Supramolecular Organization in Thin Films

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AREAS DE TRABAJO EN MATERIALES MOLEculares

- Síntesis de Moléculas y Polímeros
- Organización a Nivel Supramolecular
- Organización y/o Preparación de Fases condensadas
- Caracterización de los Sistemas, y Estudio de propiedades
- Preparación de Dispositivos y Aplicaciones
Nanoscience or Nanotechnology?

- self-assembly
- quantum effects
- molecular building blocks
- surface science
- Self-assembly or directed assembly

Nanostructured Material

Assemble from Nano-building Blocks
- powder/aerosol compaction
- chemical synthesis

'Sculpt' from Bulk
- mechanical attrition (ball milling)
- lithography/etching...
Thin-films

**Thin-film deposition** is any technique for depositing a thin film of material onto a substrate or onto previously deposited layer.

"Thin" is a relative term, but most deposition techniques allow layer thickness to be controlled within a few tens of nanometers, and some (molecular beam epitaxy) allow single layers of atoms to be deposited at a time.

It is useful in the manufacture of **optics** (for reflective or anti-reflective coatings, for instance), **electronics** (layers of insulators, semiconductors, and conductors form integrated circuits), **packaging** (aluminum-coated film).

Deposition techniques fall into two broad categories, depending on whether the process is primarily **chemical** (CVD) or **physical** (PVD).
Chemical vapor deposition (CVD)

- It is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

- Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial. These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO₂, silicon-germanium, tungsten, silicon carbide, silicon nitride, titanium nitride, and various high-k dielectrics. The CVD process is also used to produce synthetic diamonds.
Techniques for the preparation and deposition on surfaces of molecular nanostructures

Nanotechnological applications require immobilization on a surface for many of the objectives that these molecules are directed towards. Therefore, to achieve a suitable organization one must consider not only interactions between the molecules themselves but also those with the surface, which play a role of varying importance according to the system.

Different techniques are used for the preparation and deposition on surfaces of molecular nanostructures:

- Solution and Thermal Evaporation on surfaces
- The Layer-by-Layer Approach
- Langmuir–Blodgett (LB) films
- Self-Assembled Monolayers (SAMs)
Solution and Thermal Evaporation on surfaces

Deposition Techniques

- Evaporation
  - Sputtering
  - E-beam evaporation
  - Vapor deposition

  Suitable for small molecules

- Wet processing
  - Spin coating
  - Screen printing
  - Inkjet printing
  - Doctor blading

  Suitable for polymers
Thin Films

- Overall thickness of organic layers is usually less than 200nm
- Individual layers are usually between 10-60nm
- Therefore they are very delicate
  - Need to be very clean: dust
  - Sensitive to scratch
Sensitivity of Thin Films

- Figure shows a short situation

- Impurity can block electron, hole transport
- Defects site make electron/hole to recombine
- Extreme care about cleanliness
Development

- Preparing the substrate
- Depositing thin film layer
- Testing and Characterization
Vacuum Deposition

- E-beam evaporation and sputtering are for high temperature material, (both available in cleanroom)
- Sputtering is esp. useful for large substrates (Used for ITO)
- These methods can damage the organic layers
  - Organic material have low glass transition
- Vacuum evaporation by direct heating is the most appropriate for organic materials
- The pressure needed to deposit organic devices is about $10^{-5}$-$10^{-6}$ torr (760 torr = 1 atm)
- Deposition rate for organics is about 1-10A/s - usu. 6-10 A/sec
- Deposition Temperature depends on vacuum quality and material
- Substrates should be kept at low temperature during deposition
- Deposition rate is usu. Controlled by crystal monitor
Spin Coating

- Solution is dropped on the rotating substrate
- By centrifugal force, solution spreads on the substrate
- Thin film properties depend on rotation speed curve, solution, temperature, vapor pressure of material...
Spin Coating Process

- Spin rate for organic solvents that I have worked with vary between 600rpm to 4000rpm
- After spin coating each layer, the new layer should be dried in oven- preferably vacuum or nitrogen oven
- Spin coating should be done in clean room with excessive cure about cleanliness
- For better performance, spin coating can be done in a glove box (nitrogen/Arogn environment)
Thermal Evaporator

BASE PRESSURE ~ $7 \times 10^{-8}$ torr

- **E-Beam Evaporation Single Pocket**
- **Shadow Mask Storage-Exchange**
- **Independent Source Monitoring during Co-Deposition**
- **Six Thermally Heated Sources**
- **Two Independent Banks of Three Sources Each**
Double Glove Box

Moisture Level < 1 ppm
Characterization

- Devices should be kept in inert environment
- Usually testing is done in a glove-box
The Layer-by-Layer Approach

- Recently much attention has been devoted to the development of molecular assemblies of thin film based on successive deposition of alternate layers of anionic and cationic polyelectrolytes including synthetic polymers, proteins and nucleic acids, as an alternative procedure to the Langmuir–Blodgett Technique.

- The layer-by-layer deposition technique relies on the electrostatic force of attraction as an origin of the strong adhesion between the anionic and cationic layers. Therefore, the combination of polymers and biomaterials which have the same sign of electric charges and electrically neutral polymers cannot be used in this procedure.

- However, it may be possible to construct the layer-by-layer structure by means of polymers and biomaterials which have biological interactions such as protein–ligand, antibody–antigen and lectin–saccharide bindings. This would extend the scope of the layer-by-layer deposition technique in constructing the thin film assemblies composed of proteins and other biomolecules, because non-ionic polymers and even polymeric materials of the same polarity can be built into the same assemblies simultaneously through the biological interactions.
The Layer By Layer (LBL) Electrostatic Deposition

Uses:
- huge potential in coatings, electronics, sensors, controlled drug release

Materials used in LBL self-assembly:
- Polyelectrolytes
- Charged compounds such as: nanoparticles, nucleic acids, proteins, ionic dyes, viruses
- Electolytes: NaCl etc
Schematic of the Deposition Process on a Charged Substrate

PSD → DI Water → PDAC → DI Water

= PDAC
= PSS
**Electrolytes Used:**

**Anionic:** Poly (sodium 4-styrenesulphonate)  
M=70000

**Cationic:** Poly (diallyldimethylammonium chloride)  
M~100000-200000
Langmuir–Blodgett (LB) films
Método para la preparación de sólidos organizados en películas finas estructuradas en capas de espesor molecular

a) formación de una monocapa sobre la superficie del agua (o subfase).
b) transferencia sobre un sustrato sólido.
I. LA TÉCNICA DE LANGMUIR-BLODGETT (LB)

II. LAS MOLÉCULAS

III. ARQUITECTURA SUPRAMOLECULAR

IV. APLICACIONES
Step 1. The molecule of interest is dissolved in a volatile organic solvent that will not react with or dissolve into the subphase. A quantity of this solution is placed on the surface of the subphase, and as the solvent evaporates, the molecules spread forming a two-dimensional gas.

Step 2. A moveable barrier then compresses the surface of the subphase, allowing control of the surface area available to the floating layer. Generally, the state of the monolayer on the water surface is monitored by measuring the surface pressure.
Compression Isotherm

- Collapse pressure
- Collapse point
- Superficial pressure
- \( \Pi \text{ (mN/m)} \)
- Area per molecule
- \( \text{Área (Å}^2\text{)} \)
- Bidimensional solid
- Bidimensional liquid
- Bidimensional gas
Step 3. Langmuir-Blodgett (LB) films are prepared by transferring Langmuir films onto a solid substrate by vertical or horizontal lifting. Multilayers are prepared by repeated (periodic) dipping of the substrate in/onto compressed films on appropriate solutions.
The traditional means of forming an organic monolayer film is to spread an insoluble compound on an aqueous subphase, compress the film mechanically with a barrier until the molecules are densely packed and oriented approximately normal to the surface, and then to transfer this monolayer, if desired, to a solid substrate by dipping.

Langmuir Trough

The molecules for LB Films formation

Polar head

- Neutral \( \text{CH}_3-(\text{CH}_2)_n-\text{COOH} \) (-COOR, CONH\(_2\), OH, NH\(_2\),...)
- Charged: COO\(^-\), R\(_4\)N\(^+\), HPO\(_4^{2-}\), SO\(_4^{2-}\),...

Hydrophobic chain

- Aliphatic (van der waals interactions)
- Aromatics (\( \pi-\pi \) interactions)
III. ARQUITECTURA SUPRAMOLECULAR

- MONOCAPAS MIXTAS HOMOGÉNEAS
- MONOCAPAS ALTERNADAS
- EL MÉTODO SEMIANFIFÍLICO
- REACCIONES EN EL ESTADO SOLIDO: TOPOQUÍMICA

A) Reconocimiento en el plano
B) Reconocimiento entre planos
C) Centro activo
E) Requisito estructural
LB Films Drawbacks

- They are **only metastable** and tend to relax into more stable structural forms. Surface properties of LB films are most easily studied after the film has been transferred to a solid substrate, a procedure that may be complicated by changes in the structure of the monolayer during the transfer process.

- They are **not** normally **chemically bonded** to the substrate and hence are **not robust**. LB monolayers can often be removed from a substrate simply by rinsing with either aqueous or non-aqueous solvents.

- **One is restricted** to compounds that form LB films on water and that can be transferred intact to a substrate. It is, in particular, difficult to generate surfaces exposing polar functional groups at the monolayer-air interface by this technique.

- It is also **difficult to form highly crystalline monolayers** since they tend to be brittle and crack easily upon compression or during transfer.
Self-Assembled Monolayers (SAMs)

Adapted from de M. Angeles Herranz
Universidad Complutense de Madrid
Self-assembled monolayers (SAMs) provide a convenient, flexible, and simple system with which to tailor the interfacial properties of metals, metal oxides, and semiconductors. **SAMs are organic assemblies formed by the adsorption of molecular constituents onto the surface of solids** or in regular arrays on the surface of liquids (in the case of mercury); the adsorbates organize spontaneously into crystalline (or semicrystalline) structures.

Combinations of Headgroups and Substrates Used in Forming SAMs

**Adsorbed Compounds**

- **Sulfur Compounds**
  - (Ag, Cu, Pt, Hg, Fe, γ-Fe₂O₃, Au, GaAs, InP)

- **Fatty Acids**
  - (Al₂O₃, Ag, AgO, CuO)

- **Organic Silicon Compounds**
  - (Silicon oxide, Aluminum oxide, Quartz, Glass, Zinc selenide, Germanium oxide, Gold)

**Substrates**

- **Glass and Aluminum Oxides**
  - (alkysiloxanes)

- **Platinum**
  - (thiophenol and derivatives)

- **Gold**
  - (sulfur compounds)

- **Silver**
  - (sulfur compounds)

- **Copper**
  - (sulfur compounds)

- **Silicon**
  - (alkyl derivatives)

- **Mercury**
  - (sulfur compounds)
Why Is Gold the Standard?

- Gold is easy to obtain, both as a thin film and as a colloid. It is straightforward to prepare thin films of gold. Although expensive and not essential to most studies of SAMs, single crystals are available commercially.
- Gold is exceptionally easy to pattern by a combination of lithographic tools and chemical etchants.

- Gold is a reasonably inert metal: it does not oxidize at temperatures below its melting point; it does not react with atmospheric O₂; it does not react with most chemicals. These properties make it possible to handle and manipulate samples under atmospheric conditions. Gold binds thiols with a high affinity, and it does not undergo any unusual reactions with them.
Why Is Gold the Standard?

**Gold is compatible with cells**, that is, cells can adhere and function on gold surfaces without evidence of toxicity. SAMs formed from thiols on gold are stable for periods of days to weeks when in contact with the complex liquid media required.

**Thin films of gold are common substrates** used for a number of existing spectroscopies and analytical techniques. This characteristic is particularly useful for applications of SAMs as interfaces for studies in biology for cell studies.
Preparation of SAMs

- The gold **substrate** can be obtained either by using **crystal substrates** or by **evaporation** of thin Au films on flat supports, typically glass or silicon.
- Typically **concentrations** of 1-2 mM are used.
- Several different **solvents** are employed although **ethanol** is the most convenient: not toxic, cheap, easy to obtained with high purity and, able to solvate very different structures.

- Even though a self-assembled monolayer forms very rapidly on the substrate, it is necessary to use **adsorption times** of 15h or more to obtain well-ordered, defect-free SAMs.
- After the adsorption meticulous **rinsing** and **drying** are highly important.
- The monolayers obtained are thermodynamically **stable** and mechanically **robust**.
Multilayer Films Go 3-D

A combination of metal-ligand coordination and ligand-ligand aromatic interactions leads to laterally stabilized assembly of wirelike chains (purple spheres and gold crosses)

Structure of SAMs

\[ \text{Au} \quad \text{S(CH}_2\text{)}_n\text{-X} \]

25-40°
Characterization of SAMs

SAMs can be characterized by a range of techniques including:

- Ellipsometry and contact angle determination
- Transmission Electron Microscopy (TEM)
- Scanning Tunneling Microscopy (STM)
- Atomic Force Microscopy (AFM)
- Reflection Adsorption Infrared Spectroscopy (RAIRS)
- X-ray photoelectron spectroscopy (XPS)
- Electrochemistry
Reflection Adsorption Infrared Spectroscopy (RAIRS)

\[ \text{Intensity (a.u)} \]

\[ \text{Wavenumbers (cm}^{-1}) \]

- C=O
- C-O-C-
- C-S

a (n=0), b (n=3), c (n=4), d (n=5)
Materials Assembly: Self-Assembled Monolayers (SAMs)

Electroactive SAMs

\[ \Delta E = 30 \text{ mV} \]

\[ E = E^0 + \frac{RT}{\ln ([\text{ox}]/[\text{red}])} \]

Echegoyen, Diederich, et al., Chem. Mater., 2000, 14, 1721
Electroactive species trapped on SAMs

Zhang, Palkar, Fragoso, Prados, de Mendoza, Echegoyen Chem. Mater., 2005, 8, 2063
Applications of SAMs

- In biochemistry and biology: Model substrates to investigate biological membranes and cellular interactions.
- In crystallography: substrates for crystallization and to favor the nucleation of orientated crystals or to align crystals.
- In metallurgy: corrosion investigations and surface protection, covering of organic materials with metals.
- In molecular electronics for the preparation of different types of devices: rectifiers, transistors, molecular wires or switches, or to carry out conductance measurements between two metallic reservoirs.
- In electrochemistry for the investigation of systems able to generate photocurrent or for the development of sensors.
The SAM$_{AZO}$ immobilized between a transparent Au surface and a Hg drop electrode. As a result of the light-triggered isomerization between the rodlike \textit{trans} isomer (left) and the more compact \textit{cis} isomer (right), the distance between both electrodes varies, thus providing both an optoelectronic switch and an optomechanical cargo lifter.

To demonstrate and exploit this collective effect, a metal–molecule–metal junction was used, based on a Hg top electrode. Hg was chosen because it is a metal featuring a compliant liquid surface. The junction incorporates the SAM$_{\text{AZO}}$ chemisorbed on a 25-nm-thick semitransparent Au(111) electrode on a quartz support and a Hg drop coated with a SAM of dodecanethiol as the top electrode.

Gold Nanoparticles

\[ \text{HAuCl}_4 + \text{NaBH}_4 \rightarrow \text{Au} \]

Cascade structure in charge transfer!
Schematic representation of an hybrid solar cell based on a quantum dot – phthalocyanine combination.