ESRF	Experiment title: **Formation of nanostructured metallic films under Langmuir monolayers using Grazing Incidence x-ray Radiolysis**	**Experiment number**: SC1718
Beamline: ID10B	**Date of experiment**: from: 20-03-2005 to: 26-03-2005	**Date of report**: 21-07-2006
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Report:

We are developing a novel approach for synthesising ultra thin metal layer with controlled shape and thickness. This method combines the self-assembling properties of amphiphilic molecules and the radiolysis technique. In the radiolysis process, the reduction of metal ions into atoms is induced by the radicals formed by irradiation (γ-rays, e^-, x-rays) of water ($H^\bullet$, e^-_{aq}). The formed atoms further coalesce into metal aggregates[1]. In our approach, a Langmuir monolayer formed by amphiphilic molecules is deposited on the aqueous solution of a metal salt. It acts as a template for the formation of the metal layer by attracting metal ions near the interface. The irradiation needed for the radiolysis reduction is produced by the x-ray beam. To obtain ultra thin metallic layers, we use the grazing incidence geometry. In such geometry, below the critical angle, the irradiation is limited to a thin layer of about 4.5nm thickness below the air/water interface. Moreover, the x-ray beam is also used to probe in-situ the interface transformation. In preliminary experiment using silver ions (Ag^+), Grazing Incidence x-ray Diffraction (GIXD) on the liquid subphase and Atomic Force Microscopy (AFM) after transfer on silicon wafers have shown that such procedure leads to the formation of a thin silver layer of thickness 4.6±0.2nm, in perfect agreement with the estimated x-ray penetration length. We underline that this crystalline silver layer is oriented by the interface. One obtain crystals of about 10 microns lateral dimensions which present the same crystalline face parallel to the interface (2D powder)[2].

The aim of the proposal was to valid the concepts developed in this new **Surface Radiolysis** method by improving *in situ* measurements of the system and also testing the procedure for others metals (Ag, Pt), and different organic layer (Behenic Acid, Di-OctadecylAmmoniumBromide –DODAB, Semi-Fluorinated alkanes). Due to the lack of time, we did not perform the complete program.

The first point has been obtained by implementing a new measurement, the Grazing Incidence X-ray Fluorescence. For this purpose, we used a silicon drift detector (RONTEC) associated to our home build Langmuir trough which can host this detector vertically and just above (1mm) the liquid surface. It was connected to the acquisition software of the beamline. Then, by recording the fluorescence signal, we were able to follow the metal concentration at the interface. Moreover, Grazing Incidence Small Angle x-ray Scattering (GISAXS) was performed simultaneously to irradiation. The incidence on the air/water interface of the x-ray beam (12.5keV) was 1.2mrad. The scattered signal was recorded using two vertical slits (300µm and 500µm) and a vertical Position Sensitive Detector (150mm). During the irradiation process, we recorded simultaneously the scattered signal and the evolution of the fluorescence of the metal atoms in the interfacial layer probed by x-rays (a few nm thick). Figure 1 (fluorescence) and 2 (diffraction) show the case of a Behenic acid monolayer deposited on top of a silver sulphate solution. Such setup appears as very promising to control the formation of the metallic layer in the future.

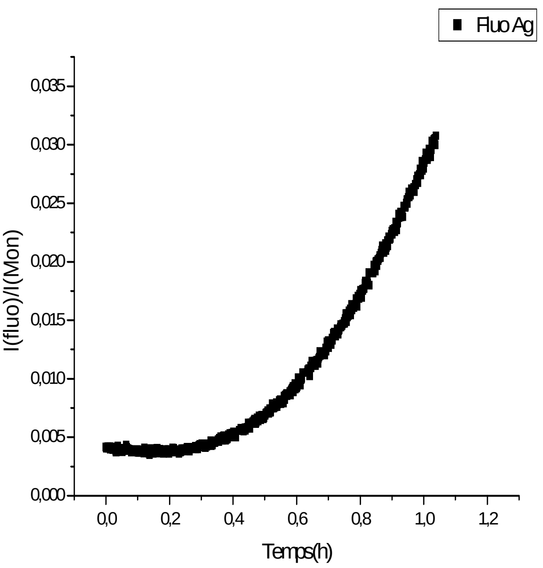

Figure 1 : *Evolution of the X-ray fluorescence intensity of Ag (2-3keV) during the irradiation of a monolayer of Behenic Acid deposited on a solution of Ag_2So_4. It shows the increase of the amount of silver in the interfacial layer.*

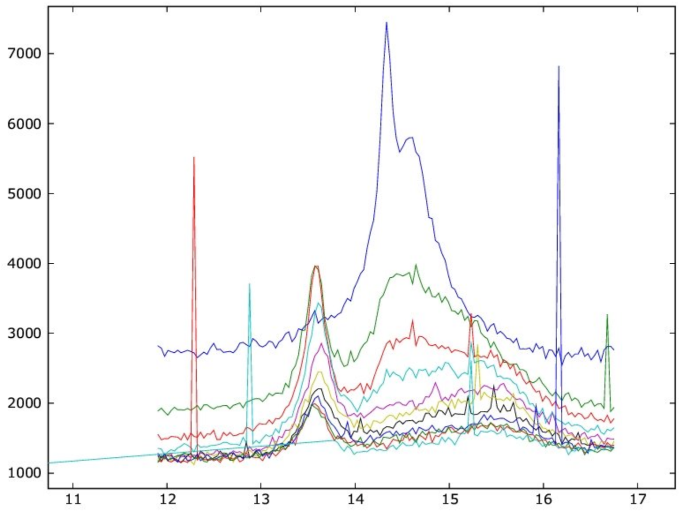

Figure 2: *GIXD spectra measured simultaneously with the fluorescence of fig. 1. On observes the disappearance of the Behenic acid (14-14nm^{-1}) and the apparition of the silver layer ones (13.5nm^{-1})*

The second point was tested by using a Langmuir monolayer of semi-fluorinated alkanes (SFA, $C_nF_{2n+1}C_mH_{2m+1}$) as template for a surface radiolysis experiment. Indeed, the absence of polar head group in the SFA molecule should remove the adsorption of silver ions at the interface and then avoid the formation of the metal layer. Surprisingly, GISAXS and fluorescence measurement have shown the formation of silver aggregates at the interface. However, the scattering and diffraction data measured simultaneously during the irradiation shown that the crystallographic structure of these domains correspond to a three dimensional powder of silver crystals (while one obtains a two dimensional powder by using a behenic acid monolayer templates). Thus the metal layer is formed by 3D crystals randomly oriented. This is confirmed by AFM measurement on transferred layers. The metallic layer appears as an aggregation of nano-spheres. Such a result is interpreted by the following meaning. The x-ray penetration into the subphase induces the radiolysis process. However, since no metallic pre-layer is formed (due to the absence of ions adsorption), one obtains spherical objects (colloids, as for usual 3D radiolysis) which remains adsorbed at the interface. Indeed, they act as “screen” for the hydrophobic organic monolayer. Then, this experiment demonstrates at least the crucial influence of the template on the structure of the metallic layer formed and validates the concepts developed in our procedure. Only suitable molecules such as fatty acids (bearing a localized charge) can lead to a homogeneous, thin, 2D oriented layer.

However, such SFA are known to form at the air water interface an hexagonal network of domains of roughly 30nm diameter [3]. Then, in collaboration chemist, SFA molecules bearing a carboxylic acid head group are currently synthesized. Using such template, we expect to form metallic layer of 5 nm thickness and 30 nm in plane network.

References :

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