ESRF	Experiment title: **Nanoscale structure of thin metallic layer grown below Langmuir monolayer by the radiolysis method.**	**Experiment number**: SC1073
Beamline: ID10B	**Date of experiment**: from: 29-01-2003 to: 04-02-2003	**Date of report**: 27-07-2004
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Report:

We are developing a novel approach for the synthesis ultra thin metal layer with controlled shape and thickness as a variation of the radiolysis technique. Reduction of metal ions into atoms is induced by the radicals formed by irradiation (γ-rays, e^-, x-rays) of water ($H^\bullet$). The formed atoms further coalesce into metal aggregates[1]. In our approach, a Langmuir monolayer made of insoluble surfactant (amphiphilic) molecules at the air-water interface 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 for the radiolysis induced reduction is made by x-rays in the grazing incidence geometry at the air-water interface. Indeed in such geometry below the critical angle, the irradiation is limited to a thin layer about 4.5nm thickness below the air/water interface. Preliminary experiment using Grazing Incidence x-ray Diffraction (GIXD) and Atomic Force Microscopy (AFM) after transfer on silicon wafers have shown that irradiation leads for silver ions (Ag^+) to the formation of a thin silver layer of thickness 4.6±0.2nm with a two dimensional organisation of the silver atoms[2]. The aim of the proposal was to measure *in situ* the nanoscopic structure of the layer since transfer on silicon wafer appears to damage the layer. 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 (8.0KeV) was 2mrad. The scattered signal were recorded using two vertical slits (300µm and 500µm) and a vertical Position Sensitive Detector (150mm).

We first explored the in-plane structure at large length scales (1nm – 1µm) of silver layer formed *in situ* by surface radiolysis. Fig 1 gives successive GISAXS spectrum before, during and after the irradiation of a Langmuir monolayer of Behenic Acid deposited on a 10^{-2}mol.L^{-1} silver solution. Initially, the GISAXS spectrum is consistent with a monolayer deposited on a liquid substrate. With time the GISAXS spectrum evolves and reveals a characteristic length scale in the system by the apparition of a broad scattering peak at $0.56nm^{-1}$. The same length scale is found in AFM images and correspond to parallel stripes. AFM phase images reveals that the stripes are made of organic molecules. Thus the Langmuir monolayer appears to be crumpled after the formation of the metal layer. For the general slope of the GISAXS spectrum, a first preliminary analysis using the DWBA approach seems to indicate that the off-specular signal is initially

determined by the thermal fluctuation of the liquid gas interface (capillary waves) covered by a Langmuir monolayer. After irradiation, the off-specular scattering seems now determined by the metal-gas interface properties, covered by a Langmuir monolayer. This analysis is still under process but the results are consistent with a dense homogeneous metal layer.

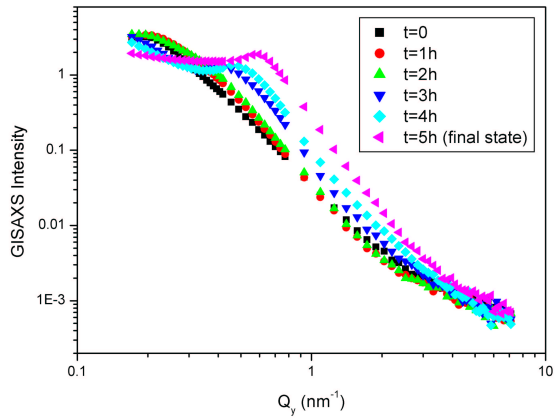

Figure 1 : Successive GISAXS spectra measured for a behenic acid monolayer deposited on the free surface of a silver ions solution during the irradiation process. The intensities are not subtracted from the background noise

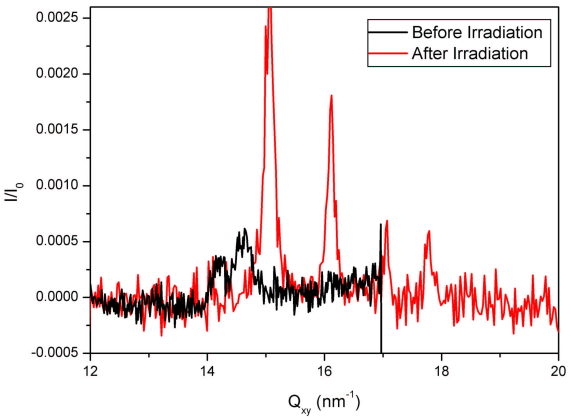

Figure 2: Grazing Incidence x-ray Diffraction spectra of a DODA monolayer deposited on the free surface of an $AuCl_4^{2-}$ solution before (black line) and after (red line) irradiation.

A second goal of these experiments was the test of other metals which are of interest for their potential application. However the corresponding ions can be both of opposite charge and need several reduction steps to reach metal forms. This is the case for gold, or platinum which are of prime importance for the application (conduction, nanocatalysis, …). For gold, the adapted ion is $AuCl_4^{2-}$. The use of such ions leads to several problems. We have to find an amphiphilic molecule able to attract the ions near the interfaces. Behenic acids is usually believed to create a negative potential which repelled the negative ions such as gold. For gold, we proposed to use DiOctadecylDimethylAmmoniumBromide (DODA) molecules, since its polar head is positively charged at the air-water interface and thus adapted to the negative ion. The other problem concerns the several reduction steps needed to reach the final atomic form of ions which have to be done by this surface radiolysis method. Fig 2. shows the GIXD spectrum of a monolayer of DODA deposited on a K_2AuCl_4 solution (10^{-2}mol.L^{-1}). Before irradiation, the spectrum is identical of the diffraction spectrum obtained on pure water[3]. After irradiation, intense and narrow diffraction peaks appear, revealing the formation of a gold, dense, organised layer. Diffuse scattering spectra (specular scattering) and GISAXS spectrum have also been measured and reveals the same phenomena as is the case of silver ions.

Theses experiments performed on ID10B enabled us to prove that the formed metal layer is dense and homogeneous and that the Langmuir monolayer remains as a monolayer onto the metal layers and crumple. The versatility of the process was also proved since positive ions and complex, negative ions ($AuCl_4^{2-}$, $PtCl_4^{2-}$) lead to the formation of metal layers by our approach, provided the correct choice of the amphiphilic molecule (fatty acid for positive ions, and DODA for negative ions). Such results are of major importance for the formation of metallic nanostructures both at 2D and 3D using soft templates and radiolysis chemistry.

References :

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