When I consider everything grows

7. THIN FILM PROCESSING AND DEVICE FABRICATION

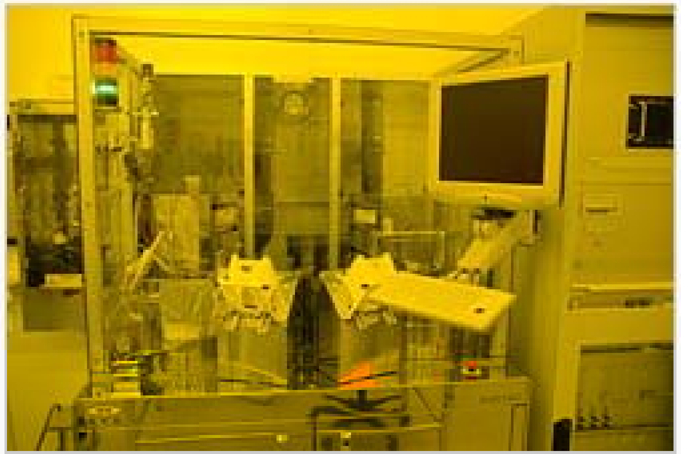
Source
No Spec: Text
W: Wikipedia

A spin coater (Laurell Technologies model shown) used to apply photoresist to the surface of a silicon wafer.

Spin-Coating

- Established method for photoresist (PR) coating
- Suitable for coating polymers, oligomers, and some molecules like phthalocyanine
- Typical concentration range 5-30 wt%, 1500-3000 rpm for several μm thick film.
- Film thickness depends on the concentration and spin speed

$$d = \left(\frac{\eta}{4\pi\rho\omega^2}\right)^{1/2} t^{1/2}$$



EVG 120 fully automated photoresist coater-developer under inactinic light at LAAS technological facility in Toulouse, France.

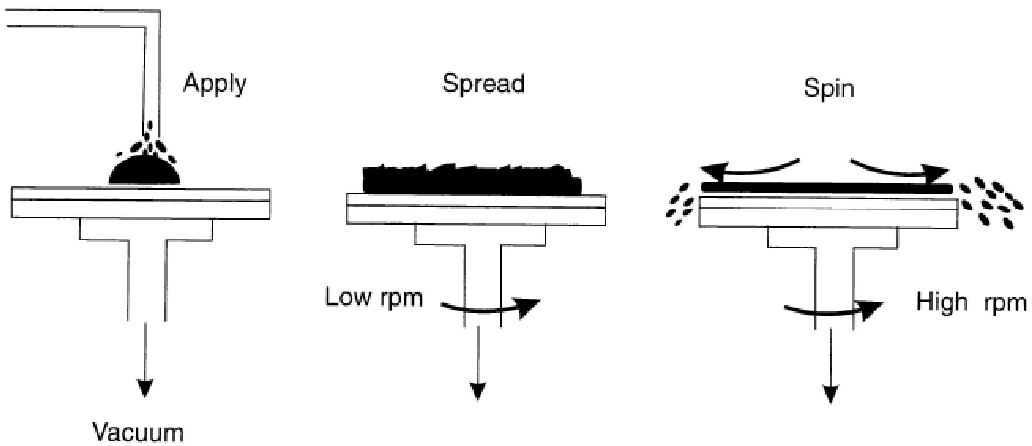


Figure 7.1 Schematic diagram of spin-coating.

Thermal Evaporation

- Use of shadow mask is possible if the mean free path (λ) is much greater than the source-substrate distance
- Film thickness sensor is used (Quartz crystal thickness monitor)

Langmuir expression of rate of evaporation Γ (in $kgm^{-2}s^{-1}$)

$$\Gamma = P(\frac{M}{2\pi RT})^{\frac{1}{2}}$$ where P is the vapor pressure (Nm^{-2})

Mean free path (λ)

$$\lambda = \frac{k_B T}{P\pi d^2 \sqrt{2}}$$ where d=0.2 nm (He), 0.5 nm(H_2O) etc

(λ is ~10 cm at 10^{-3} mbar and 10^4 cm at 10^{-6} mbar)

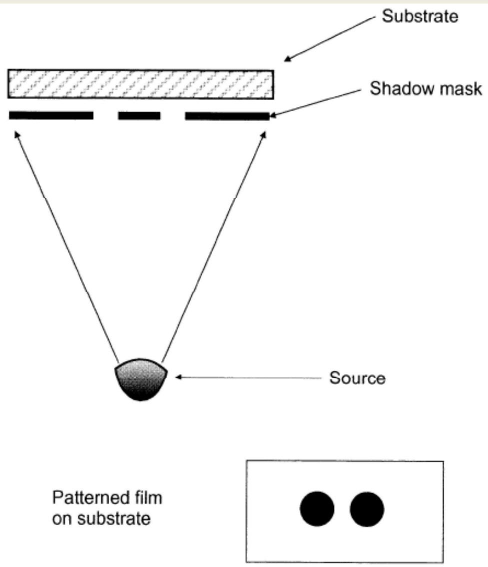


Figure 7.2 Use of a shadow mask to pattern an evaporated thin film.

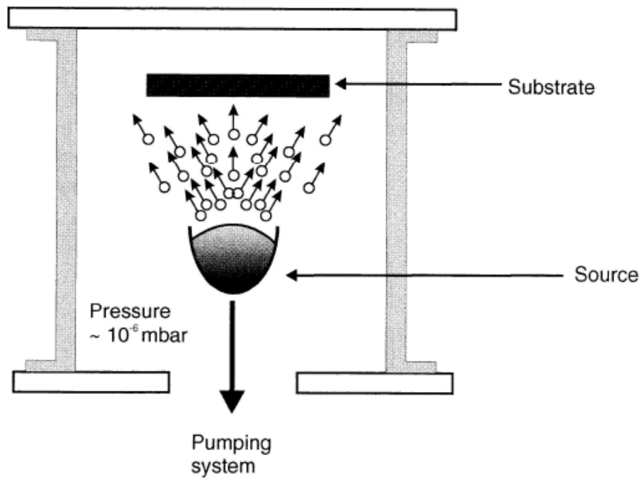


Figure 7.3 Vacuum evaporation system. Evaporating atoms or molecules traverse the space between the source and the substrate at reduced pressure.

- ## Different Evaporation Methods:

  Resistive heating: 1-10 nm min^{-1}

  Arc evaporation

  RF heating

  Electron bombardment

  Laser ablation

  Flash evaporation

Processes after reaching the substrate

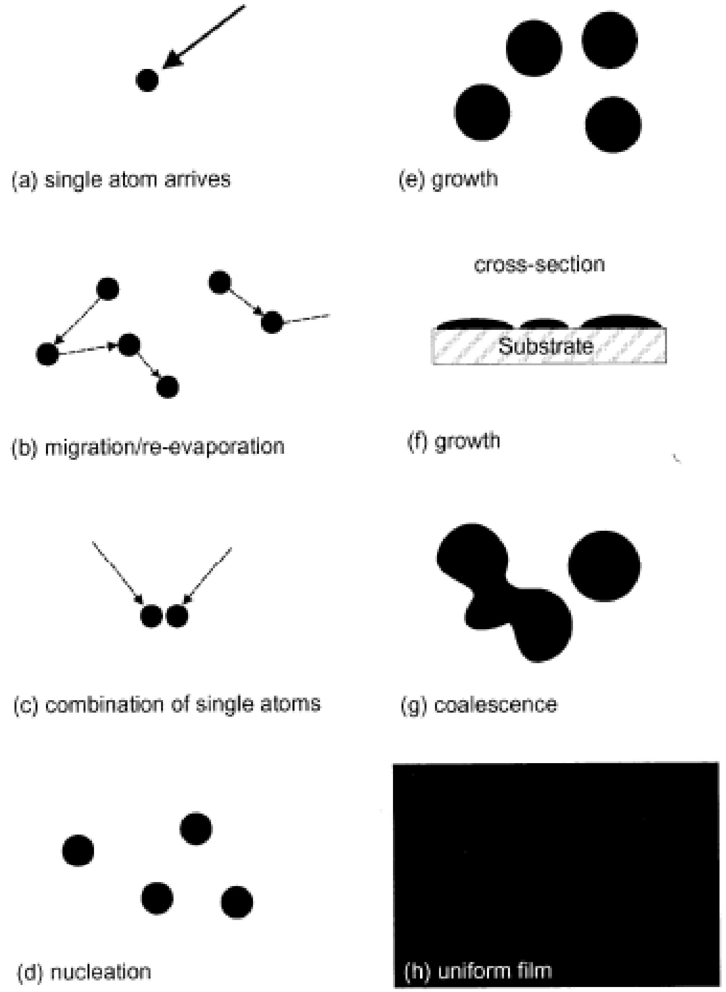


Figure 7.5 Stages of growth of an evaporated thin film. Reprinted with permission from Leaver KD, Chapman BN, *Thin Films*. Copyright (1971), Taylor and Francis.

Pentacene on glass, 40 nm

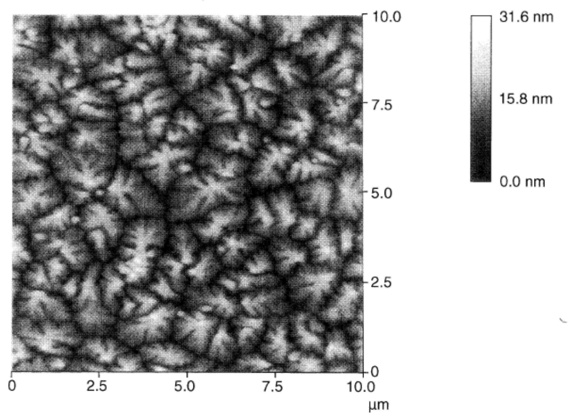
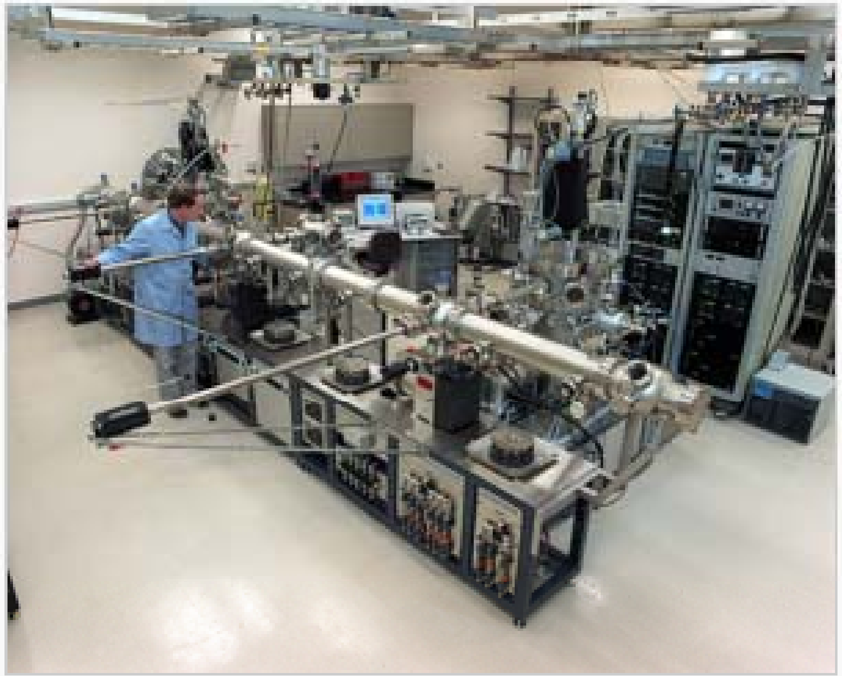


Figure 7.6 Atomic force microscope image of an evaporated film of pentacene, thickness ~40 nm [10]. Reprinted with permission from Dan Kolb.

Molecular Beam Epitaxy (MBE)

- Similar to the vacuum evaporation but employs ultrahigh vacuum (10^{-9} mbar) to eliminate the scattering. Makes the epitaxial growth of crystalline film, multiple quantum well etc possible
- Directs the controlled beams of the required molecules (in Knudsen cells) towards a heated substrate
- Very slow process, usu single monolayer per second
- GaAs crystal, phthalocyanine, perylene, etc. Usually cleaved surface of MoS2, HOPG and alkali metal halides are used as epitaxial substrate.



The Molecular Beam Epitaxy System in the William R. Wiley Environmental Molecular Sciences Laboratory is used to grow and characterize thin crystalline films of oxides and ceramics to understand in detail the chemistry that occurs on oxides and ceramic surfaces.

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Sputtering

- Sputtering is based on the momentum exchange of accelerated ions incident on a target (cathode for Ar^+ ion); produced secondary electron are accelerated to anode and help to maintain the plasma
- Source of ion: glow discharge, optimum pressure is 25-75 mbar.
- For insulating source material, RF instead of DC sputtering is used.
- Metal targets usually: polymer target is also possible

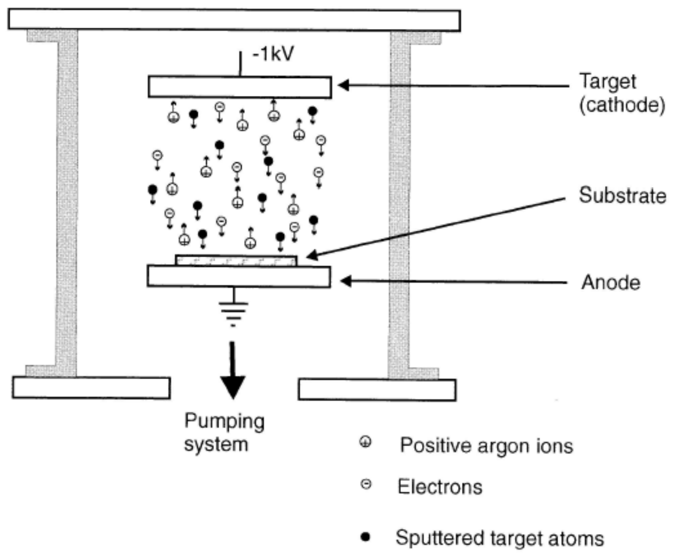
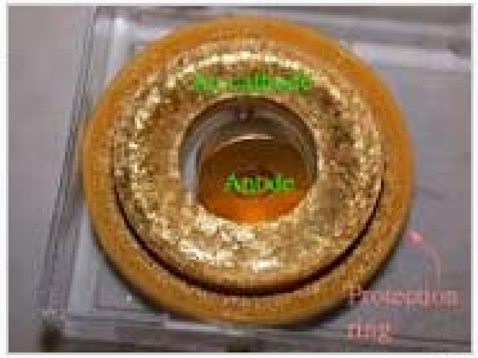


Figure 7.9 Sputtering system. A target, held at a negative potential, is bombarded with positively charged ions.



A typical ring-geometry sputter target, here gold showing the cathode made of the material to be deposited, the anode counter-electrode and an outer ring meant to prevent sputtering of the hearth that holds the target.

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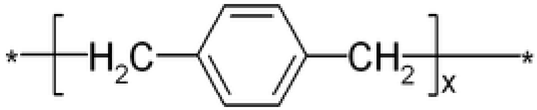
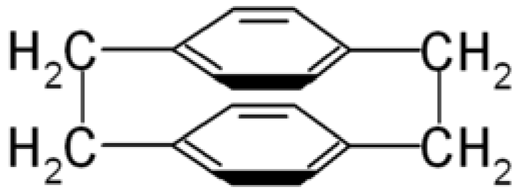
Chemical Vapor Deposition (CVD)

- Parylene (poly-p-xylylene): by pyrolysis of p-xylylene dimer at 600 ^{o}C
- Conformal coating on circuit board: insulating & moisture protection
- Preserving archival papers

Picture of one of the original pieces of SCS Parylene coating equipment.





http://www.scscoatings.com/parylene_knowledge/history.aspx

PECVD and MOCVD

- Plasma Enhanced CVD (PECVD): Plasma polymerization: Glow discharge polymerization
- MOCVD (Metallorganic) CVD: film deposition on a heated substrate

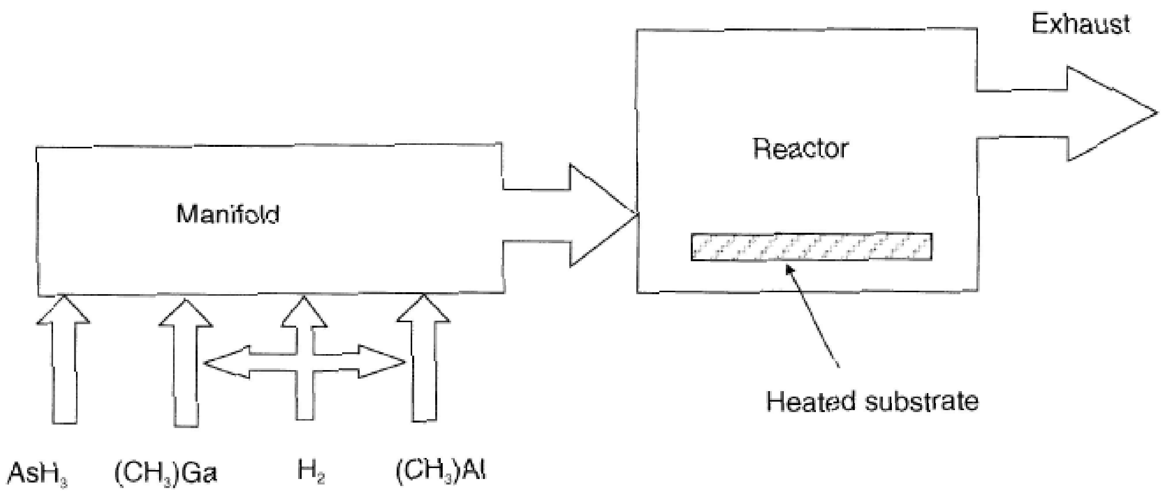


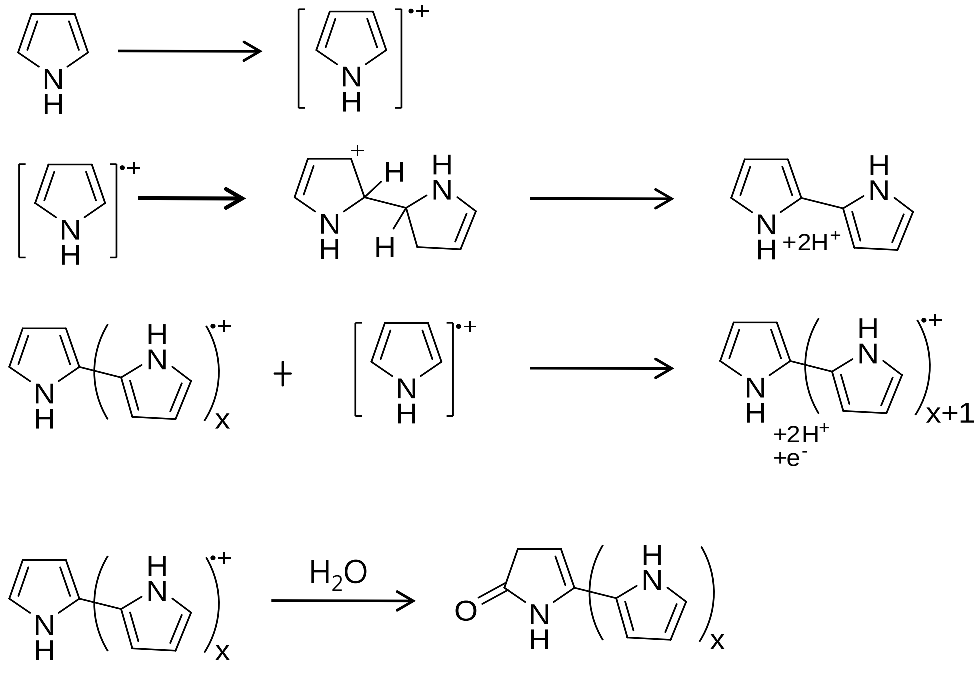
Figure 7.10 Schematic diagram for metallorganic chemical vapour deposition. The example depicts the arrangement to form thin films of the compound inorganic semiconductor alloy AlGaAs.

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4$$

takes place at 700 °C and epitaxial growth happens

Electrochemical Methods

- Electroplating of metals: deposition on the cathode, anode generation of cation (anodization)
- Electrochemical polymerization via anodic oxidation
- Electroless deposition: e.g. Ag or Ni on polymer surface; catalytic activity of the polymer surface



Electropolymerization of pyrrole

Inkjet Printing

- Direct-write fabrication method; wet-processing, reel-to-reel process
- Typical size of nozzle 20-70 μm, droplet size 4-180 pl, viscosiy 2 cP, surface tension 40 mNm-1; clogging of nozzle with partially dried ink is prevented by adding water miscible ethylene glycol 10-20 %

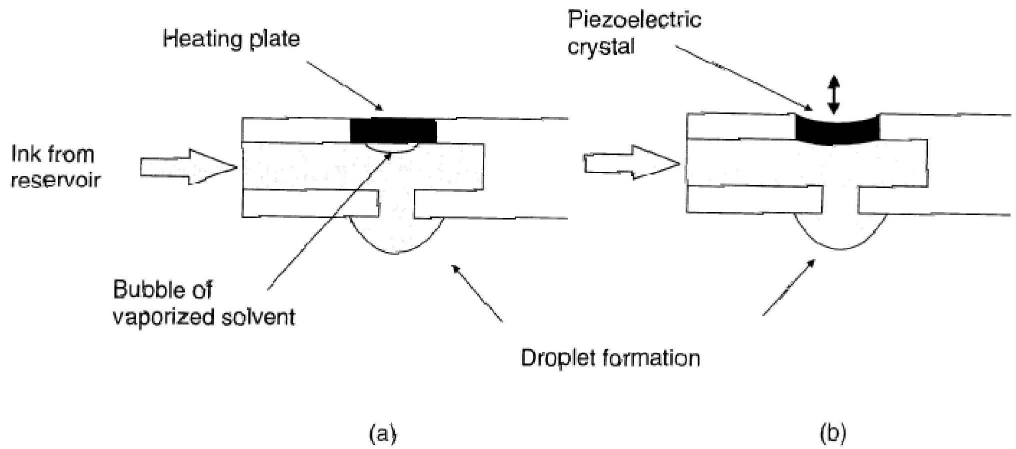


Figure 7.11 Inkjet print heads: (a) thermal (bubble-jet) operation; (b) piezoelectric operation.

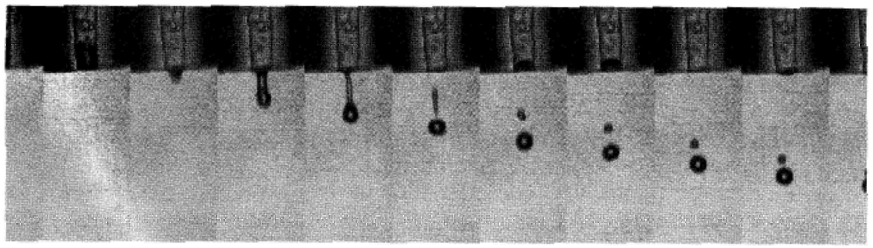


Figure 7.12 Ejection of drops from print head [22]. Nozzle size = 50 μm. Reprinted with permission from David Morris.

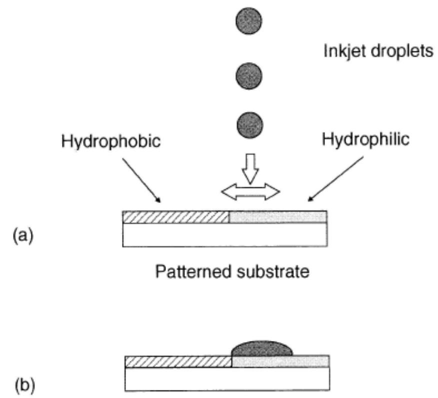
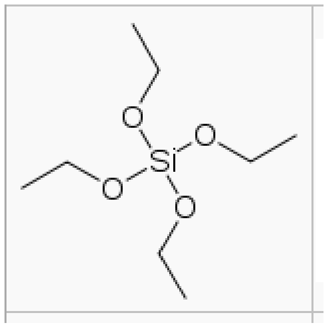


Figure 7.14 Use of surface treatments to define patterns for ink-jet printing.

Sol-Gel Processing

- Hydrolysis of alkoxide in a water-alcohol mixture system, followed by polycondensation
- Xerogel, Aerogel

TEOS



$Si(OC_2H_5)_4 + 2\ H_2O \rightarrow SiO_2 + 4\ C_2H_5OH$

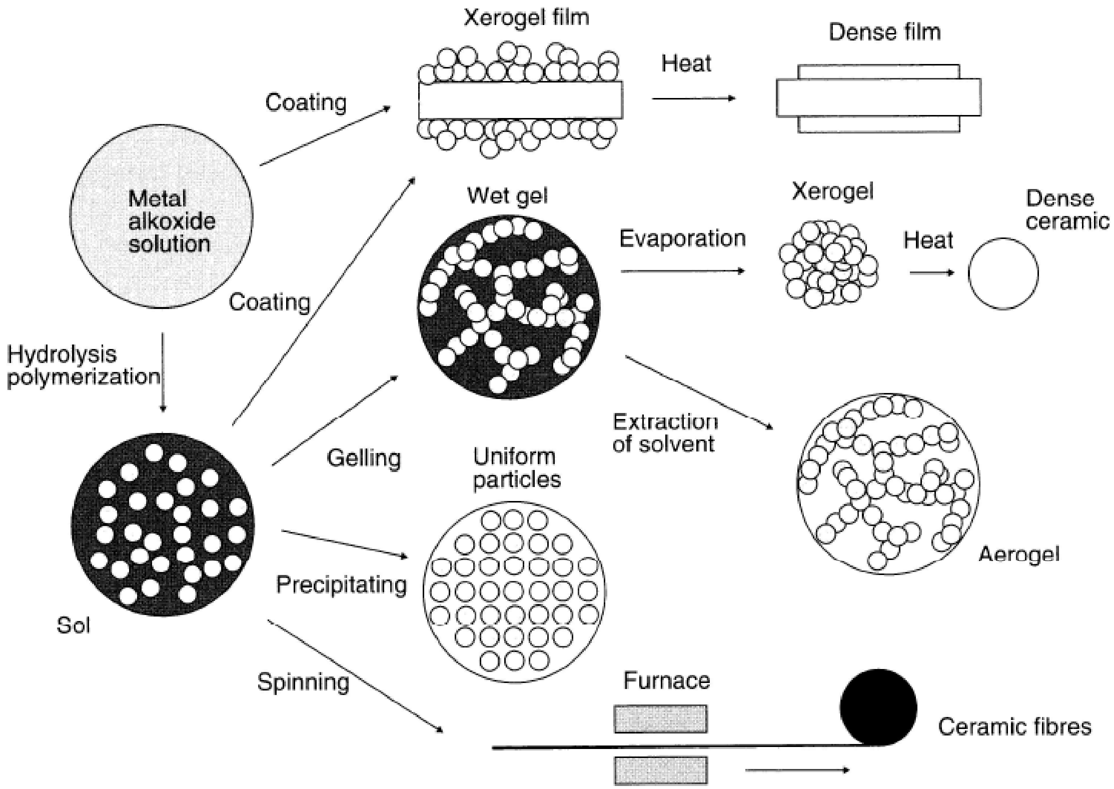


Figure 7.15 Sol–gel technologies and products. Reproduced from *Sol–Gel Science: the Physics and Chemistry of Sol–Gel Processing*, Brinker CJ, Scherer GW, p. 1 Copyright (1990), with permission from Academic Press.

Langmuir Blodgett(LB) Technique

- Monolayer of amphiphilic compound on an air-water interface
- (2-D)G(gaseous state), E(expanded monolayer phase), C(condensed phase)
- At C phase: area per molecule equals the cross-sectional area of it (0.19 $nm^2 molecule^{-1}$)

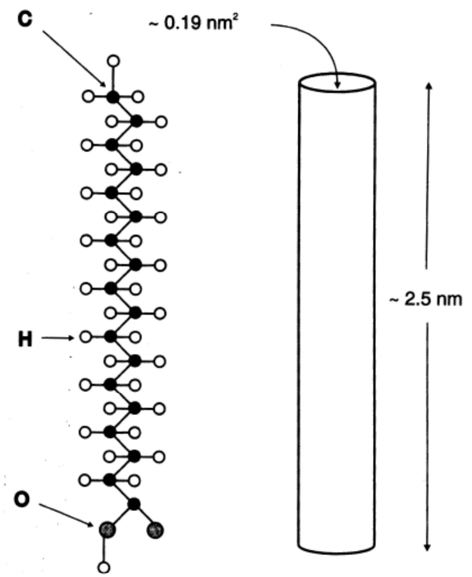


Figure 7.16 Chemical structure for *n*-octadecanoic acid (stearic acid). The approximate geometric shape and dimensions of the molecule are shown on the right.

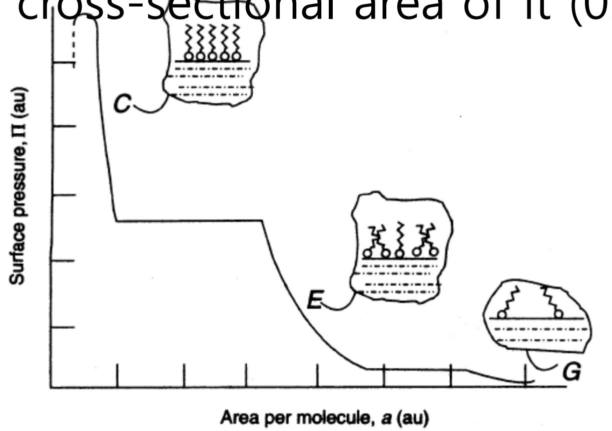


Figure 7.17 Surface pressure, Π, versus area per molecule, *a*, isotherm for a long-chain organic compound. The surface pressure and area are in arbitrary units (au). Reprinted from Petty MC, *An Introduction to Langmuir–Blodgett Films*, p. 18. Copyright (1996), Cambridge University Press.

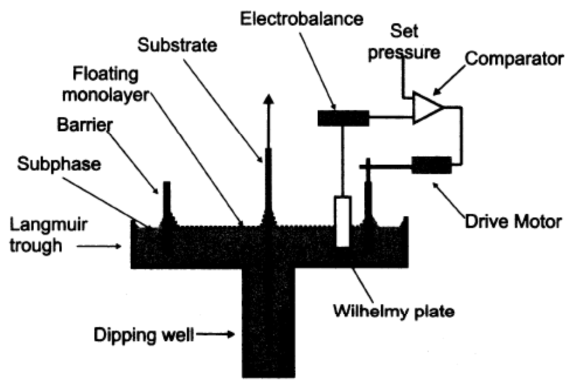


Figure 7.22 Schematic diagram of equipment for Langmuir–Blodgett film deposition.

Wilhelmy Plate

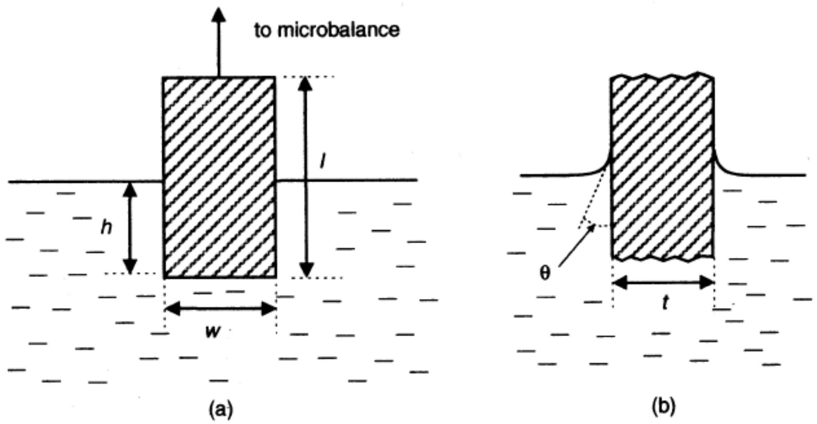


Figure 7.19 A Wilhelmy plate: (a) front view; (b) side view.

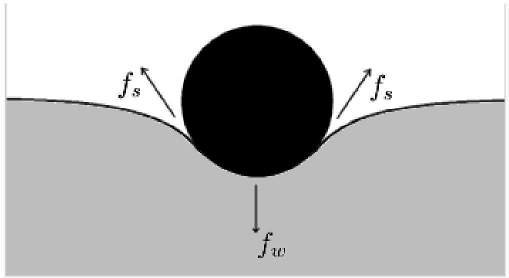
$F = \rho_w glwt + 2\gamma(t+w)\cos\theta - \rho_L gtwh$

where γ is the surface tension of the liquid

ρ_w is the density of the material

Usual procedure is to choose a plate that gives θ=0 (complete wetting) and measure the change in F for a stationary plate

$$\Delta\gamma = \frac{\Delta F}{2(t+w)} \approx \frac{\Delta F}{2w}$$



Surface Tension (force/length, mNm^{-1})

Sphere has the smallest possible surface area to volume ratio

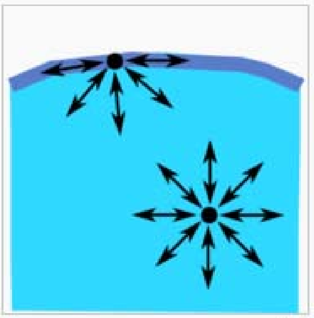


Diagram of the forces on a molecule of liquid.

A soap bubble balances surface tension forces against internal pneumatic pressure.

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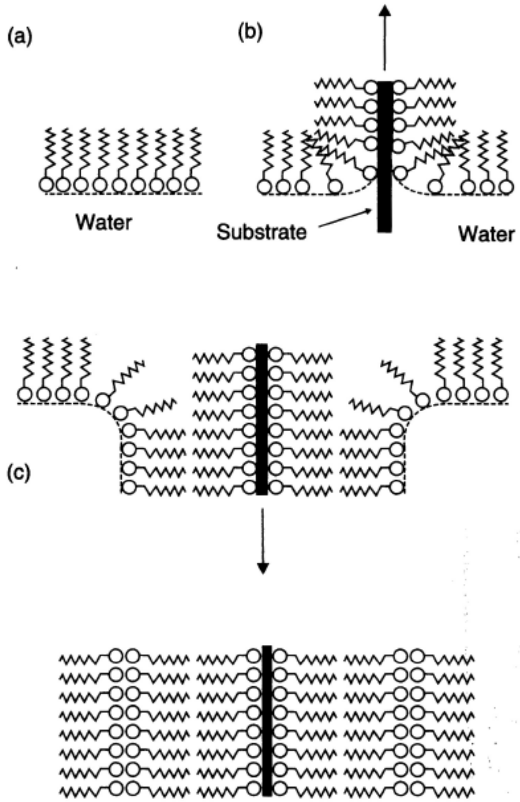


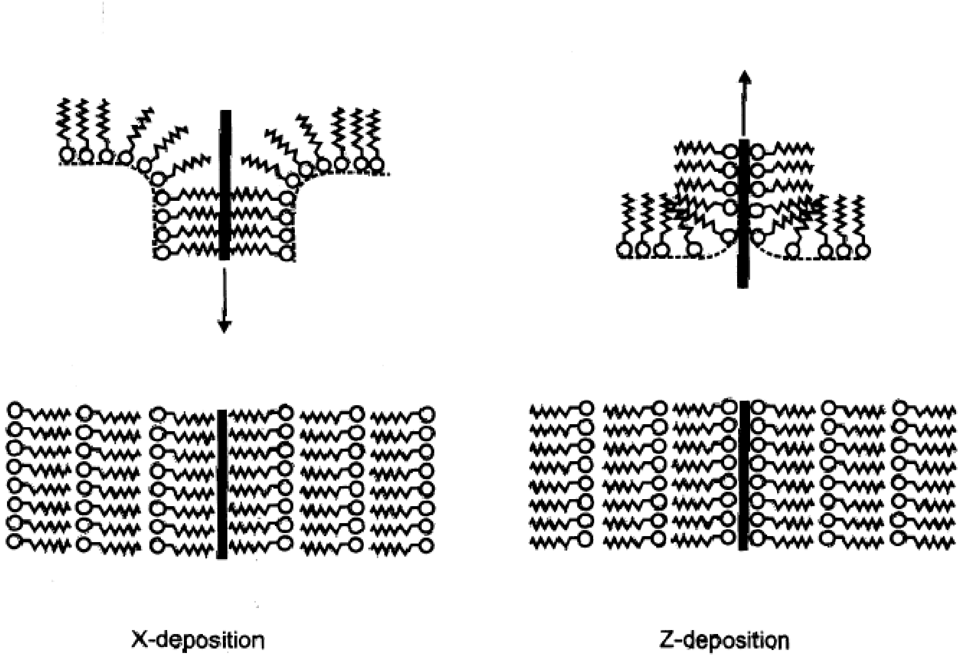


Figure 7.21 X-type and Z-type Langmuir–Blodgett film deposition.

Transfer ratio τ (also called as deposition ratio)

$$\tau = \frac{A_L}{A_S}$$

A_L is the decreased monolayer area on water surface

A_S is the coated area on the substrate

$0.95 \le \tau \le 1.05$ is fair

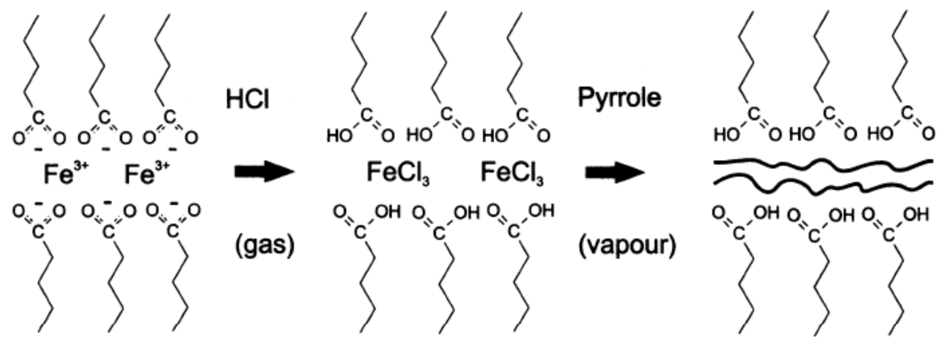


Figure 7.26 Idealized solid-state reactions of ferric stearate multilayers with HCl and pyrrole vapour to form a conductive polymer film within the fatty acid matrix [39].

Chemical Self-Assembly

- Strong interactions btw the head group of the self-assembling molecule and substrate, resulting in a chemical bond formation
- R-Si(Cl)$_3$ and Surface-OH; R-SH and Au; RCOOH and AgO/Ag to give $-CO_2^-Ag^+$

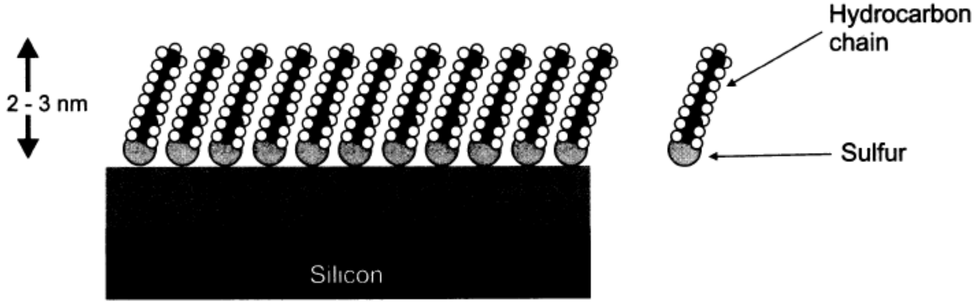


Figure 7.28 Self-assembled monolayer film of an alkanethiol on an Au-coated substrate.

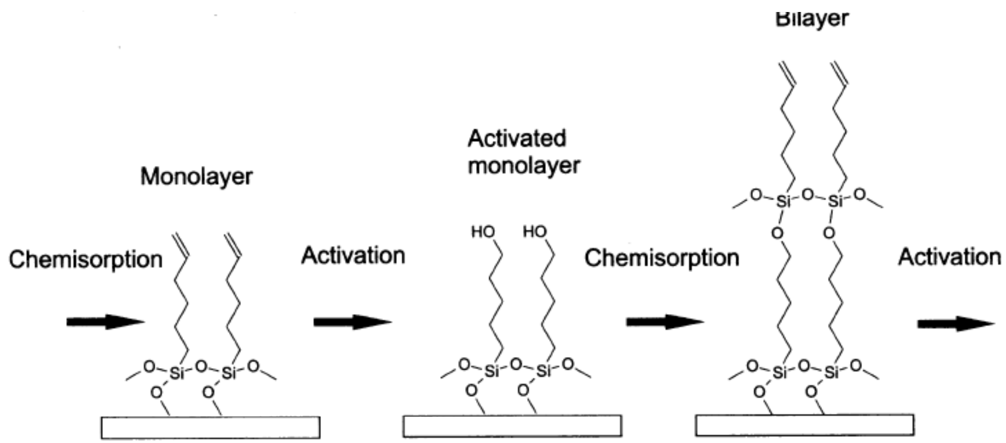


Figure 7.29 Preparation of a chemically attached polymeric multilayer. Reprinted from *Thin Solid Films*, **99**, Netzer L, Iscovici R, Sagiv J, 'Adsorbed monolayers versus Langmuir–Blodgett monolayers–why and how, I: from monolayer to multilayer, by adsorption', pp. 235–241, Copyright (1983), with permission from Elsevier.

Electrostatic Layer-by-Layer Deposition (LBL)

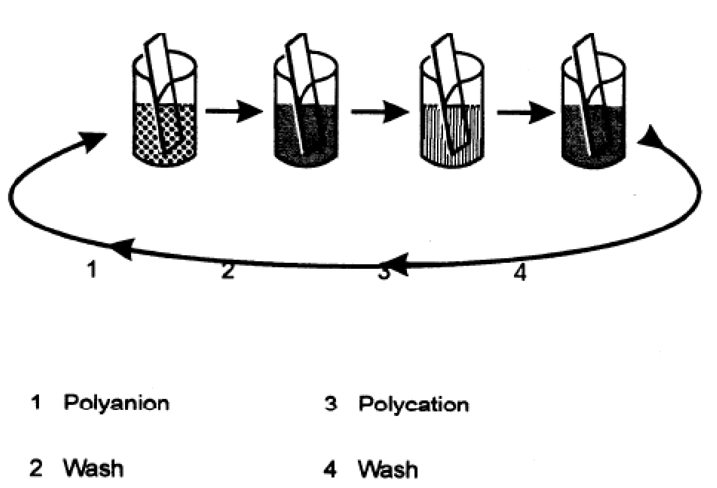
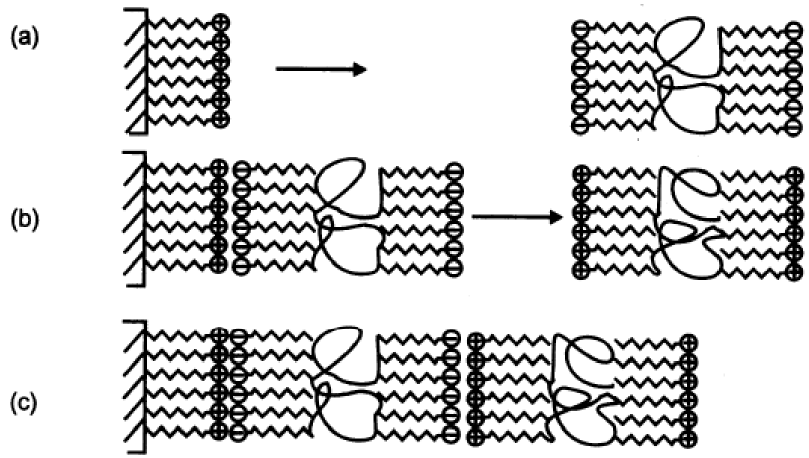
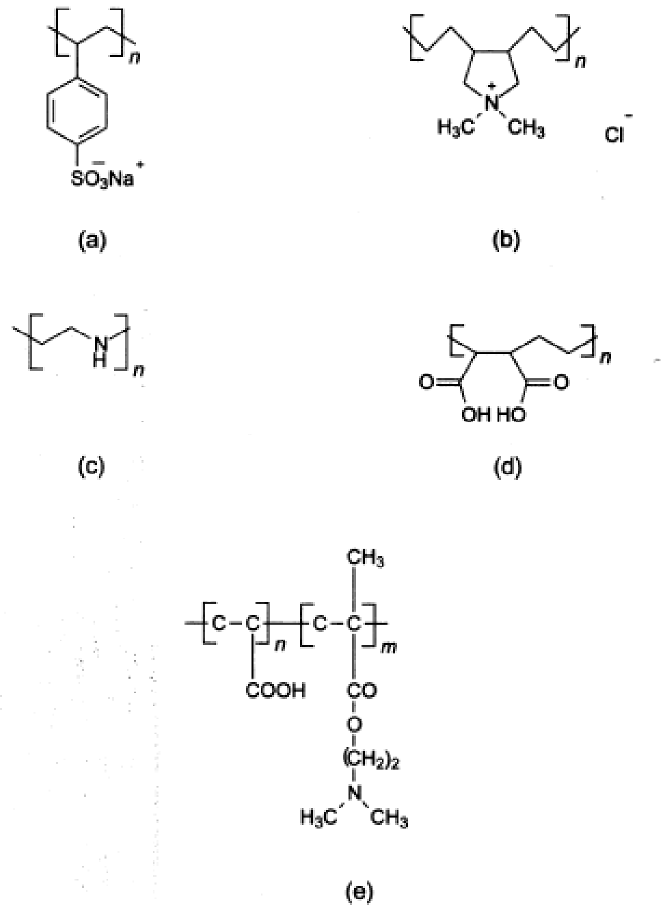


Figure 7.31 Layer-by-layer electrostatic deposition in a series of beakers.





.30 Types of polyelectrolyte: (a) sodium poly(styrene sulfonate) (PSS); (b) poly(diallyldi-
ımoium chloride) (poly-DADMAC); (c) polyethylenimine (PEI); (d) poly(ethylene-*co*-maleic
IAE); (e) a copolymer formed from acrylic acid and dimethylaminoethyl methacrylate. (a), (b)
ples of strong polyelectrolytes; (c), (d) are weak polyelectrolytes; and (e) is a polyampholyte.

Photolithography

- Positive and negative resist
- Hg lamp (365 nm) to KrF (248 nm) to ArF(193 nm)

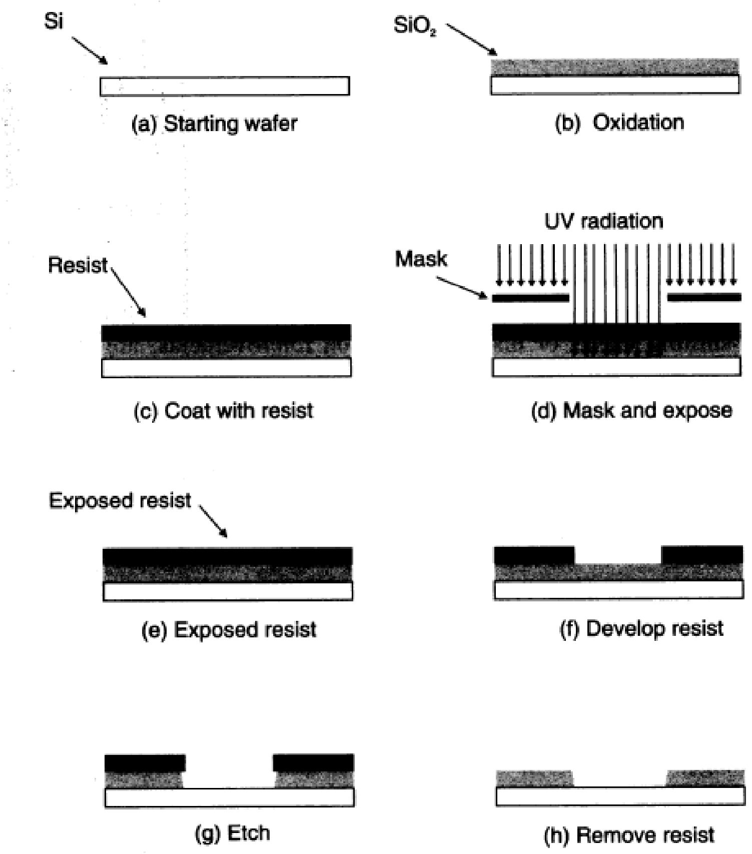
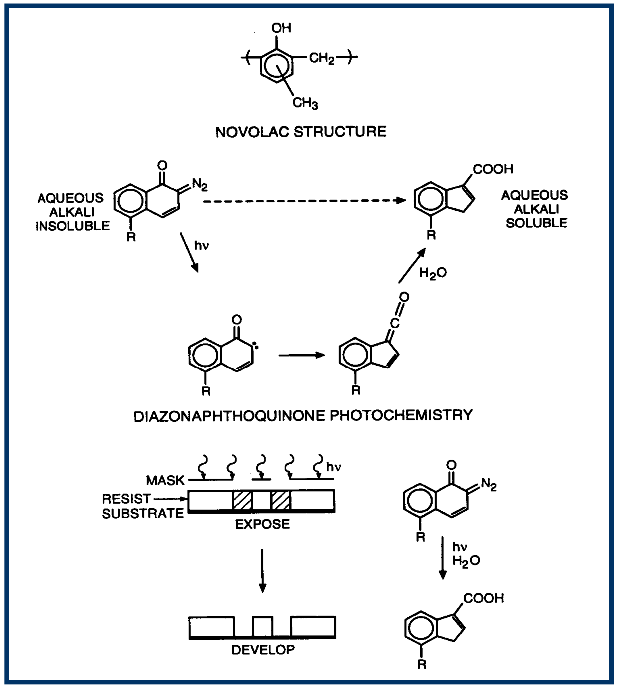


Figure 7.35 Schematic diagram of the process of photolithography.



Soft Lithography

- In technology, soft lithography refers to a family of techniques for fabricating or replicating structures using "elastomeric stamps, molds, and conformable photomasks"
- Used for features from micro to nanometer size
- Soft lithography includes the technologies of Micro Contact Printing (μCP), replica molding (REM), microtransfer molding (μTM), micromolding in capillaries (MIMIC) and solvent-assisted micromolding (SAMIM) (From Xia et al.) Patterning by etching at the nanoscale (PENs) One of the soft lithography procedures,

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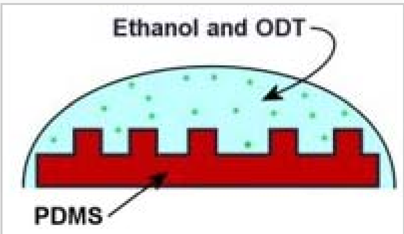


Figure 1 - "Inking" a stamp. PDMS stamp with pattern is placed in Ethanol and ODT solution

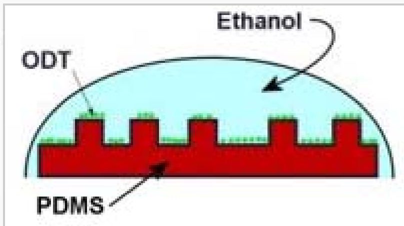
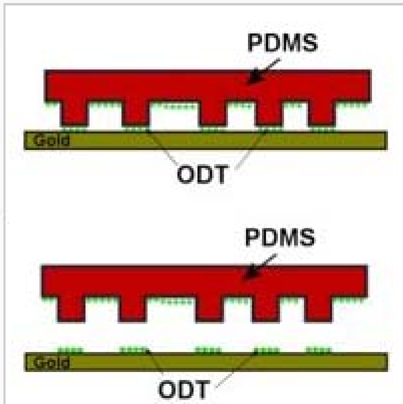


Figure 2 - ODT from the solution settles down onto the PDMS stamp. Stamp now has ODT attached to it which acts as the ink.



HW #3 Report on the Soft Lithography: Due by November 19

Dip-Pen Nanolithography

- Dip Pen Nanolithography (DPN) is a scanning probe lithography technique where an atomic force microscope tip is used to transfer molecules to a surface via a solvent meniscus. This technique allows surface patterning on scales of under 100 nanometres
- The transfer of a molecular 'ink' from a coated AFM tip to a substrate was first reported by Jaschke and Butt in 1995. The technique was further developed by a research group at Northwestern University led by Chad Mirkin [1] who also introduced the term "DPN".

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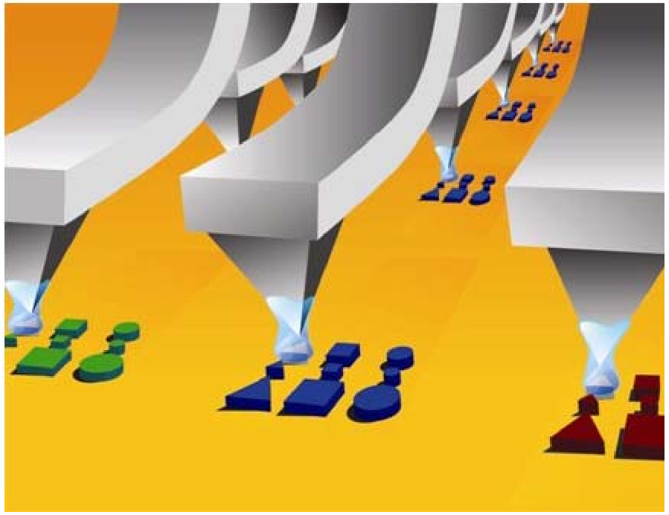

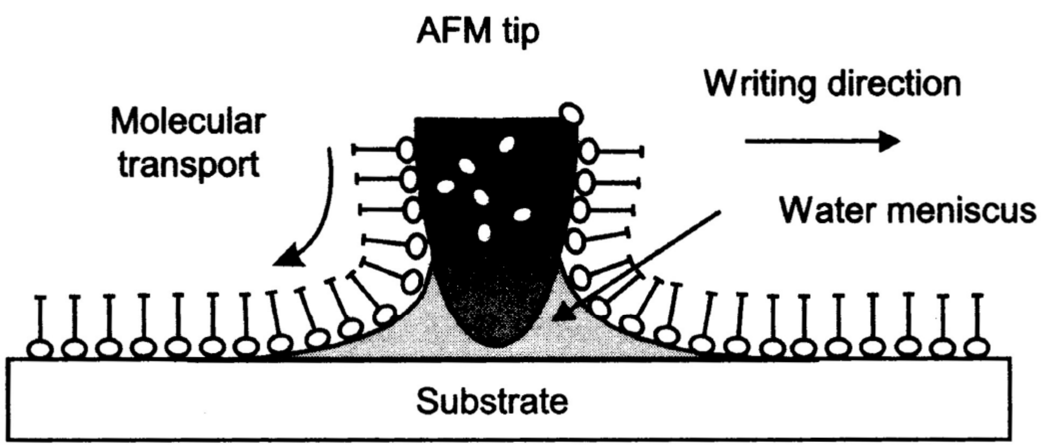

Figure 7.42 Dip-pen nanolithography.

Gravure Printing for Flexible Electronics

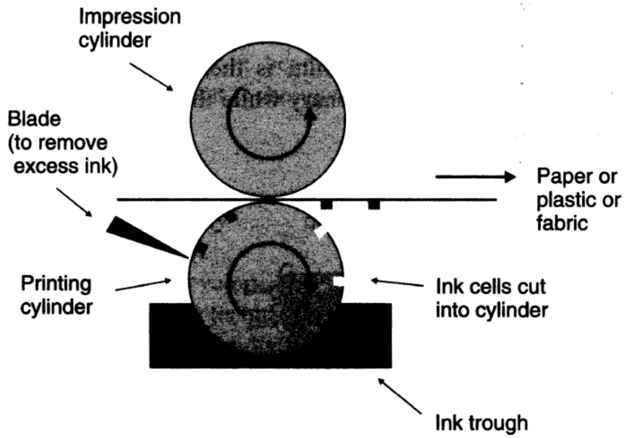

Figure 7.43 Schematic diagram of gravure printing where the ink is held in a recess etched or cut into the printing roller.