Advanced *in situ* µGISAXS investigation of drying kinetics of colloidal gold suspensions on chemically modified silicon surfaces.

M. Schwartzkopf, B. Heidmann, G. Santoro, S. Yu, J. Perlich, G. Herzog, J. F.H. Risch, R. Mannweiler, R. Gehrke and S.V. Roth

Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607 Hamburg, Germany

Nanostructured gold films are crucial materials for a large variety of current applications like solar cells of hybrid and colloidal multilayers, bioanalytical assays, waveguides in optical circuits, antibacterial and reflective coatings, nanocatalysts, bioelectronics and gas sensors [1-4]. Their applicable key characteristics, like chemical reactivity, electrical and optical properties are strongly influenced by the structural distribution of the nanoparticles and the interactions occurring at the metal-substrate interface [1-4]. The advantage of the self-assembly and easy processability of gold colloids have enabled the low-cost fabrication of integrated micro- and nanosystems with a high degree of complexity and functionality. Installing regular arrays on mesoscopic length scales is thereby essential in the field of applied nanotechnology. In general, the specific nature of colloid-substrate interaction that causes self-assembly is still far from being completely understood.

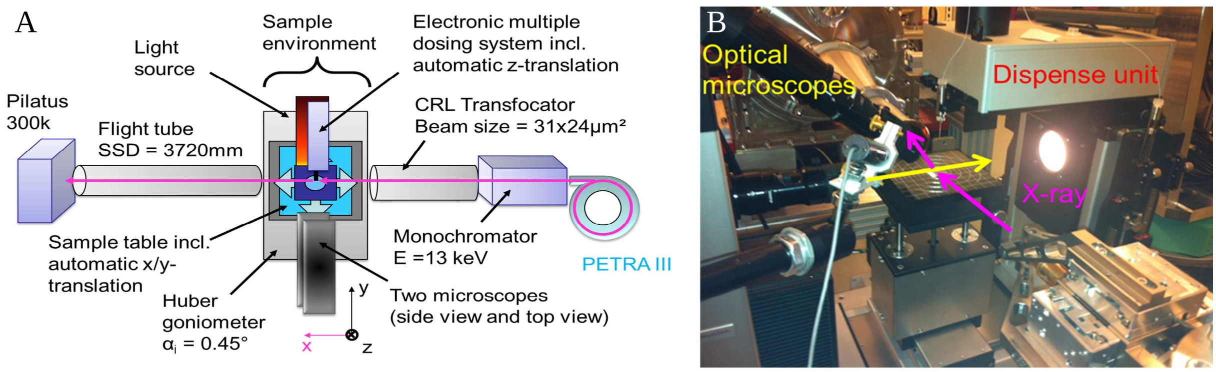

Figure 1. (A) Scheme of advanced µGISAXS setup including parameters (top view). **(B)** Photograph of the sample environment at P03/ MiNaXS beamline at PETRA III.

Microfocus grazing incidence small-angle X-ray scattering (µGISAXS) is a powerful tool for *in situ* measurements of a large variety of surface processes on the nanoscale like physical vapor-deposition, evaporation-mediated self-assembly or adsorption phenomena in laminar flow conditions [1-4]. We utilize the µGISAXS technique to investigate solvent-evaporation-mediated preparation processes in real time and measure *in situ* adsorption and self-assembly kinetics. In this study, we introduce an advanced drop-casting deposition technique by installing a remote-controlled contact angle measuring device (OCA35; Dataphysics) at the P03/ MiNaXS synchrotron beamline at PETRA III (Fig. 1) [5]. The very promising combination of the µGISAXS setup with a contact angle measuring device enables the unique possibility to perform *in situ* drop casting experiments more accurate and flexible. The electronic multiple dosing system and the automatic sample table enable the precise deposition of droplets with defined volumes onto nanostructured surfaces. This permits on the one hand the opportunity to change the droplet drying conditions during the measurement by adding additional solutions (e.g.: other colloids, surfactants, salts or changes in pH values) on the same position. It also opens up the possibility to initiate and investigate chemical reactions under defined boundary conditions. On the other hand, it is possible to investigate adsorption phenomena without using a specific microfluidic cell by simply moving the droplet attached to the needle along the surface, especially over the X-ray footprint. Furthermore, this setup allows to investigate the influence of wetting behaviour, surface energy and roughness on drying kinetics during colloidal self-assembly. The incident angle is below 0.5 degree and will not disturb the drying kinetics.

In our first experiment, the collective self-assembly of gold nanoparticles (AuNP) was examined on chemically modified silicon substrates (Si-R) as a function of differences in their surface chemistry (Fig. 2A). The aim of the experiment was to describe self-assembly of gold nanoparticles and chemical dynamics at liquid-surface interfaces. The broadening of the Yoneda peak and the occurrence of a ring-like intensity distribution indicates the presence of nanoparticles and the success of the deposition experiment (Fig. 2C). We were able to identify different stages of the drying process in the temporal evolution of detector cuts, namely nucleation (N), diffusion (D), precipitation (P) and compaction (C) (Fig. 2D) [3]. The out-of-plane cuts along the silicon Yoneda peak can be considered as an adsorption isotherm (Fig. 2E).

We expect that this work will contribute to explaining the deposition mechanism of noble metals on various substrates by determining the effect of surface polarities. This study takes also part in fundamental research to retrieve kinetic information of the difference between physisorption and chemisorption by measuring adsorption isotherms of surface-modified and pH-sensitive adsorbents and adsorbates via *in situ* µGISAXS investigations. These results are extremely valid for describing industrial processes like heterogeneous catalysis or solid phase synthesis.

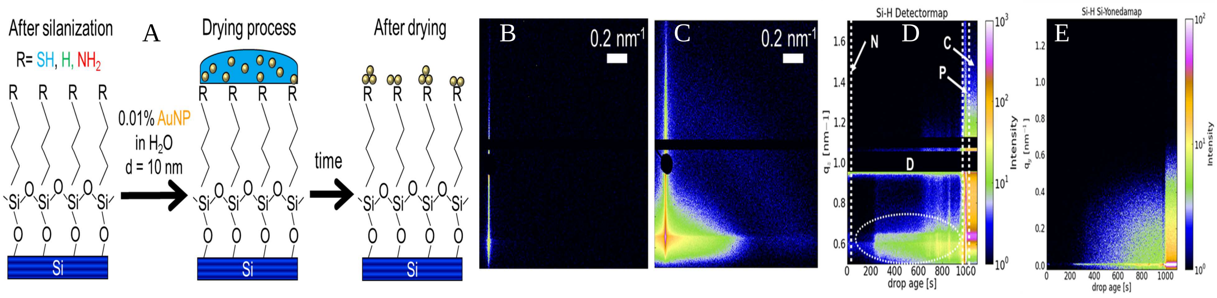

Figure 2. (A) Scheme of the experimental principle. **(B)** and **(C)** µGISAXS patterns taken before and after the droplet drying experiment with gold nanoparticles (10 nm diameter) for R=H. **(D)** Temporal evolution of detector cuts (vertical line cuts) with different drying regimes. **(E)** Out-of-plane cuts (horizontal line cuts) along the silicon Yoneda peak can be considered as an adsorption isotherm.

* e-mail: Matthias.Schwartzkopf@desy.de

References

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