ESRF	**Title** Growth of regular arrays of metal clusters on a nanostructured alumina ultrathin film	**Experiment number**: 32-03-635
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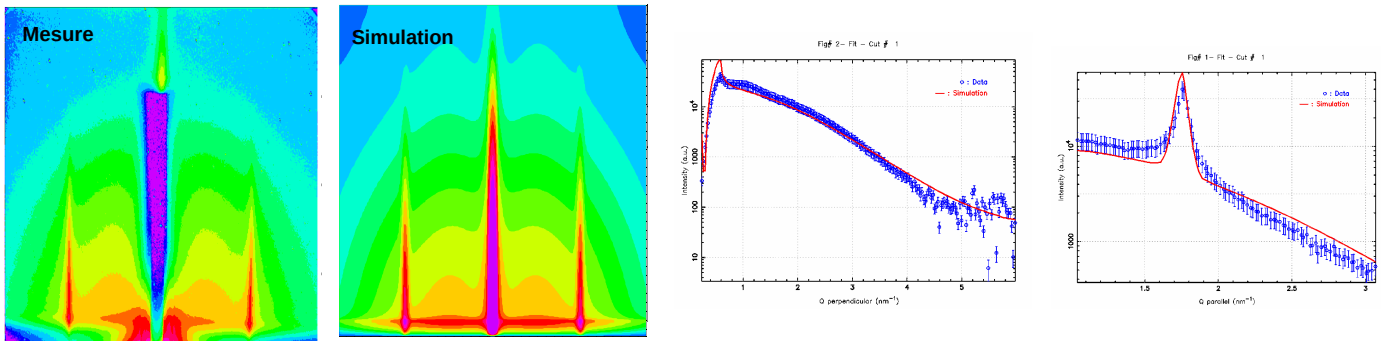
The purpose of this experiment was to study *in situ* the growth and the long range order of Pd and PdAu clusters on a nanostructured alumina ultrathin film on a Ni_3Al (111) surface. From previous STM and AFM works we knew that these alumina thin films are nanostructured [1, 2] and can be used as templates to grow hexagonal arrays of clusters [3,4]. However in these experiments the clusters were observed sequentially by STM or AFM after deposition of Pd and Au. Images showed a very good order but information gained by these techniques were only local and not in real time. For applications, these arrays of clusters must have a good order on the whole ($1cm^2$) sample. Thus the purpose of this campaign of GISAXS measurements was to characterize *in situ*, in real time as function of the amount of deposited atoms the long-range order quality of the clusters lattice and their morphology at the nanometer scale.

The alumina films were grown on the *in situ* cleaned Ni_3Al (111) surface using the SUV set-up of the BM32 beamline. First we have studied in real time the growth of Pd on the alumina film at RT. GISAXS patterns showed that already at low coverage (0.05 nm) ordered arrays of clusters with a narrow size distribution were obtained. Moreover GISAXS patterns obtained at various azimuth showed that the clusters were aligned in three directions at ±120° with two orientational domains rotated by 24°. These results already show that the Pd clusters are organised in a regular hexagonal lattice on the whole sample. In order to get more precise information on the organisation of the clusters we have simulated the GISAXS patterns using the IsGISAXS software [5].



(a) (b) (c) (d)

Figure 1: GISAXS experiment on an array of Pd clusters grown on a nanostructured alumina film on Ni3Al (111) surface. Experimental (a) and simulated (b) GISAXS patterns. Experimental and simulated intensity cuts in the perpendicular (c) and parallel (d) directions of the surface.

Figure 1(a-d) displays a comparison between experimental and simulated GISAXS results for a thickness of 0.1 nm of deposited Pd. The agreement between experiment and simulation is very good. The best fitted spectra has been obtained with hemispherical clusters of 0.95 nm mean radius, 0.25 relative size dispersion and 0.625 aspect ratio (height/diameter), sitting on an hexagonal lattice of 4.14 nm lattice parameter. The size and the aspect ratio of the clusters are in agreement with our STM results, keeping in mind that STM measurement of diameter have some uncertainty due to the tip/sample convolution effect [6]. Concerning the lattice, it corresponds exactly to the periodic structure of the underlying reconstructed alumina surface [1,2]

as observed by STM and AFM. From the fit of the full width at half maximum of the narrow scattering rods of the Pd clusters lattice, it is clearly put in evidence that the clusters are long-range ordered (200 nm correlation length) on the whole sample area. This analysis has been completed by the measurement of a full 3D map of reciprocal space by GISAXS rotating the sample by steps of 1° over a total angular range of 60°. In Fig. 2 is shown a 2D projection of this map in the surface plane. It exhibits clearly the two main spots arising from the two variants of the hexagonal lattice of Pd clusters rotated by 24°.

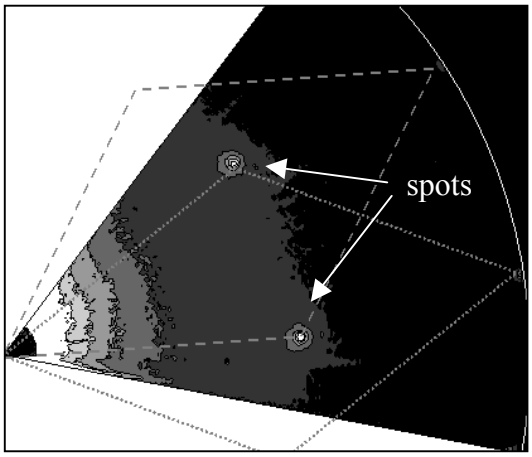


Figure 2: Map of the reciprocal space in the surface plane deduced from 60 GISAXS images measured at different angles. The two spots correspond to the "Bragg" peaks of two hexagonal lattices of Pd clusters rotated by 24°.

Later on we have performed the same measurements on a assembly of AuPd bimetallic clusters. The clusters were grown by a two-steps process previously developed [7] in our lab (CINaM). First a lattice of Pd clusters is grown on the alumina film, then Au is deposited on the surface. It has been shown by STM that gold atoms selectively attach on the previously grown Pd clusters (i.e. there is no nucleation of pure gold clusters). Repeating this experiment on the SUV apparatus a regular lattice of bimetallic clusters extending on the whole sample has been grown and characterized by GISAXS. These results will be published in a forthcoming article [8].

In summary sample preparation of Pd and PdAu clusters on top of a thin alumina film have been well reproduced on the SUV apparatus. GISAXS measurements have been performed *in situ* and in real time providing a detailed characterization of the clusters shape/size and long order. At some deposit, a complete set of GISAXS patterns measured for different orientations of the sample surface have been performed, providing a complete 3D map of reciprocal space of the Pd clusters lattice.
However due to lack of time, the internal structure of the PdAu bimetallic clusters have not been obtained (core-shell structure?) as well as the stability of the clusters as function of temperature and gaseous environment. Further experiments will be necessary to elucidate these two points. We plane to perform anomalous GISAXS measurements to extract the internal structure of the PdAu clusters changing the electronic density of Au or Pd atoms close to absorption edges. Moreover temperature/gaseous environment - dependent measurements will be necessary to check the stability of the organisation of the clusters at high temperature.

References

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