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KSV NIMA [Technology Note] 2

What and why: Langmuir-Blodgett films

This note describes the basic theory, measurements and applications of Langmuir-Blodgett and Langmuir-Schaefer films.

Langmuir-Blodgett and Langmuir-Schaefer films

Early in the 20th century, Irving Langmuir and Katherine Blodgett founded the science of Langmuir-Blodgett films by examining the transfer of Langmuir monolayers onto substrates. In a LangmuirBlodgett experiment, a Langmuir monolayer is held at constant surface pressure while transferring it onto a solid substrate. The density, thickness and homogeneity properties of the monolayers are preserved when transferring the Langmuir film. This gives the possibility to make organized multilayer structures with varying layer compositions.

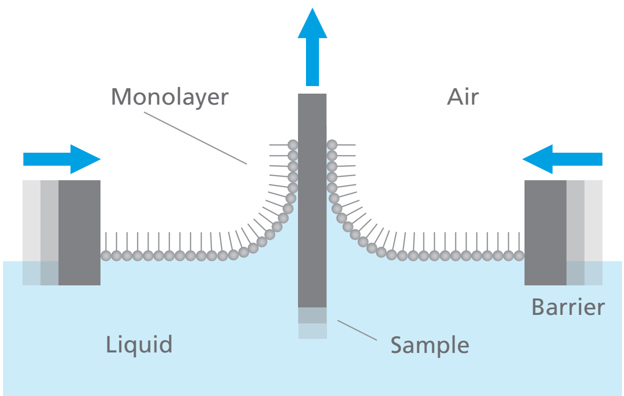
There are two main approaches to fabricating a Langmuir film on a solid substrate (Figure 1). In the case of Langmuir-Blodgett (LB) deposition, the solid substrate is dipped vertically through the Langmuir film. The Langmuir film has to be fabricated using a LangmuirBlodgett trough top with a sufficient well size for the substrate. The Langmuir-Schaefer (LS) technique (Figure 2) can be performed with a Langmuir trough top as the sample is dipped horizontally and no additional depth is required below the monolayer. Repeated deposition can be achieved to obtain well organized multilayers on a solid substrate. Special Langmuir-Blodgett Deposition Troughs such as the KSV NIMA Alternate-Layer Langmuir-Blodgett Deposition Trough are designed for fully automatic LB multi-deposition from 2 different Langmuir films.

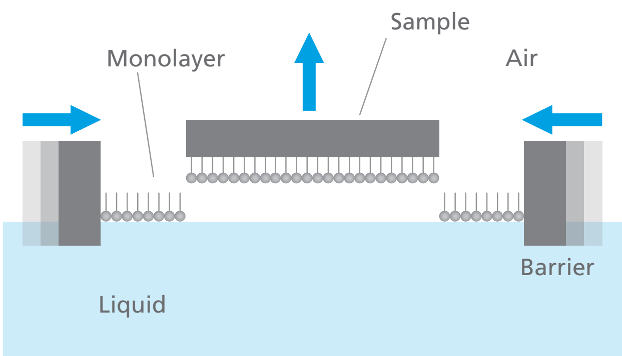
Requirements for deposition

LB deposition is traditionally carried out in the solid phase. This ensures that the surface pressure is high enough for sufficient cohesion in the monolayer and ensures the build-up of homogeneous multilayers. The surface pressure value that gives the best results depends on the nature of the monolayer and is usually 10 - 40 mN/m. When the solid substrate is hydrophilic (glass, SiO_2 etc.) the first layer is deposited by raising the solid substrate from the subphase through the monolayer, whereas if the solid substrate is hydrophobic (HOPG, silanized SiO2 etc.) the first layer is deposited by lowering the substrate into the subphase through the monolayer.

There are several parameters that have an effect on what type of LB film is produced. These are the nature of the spread film, the subphase composition and temperature, the surface pressure and the deposition speed as well as the type and nature of the solid substrate. The quantity and quality of the deposited monolayer on a solid support is measured by transfer ratio, t.r., defined as the ratio between the decrease in monolayer area during a deposition stroke, and the area of the substrate. For ideal transfer the t.r. is equal to 1.

The LB film can be characterized to obtain additional information and to check the quality of the deposition. Commonly used techniques are for instance PM-IRRAS (FTIR spectrometry), Surface Plasmon Resonance, Quartz Cristal Microbalance, Ellipsometry, Vibrational spectroscopy, UV-VIS absorbance spectroscopy, X-ray reflectometry etc.





[Figure 1]: Illustrations of Langmuir-Blodgett and Langmuir-Schaefer deposition

Key application areas

The Langmuir-Blodgett technique is one of the most versatile methods for the preparation of thin films as it enables precise control of the monolayer thickness, homogeneous deposition of the monolayer over large areas and the possibility to make multilayer structures with varying layer composition. The deposition technique offers the possibility to fabricate for example functional coatings, supported bilayers of phospholipids, and novel coatings of nanotubes, nanowires and graphene.

Modelling of biomembranes

Whereas Langmuir monolayers provide a way to model phospholipids on liquid surfaces, LB and LS techniques can be used to transfer the layers onto a solid substrate. This offers a valuable way to prepare supported bilayers of phospholipids with varying lipid composition.

- Supported phospholipid model structures
- Biomolecular interactions

Organic and inorganic coatings

Coatings that respond to changes in their environment can significantly alter the surface properties of different materials. LangmuirBlodgett technique offers the possibility to fabricate and control monolayer deposition in application areas such as

- Smart coatings
- Nanoparticles, -wires and nanoscale coatings
- Nonlinear optics

Electronic industry

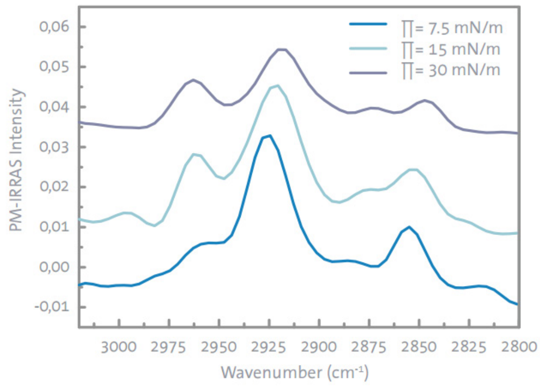
Conductors, semiconductors and dielectric materials exhibit different properties depending on their composition. Langmuir-Blodgett deposition can be used to transfer high-quality molecular layers of a variety of materials in electronic industry. Examples include

- Carbon -based nanoparticle applications
- Fuel and solar cells
- Semiconductor devices and material quality

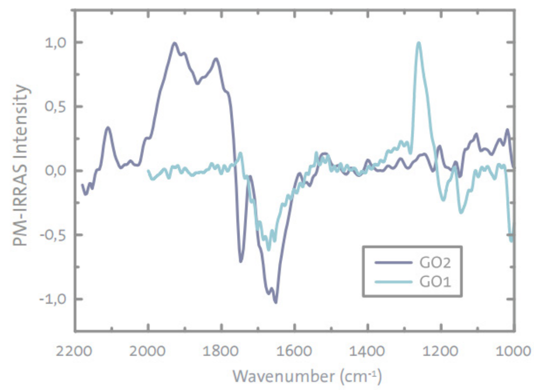
Sensors

Generally, sensors require a large surface-to-bulk ratio for sufficient sensitivity and reversibility. For sensor applications, Langmuir-Blodgett deposition allows careful control of orientation and surface properties. Sensors based on LB films include

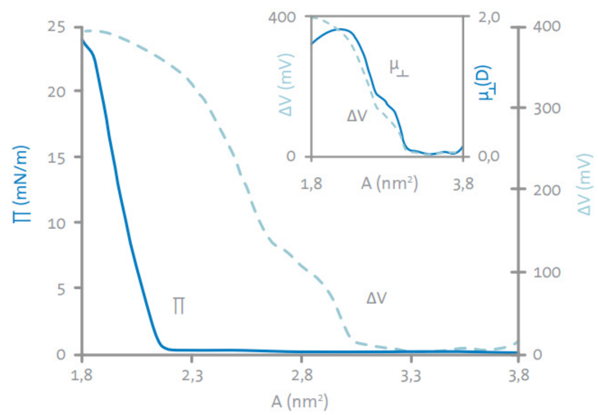
- Volatile organic compound sensors
- Biosensors
- Ion sensors



[Figure 2]: Phospholipid deposition. DPPC monolayers were deposited on gold coated glass slides at different surface pressures (∏) and analyzed using PM-IRRAS. The monolayer packing density (surface pressure) effect was clearly seen especially at the methyl group region (~3000 cm^{-1}), but also at the carbonyl (~1750 cm^{-1}) and phosphate group (~1000-1200 cm^{-1}) vibrations. Observed peak intensity ratio change indicates that the molecule orientation changes as a function of surface pressure.



[Figure 3]: Graphene characterization. PM-IRRAS was used together with a Langmuir trough to measure two different types of floating graphene oxide layers prepared on a water subphase. The C=O stretches of the two layers oriented differently (1750 cm^{-1}) in the floating layer. The spectra shows that GO_2 has much more complex structure, probably from having more defects in the graphene layer.



[Figure 4]: Ion sensors. The graph displays the surface pressure - area (∏-A)-isotherm and surface potential ΔV and dipole moment $\mu_\perp$(inset) of a calixarene monolayer in the presence of copper ions in the subphase. It can be observed that the effective dipole moment reaches a maximum at the gas-liquid phase transition. The effect was preserved for LB layers deposited on aluminum substrate. Adapted with permission from Langmuir 2010, 26(13), 10906–10912. Copyright 2010 American Chemical Society.

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