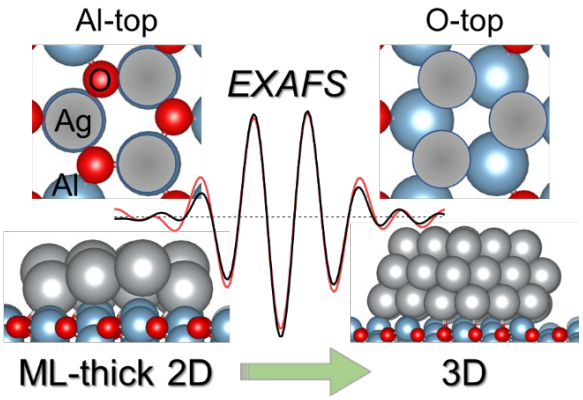

Figure 1. Transition of registry and dimensionality in epitaxial Ag/α-Al_2O_3(0001) clusters

[1] Lazzari, R., Jupille, J., Cavallotti, R., Chernysheva, E., Castilla, S., Messaykeh, M., Herault, Q. & Meriggio, E. (2020). *ACS Appl. Nano Mater.* **3**, 12157

[2] Lazzari, R., Goniakowski, J., Cabailh, G., Cavallotti, R., Trcera, N., J. Jupille & Lagarde, P. (2016). *NanoLetter*. **16**, 2574.

[3] Lazzari, R., Goniakowski, J., Cabailh, G., Cavallotti, R., Jupille, J., Trcera, N. & Lagarde, P. (2023). *NanoScale*. **15**, 15608.