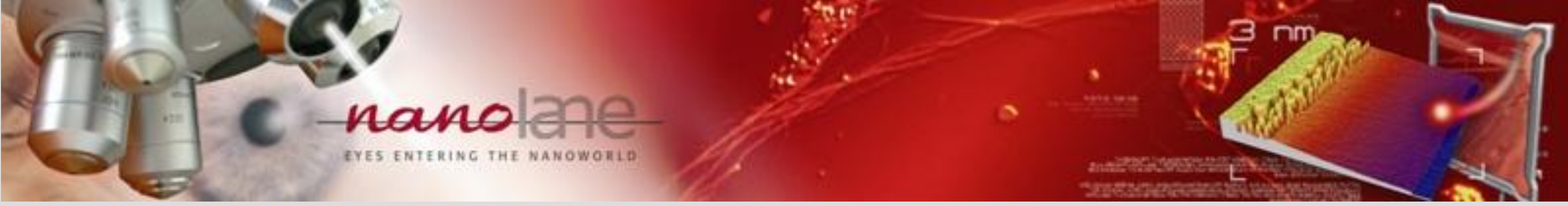
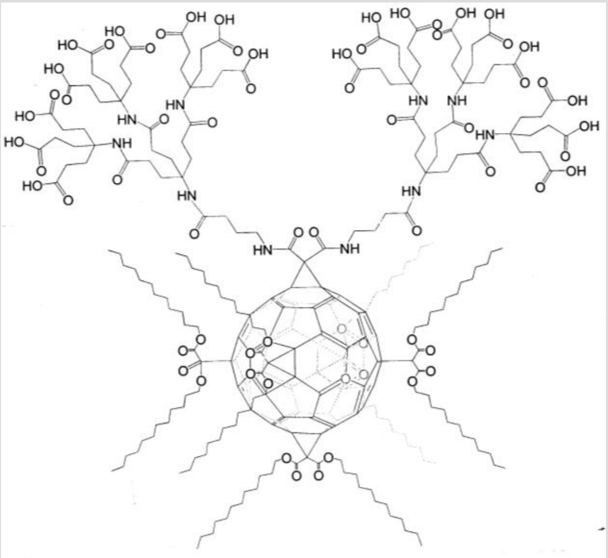


SARFUS: Evaluation of Langmuir-Blodgett-type organic thin films

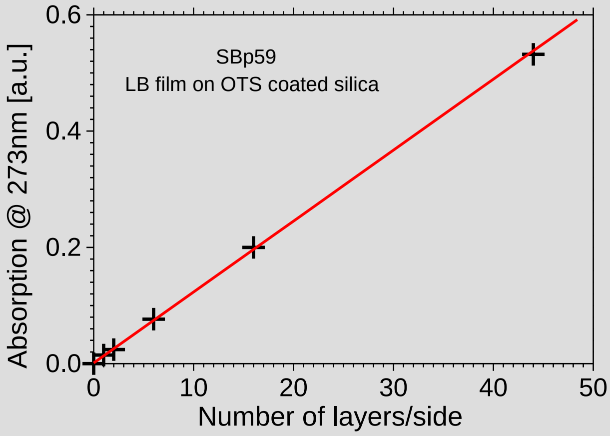
Collaboration: JL.Gallani (IPCMS, Strasbourg, FRANCE),
A.Hirsch (Institut für Organische Chemie, Erlangen, GERMANY)

The Langmuir-Blodgett (LB) technique is a simple method that enables the preparation of organic thin films on solid substrates with excellent control of the structural parameters. It is possible to prepare mono- or multi-layer films while knowing the orientation of the molecules within. These LB films can be used in fundamental science (thermodynamic, layer-object interaction, electron transport, magnetism, intermolecular energy exchanges) as well as in practical science (tribology, organic diodes and transistors, nonlinear optics, photovoltaic devices). Even though their overall quality can roughly be assessed through measurement of the "transfer ratio", subsequent measurements such as AFM (Atomic Force Microscopy) or X-Ray diffraction are mandatory in order to get precise quantitative data on the film's thickness and roughness. These measurements unfortunately require expensive apparatus and are time consuming (1 to 2 hours). Moreover, in some cases the transfer seems to proceed correctly but the quality of the films still is not good enough for X-Rays to be used, which leaves only AFM for getting reliable data.

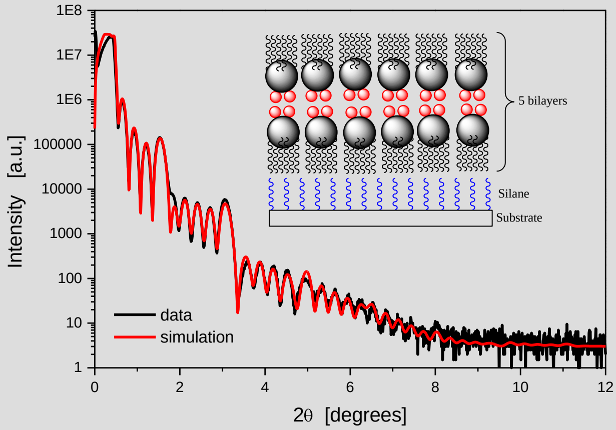
The optical imaging process Sarfus (using specific substrates called Surfs®) allows to obtain useful information such as long distance flatness and roughness, presence or absence of defects, spontaneous formation of supramolecular structures (bilayers, micelles, crystals). Sarfus enables local measurement of the optical thickness of the film with a vertical resolution of 0.1nm, the lateral resolution remaining that of a conventional optical microscope. The example below gives an illustration of the possibilities of these techniques.
Multilayer LB films have been prepared with the molecule drawn below[1] (P. A. Hirsch, Uni. Erlangen). Spectrometric measurements show that the deposition of LB layers is regular (rightmost figure).

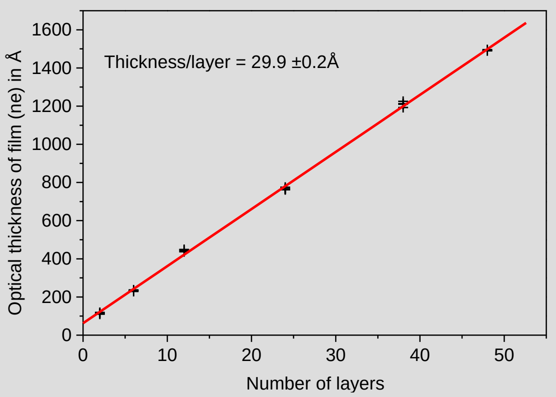


[1] The different functional groups are not drawn to scale.

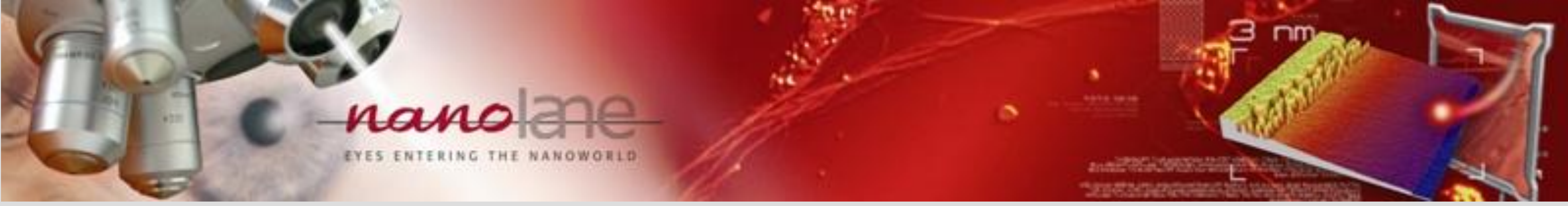


Grazing incidence X-Ray measurements (hereafter) show that the quality of the layers is very good and that each layer is, on average[2], 28,2 ± 0,6Å thick. Ellipsometry measurements provided the value of the refraction index (n=1,58) and an average layer thickness (below, right) of 29,9 ± 0,2Å, value slightly larger than the one measured with X-Ray, probably because of the silane layer deposited on the substrate.

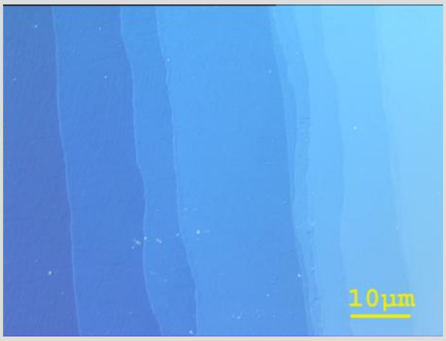


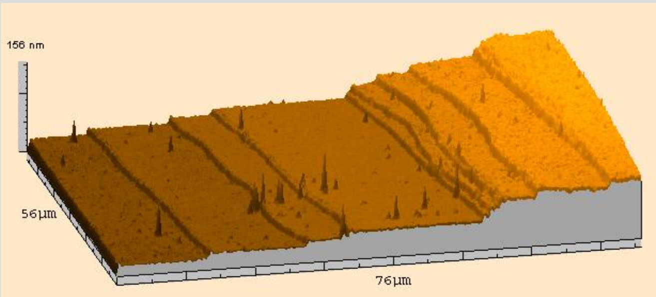


[2] The rather large incertitude given corresponds to an interval containing 90% of the samples tested. For a given sample the incertitude on the thickness of the layers is of the order of 0.1Å ; the different samples gave values between 27,6 and 28,7Å.

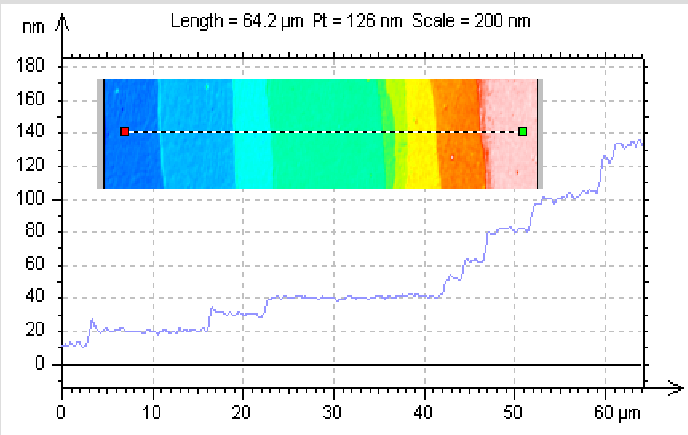


The Sarfus observations have been performed on multilayer samples, just at the silicon/LB film boundary. In this region the LB technique inherently create "steps". Selective reflection of white light by the layers produces a rainbow effect on this part of the film, easily seen with the naked eye (see picture herafter). The observations confirm the presence of these steps, each one actually corresponding to a bilayer.





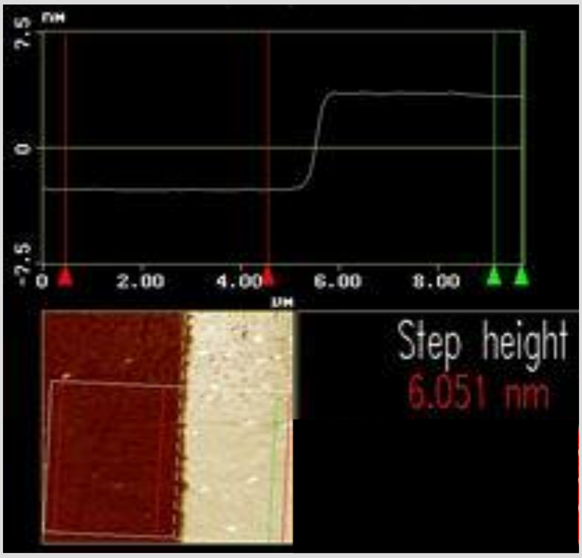
If a picture is scanned along a line (dotted line in the picture), the height profile is determined along this line.



Use of the 3D-Sarfus technology enables one to calculate back to the thickness of the steps (n*t), this gives a value of 63 ± 7 Å (see table hereafter), in perfect agreement with the X-Ray measurements.

Step	Optical thickness n*t (Å)	Thickness t (Å) (n=1.58[3])
S1-S2	89	56
S2-S3	106	67
S3-S4	96	61
S4-S5	92	58
S5-S6	109	69
S6-S7	212	67[4]
S7-S8	208	65[4]
Mean (S1-S6)	**-**	**63**

The last proof of the quality of the optical measurements is brought by AFM measurements. The picture on the left has been taken on a 10 × 10 µm2 zone, and as before at the film/substrate boundary. After calibration of the piezo tube of the AFM a step height of 60Å is measured, corresponding once again to the thickness of a bilayer.



Contribution/advantages of Sarfus

- Direct visualisation of the quality of the layers
- Rapid step height measurement
- Non-invasive/non contact technique
- No labelling/pretreatment of the sample

[3] Optical index determined by ellipsometry
[4] Thickness calculated considering a bilayer