EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Determination of the diffuse layer formed during Rare Earth Elements adsorption on organosilanes monolayers having specific functionalities for the understanding of REE extraction	**Experiment number**: 32-02 831
Beamline: BM32	**Date of experiment**: from: 09/06/2021 to: 14/06/2021	**Date of report**: 04/05/2018
Shifts:	**Local contact(s)**: Samuel TARDIF	*Received at ESRF:*

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Report:

This study is in the context of Rare Earth Elements (REEs) recycling and, more particularly, dedicated to the understanding of the interactions between REEs and the specific functions of new promising organosilanes used in the elaboration of hybrid materials. The aim of this study is to characterize by using Hard X-ray reflectometry (27 keV), the diffuse layer formed during REEs adsorption as a function of the pH at the surface of model systems made of organosilane monolayers. Such experiments coupled with analysis performed in our laboratory will allow the determination of the processes occurring during REEs extraction, which is of interest for the industrial use of these new hybrid materials.

Sample preparation and analysis

Samples were prepared in our laboratory. Silicon wafers were first activated by refluxing in HNO_3 during 1 hour and then grafted with the molecules M1, M3 and M4 (Figure 1) in toluene during 5 hours.

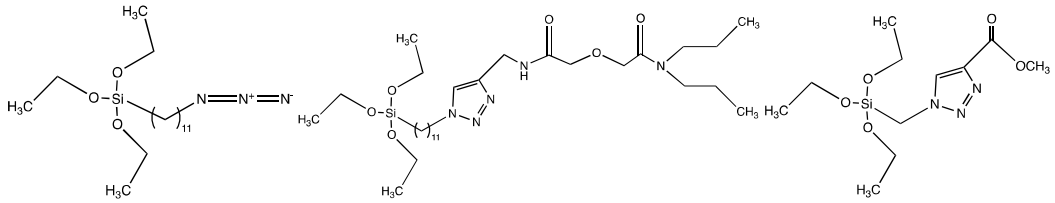

Figure 1: Organosilanes grafted on activated silicon wafers. Left to right M1, M3, M4

Four samples refered as SiO_2 (activated silcon wafer), M1, M3 and M4, were analyzed by hard X-ray reflectometry at 27 keV to allow the X-ray transmission through the solution using the following protocol. First, the samples were characterized in water until the X-ray reflectivity signal does not evolve (few hours). Afterwards, water was replaced by $NdCl_3$ solution at 0.1 M at pH=4, 3, 2 and 1. Such procedure was required to correctly measured the impact of ion presence at the surface of the sample on the reflectivity signal.
Measurements were performed from $-0.2 < \theta < 2$. Scans were taken continuously until there were no more visible changes between reflectivity curves.

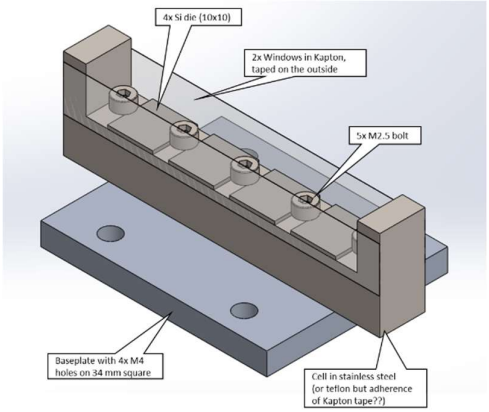

Figure 2: Cell used for the in situ X-ray raflectivity analysis of the samples fixed using two screws and filled with the appropiate solutions.

Results

Five experiments were performed. During the first and the second experiments, the samples were degraded under the X-ray beam (black trace of the X-ray beam at the surface of the samples). To preserve the sample surfaces, Cu absorbers were added. For the third experiment, the beam was stopped during the samples analysis for few hours, thus, the data were not usable. For the fourth experiment, the duration of one X-ray reflectivity

measurement/sample was unfortunately too long to characterize the kinetics of Nd adsorption. Finally, the last experiment has given workable analyses and are presented on the Figure 3.

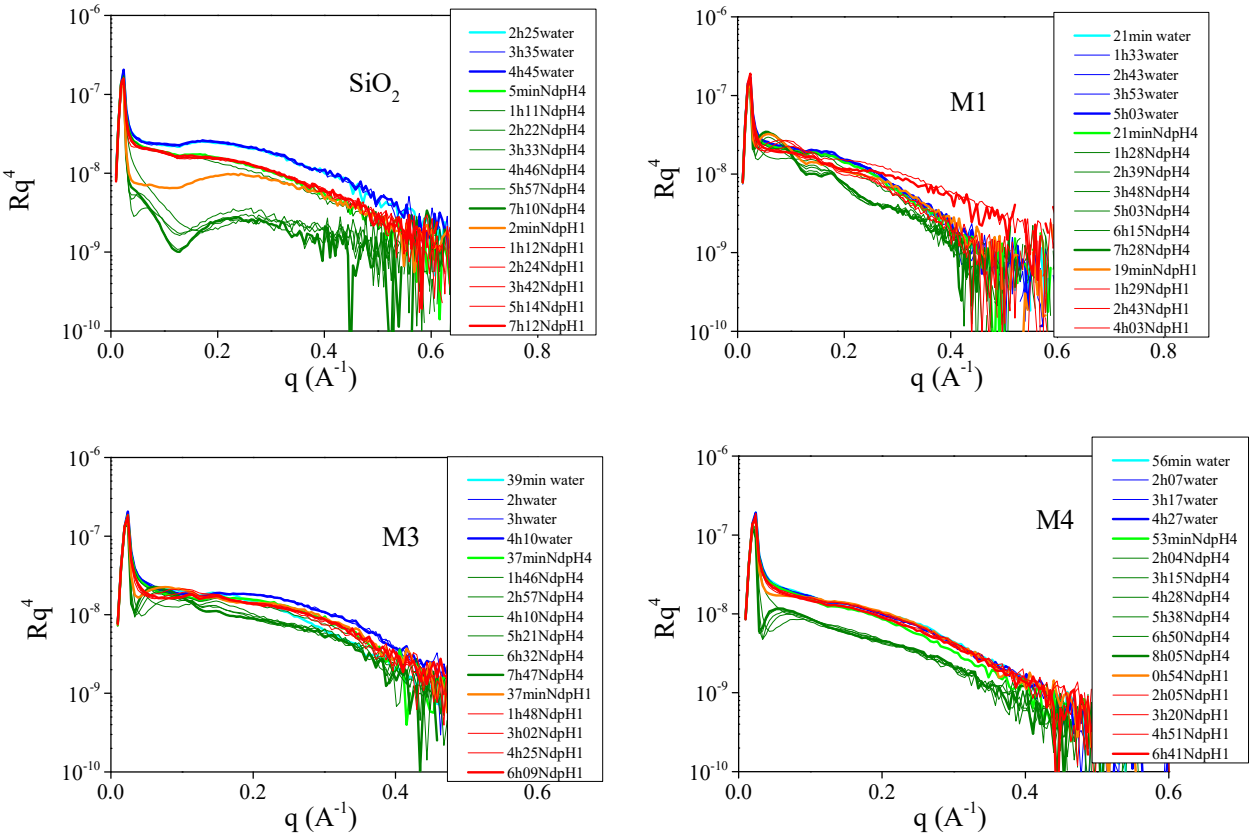

Figure 3: Evolutions of the X-Ray Reflectivity curves of samples SiO_2, M1, M3 and M4 in water, $Nd(NO_3)_3$ at 0.1M at pH=4 and pH=1.

The data obtained during this last experiment hilight several results. First, the sample surfaces are not modified in water even after more than 4 hours. For the grafted surfaces, it means that molecules are stable regarding their hydrolysis at a neutral pH. Second, the X-ray reflectivity evolutions depend on the grafted molecules and the pH of the $Nd(NO_3)_3$ solution attesting of the different interactions existing between Nd^{3+} and the functional groups of the molecules.

Perspectives

These data will be fitted to obtain the evolution of the density profiles perpendicular to the surface during the kinetics of Nd^{3+} adsorption and the results will be related to the on-going analyses perform in our laboratory such as Atomic Force Microscopy peak force measurements, *in situ* ATR-FTIR and atomistic modeling.