ESRF	**Experiment title:** Following in real time kinetics of growth and ripening of oxide supported metal nanoparticles: the case of $Au/Al_2O_3(0001)$	**Experiment number**: SI-1862
Beamline: ID03	**Date of experiment**: from: 22/07/2009 to: 28/07/2009	**Date of report**: 31/08/09
Shifts: 21	**Local contact(s)**: Roberto Felici	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

R. Lazzari*
J. Jupille*
H. Cruguel*
G. Cabailh*
Institut des Nanosciences de Paris, CNRS, Paris, France
M-C. Saint-Lager*
I. Laoufi*
S. Garaudee*
Institut Néel, CNRS, Grenoble, France

Report:

The growth and the ripening of supported nanoparticle assembly involve a huge number of microscopic phenomena [1] such as atom arrival, reevaporation, surface diffusion of adatoms or clusters, atom binding and clustering, trapping on defects, coalescence of clusters etc... From the knowledge of the typical time scales or energies of such phenomena, either the famous complex rate equations of nucleation and growth [2] or extended kinetic Monte-Carlo simulations [3] can describe the evolution of the size distributions and density of particles. An experimental check of those modeling and the determination of the relevant energy barriers can be achieved only by analyzing growth over a large range of temperatures and evaporation fluxes.

The present project was based on the capability of recording GISAXS patterns which could be considered as snapshots of the growing film on wide temperature and flux ranges, even in the extreme conditions combining high flux and high substrate temperature, *i.e.* with a high surface mobility. This leads to information on mass transport, condensation processes [1,2,3], cluster mobility [4] and ripening mechanism [1]. The chosen system is $Au/Al_2O_3(0001)$ which is expected to be an archetype of Volmer-Weber growth with poor adhesion and abrupt interface on a vacancy-free surface.

In-vacuum guard slits after the beryllium entrance windows and a beam stop after the exit windows on the UHV chamber of ID03 were installed. These latter are necessary to remove the unwanted background scattering of the Be windows in order to get accurate measurements for the smallest nanoparticles and to go as far as possible in reciprocal space in the uncorrelated Porod's regime where scattering is sensitive only to the particle form factor. With the combination of the brilliance of the undulator of ID03 and the low readout of FRELON high-speed camera of the ESRF detector pool, exposure times between 1 and 20 seconds per frame were obtained. Such an acquisition rate was unachievable during our previous runs on the bending magnet beamline BM32.

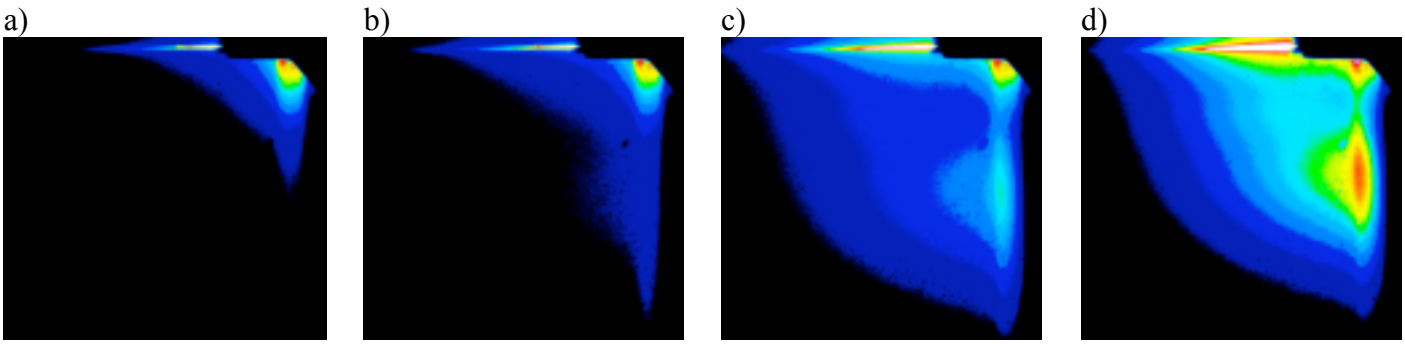

Figure 1. GISAXS measurements of the growth of Au nanoclusters on the silica surface at room temperature with a Au flux of 1Å.min^{-1}. Snapshots for different thicknesses are shown: a) 1Å, b) 2Å, c) 4Å and d) 6Å

Al_2O_3(0001) surfaces were prepared by annealing under vacuum at 1200K. Gold was thermally evaporated from a Knudsen cell which flux is calibrated *in situ* with quartz microbalance and with X-ray reflectivity at the end of each deposition. Between each deposition run, gold was removed from the surface by a simple annealing under vacuum at 1200K [5]. Initially the growth of Au on Al_2O_3(0001) was studied at 300K. Unfortunately, slight calcium contamination due to segregation from the bulk was observed with Auger spectroscopy. Thus it was decided to change substrate to amorphous silica whose surface preparation is somehow similar to crystalline alumina.

Series of growths up to a thickness of several nanometers at different temperatures (from 300 to 670 K) and evaporation rate (from below 0.01 up to 1-2 nm/min) were preformed on the silica substrate (example in figure 1). We were able to perform high-speed data acquisition and 'live' measurement thus (avoiding stepped deposition and spurious sintering.

After initial comparison between the two substrates, the growth mode observed for gold on amorphous silica differs from what has been seen on crystalline alumina. On the latter at 300 K, at a flux of ~ 0.015 nm.min^{-1} Au, 3D Au clusters rapidly form, as expected in the case of a poor wetting. In contrast, on silica, a delay in the appearance of Au nanoparticles indicates a partial wetting of the silica surface, though its roughness is very low as checked with reflectivity. A first explanation would be the high density of nucleation centres on an amorphous substrate It is only by deposition at higher temperature (500 K and above at 0.015 nm.min^{-1}) that the growth is 3D from the very beginning. The Au film is also observed to dewet upon desorption. Somewhat similar observations were made in the case of Ni/silica [6]. Also, different growth modes were also observed for different fluxes.

The current dataset is undergoing thorough analysis using the IsGISAXS software [6] and will lead to an initial understanding of the growth mode and ripening of Au on the silica surface. However to obtain a full understanding further beamtime is required to obtain a complete dataset exploring more substrate temperatures (below 300K), higher deposition rates and sintering kinetics.

[1] M. Zinke-Allmang, Thin Solid Films 346 (1999) 1
[2] J. Venables, Phil. Mag. 27 (1973) 697 and « Introduction to Surface and Thin Film Processes », Cambridge University Press (2000)
[3] P. Jensen, Rev. Mod. Phys. 71 (1999)1695 and P. Meakin, Rep. Prog. Phys. 55 (1992) 157
[4] J. Carrey, J.-L. Maurice, F. Petroff, and A. Vaurès, Phys. Rev. Lett. 86 (2001) 4600
[5] I. Besdeza, E. G. Gontier-Moya and A. W. Imre, Appl. Phys. A 81 (2005) 673
[6] R. Felici et al. Phys. Rev. B 79 (2009) 155443
[7] R. Lazzari, J. Appl. Cryst. 35 (2002) 406; IsGISAXS: http://www.insp.jussieu.fr/axe2/Oxydes/IsGISAXS/isgisaxs.htm