

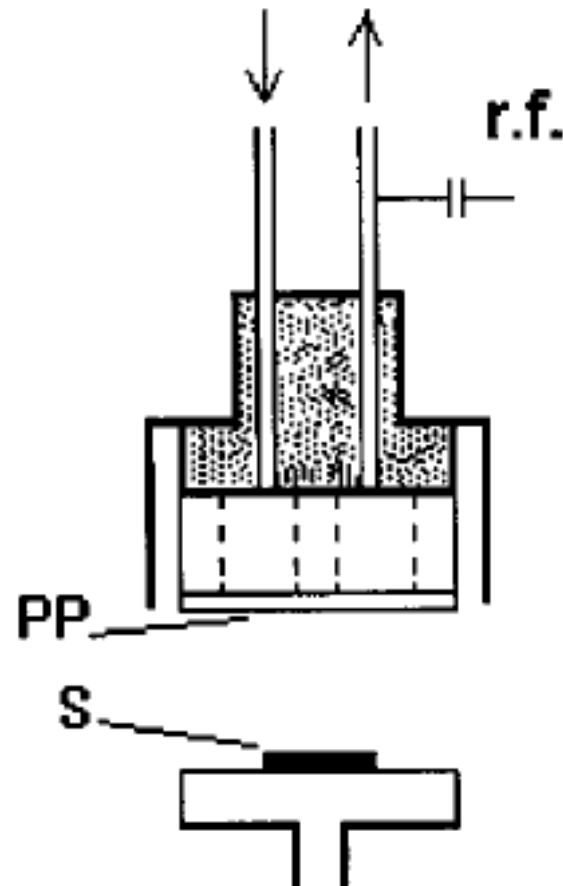
Thin film deposition on polymers and deposition of polymer thin films

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Sputter deposition of polymers

Need RF-sputter,
so that there is
no charging of the target

Deposition rates ~ 0.6 nm/s
(slightly lower than metals)



Self-sputtering of PTFE (CF₂)_n

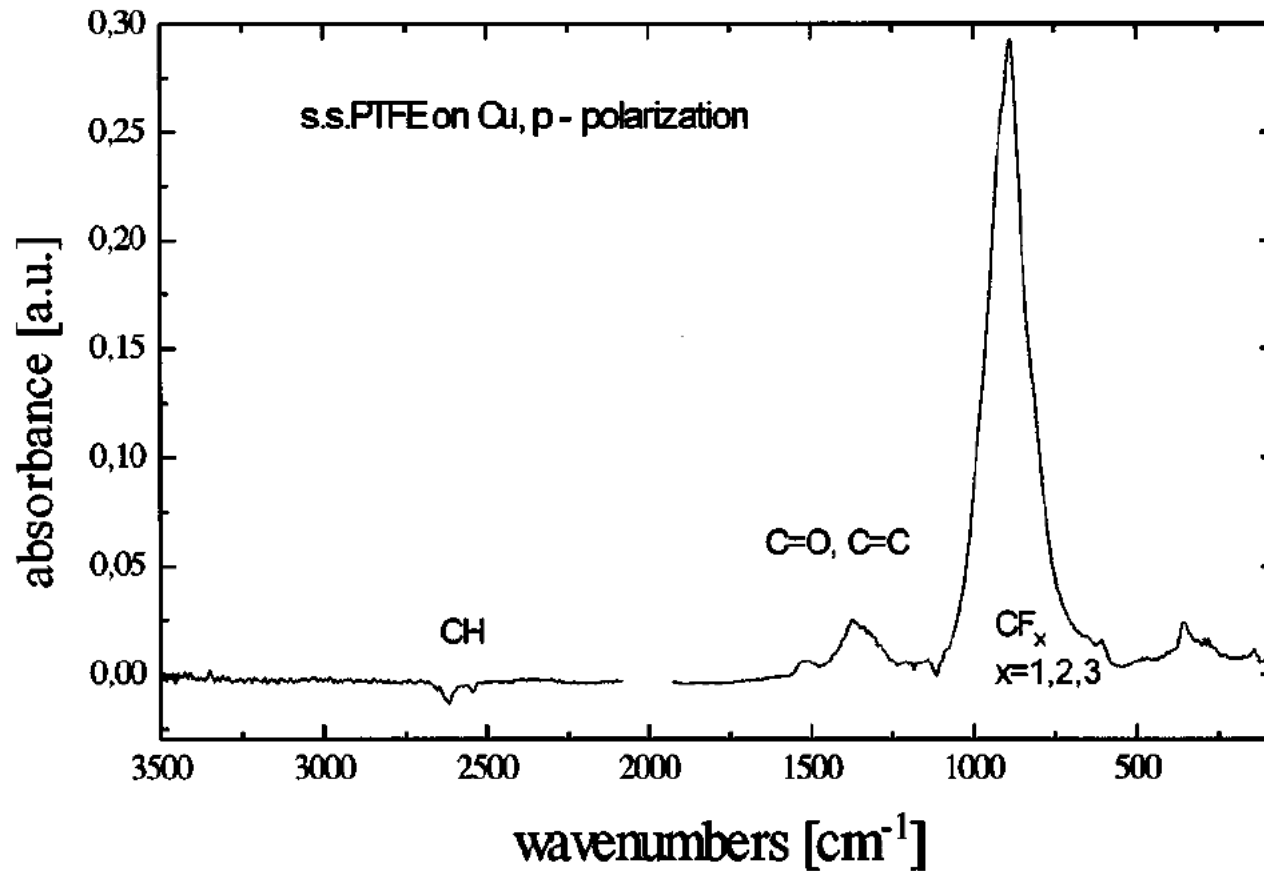
Organic films that can be best described as *fluorocarbon plasma polymers (Teflon-like)* were prepared in the so called self-sputtering mode.

In this case argon was used to initiate the discharge that continued to be maintained by the volatile fragments when the argon supply was shut off.

RF sputtering of PTFE was also performed in argon.

Because sputtered fluorocarbon films were found deficient in fluorine, RF sputtering of PTFE in a CF₄-Ar mixture was used and shown to give stoichiometric films.

FTIR-analysis of PTFE film



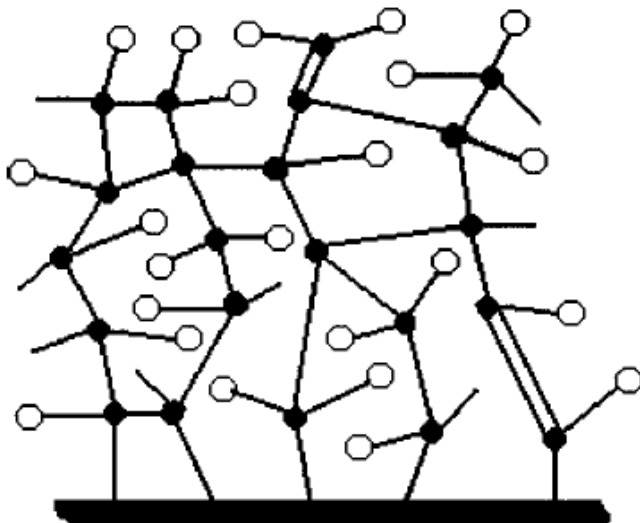
XPS-analysis of PTFE-film

TABLE I. Composition of films of PTFE sputtered in nitrogen (E4) and argon (G1).

Sample	Power (W)	Pressure (Pa)	XPS analysis				F/C
			O (at. %)	C (at. %)	N (at. %)	F (at. %)	
E4 (N ₂)	200	11	5.8	38.1	11.1	44.9	1.18
G1 (Ar)	200	9.2	1.1	44.3	0.7	53.8	1.21

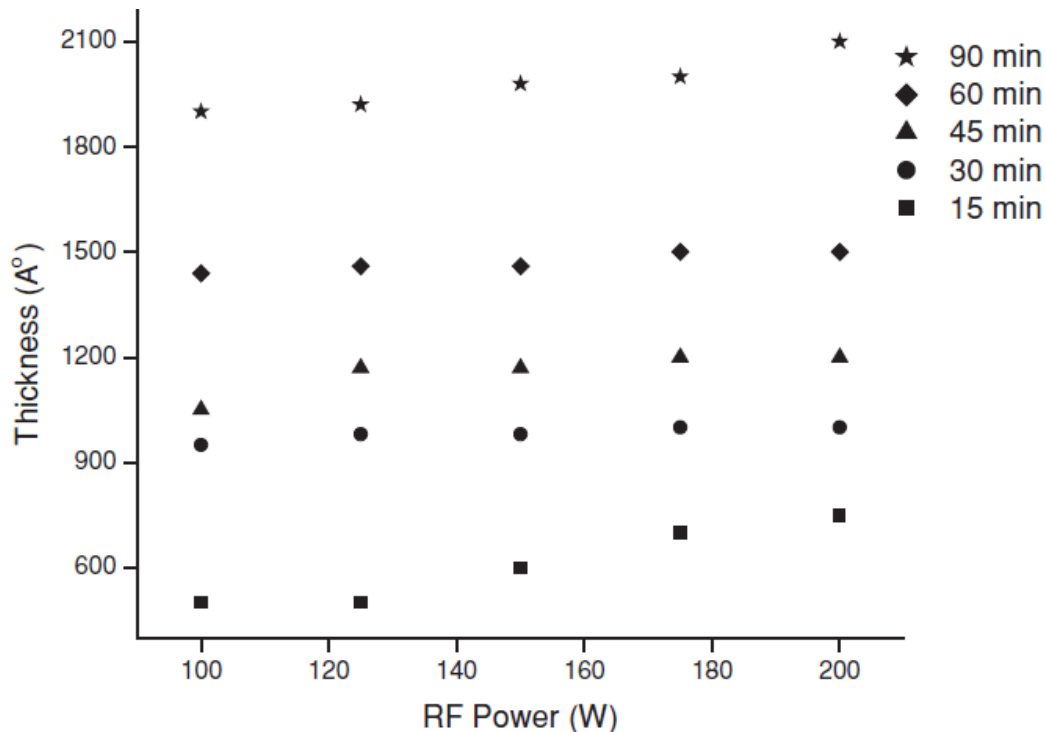
Film structure

- These F-rich fluorocarbon plasma polymer films were stable at 450°C for 4 h.
- Even after 24 h at 450°C no crystalline structures were observed by x-ray diffraction, i.e., the films appeared to be amorphous.



(○) fluorine, (●) carbon

Another PTFE sputter process



Thickness @ 30 min \approx 1000 Å

Thickness @ 90 min \approx 2000 Å

If linear deposition rate \rightarrow should be 3000 Å !

“Negligible increase in thickness beyond a certain time duration may be because of the possible equilibrium established between deposition and etching of the film.”

XPS analysis of PTFE film

Assignment	15 min	45 min	90 min	Bulk PTFE [29]
	(A) Deposition power 200 W			
C1s	285	285	285	285
C–CF	286.6	286.4	286.4	287.3
C–F	289.1	288.6	288.0	289.5
CF ₂	–	–	290.8	292.1
CF ₃	–	–	292.6	294.0
F–C	687.2	687.3	687	687.7
F1s	690.1	690.5	690.4	690
F/C ratio	0.5	0.89	1.2	2

XPS vs. sputtering power

Assignment	100 W	150 W	200 W	Bulk PTFE
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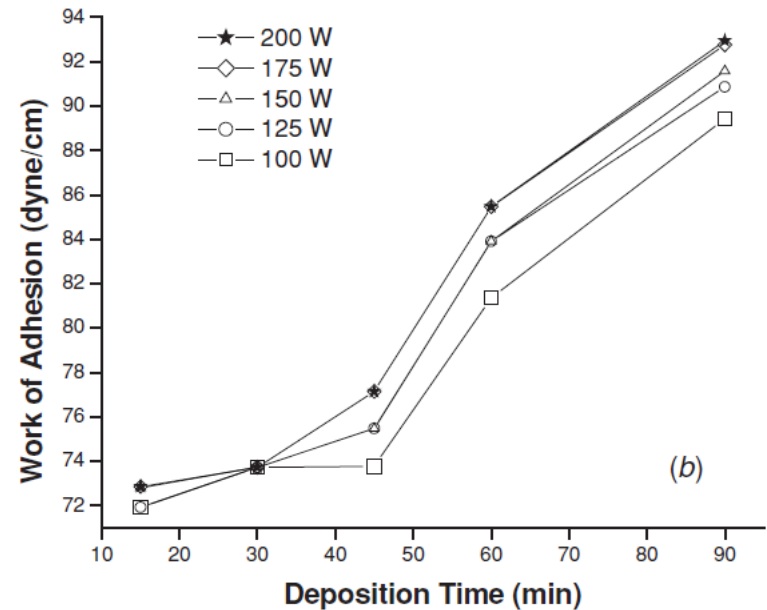
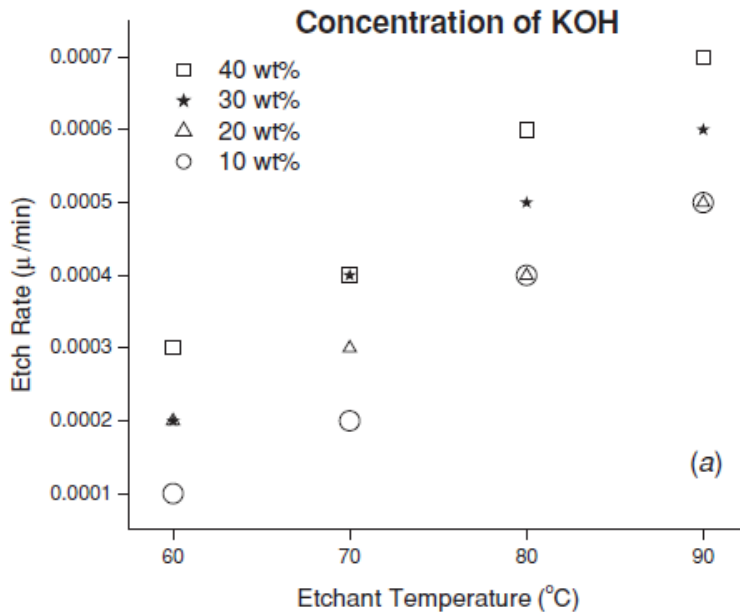
(B) Deposition time 90 min

C1s	285	285	285	285
C-CF	286.6	286.6	286.4	287.3
C-F	288.8	288.3	288.0	289.5
CF ₂	–	–	290.8	292.1
CF ₃	–	–	292.6	294
F-C	687.4	687.6	687	687.7
F1s	690	690.2	690.4	690
F/C ratio	0.51	0.98	1.2	2

Sputtered Teflon as etch mask

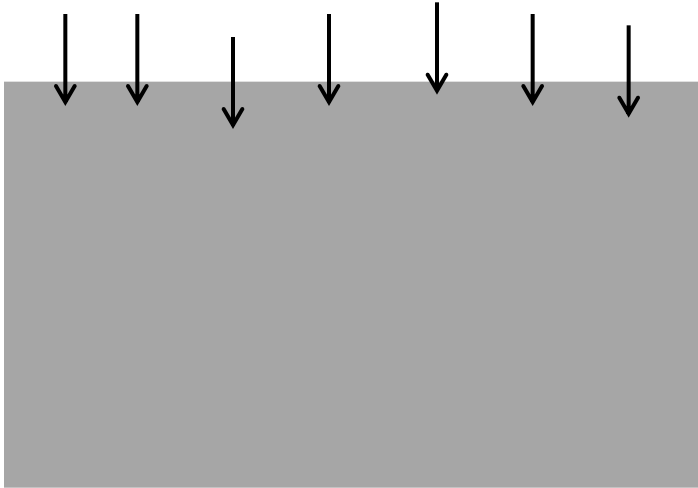
Not attacked by hot KOH

Has good adhesion to Si



Rate Si: rate PTFE =
 $1 \mu\text{m}/\text{min} : 0.0006 \mu\text{m}/\text{min} = 1700:1$

Film effects on substrate

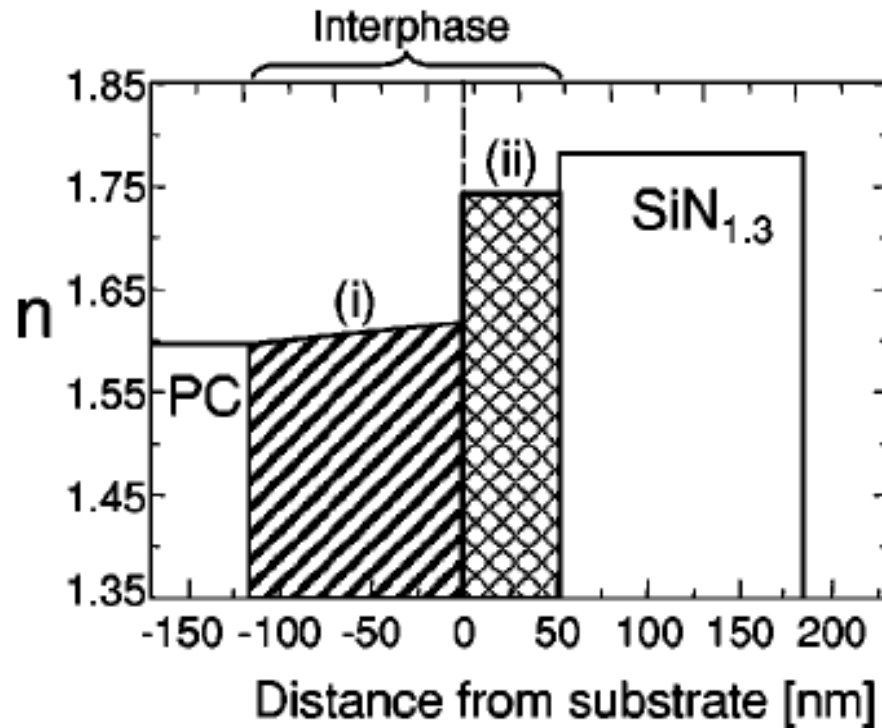


Sputtering (and PECVD and other energetic deposition process) will implant atoms into substrate.

Penetration of sputtered film atoms can be 50 nm in polymers.

This improves adhesion, which is important since polymers do not readily form bonds with deposited metals or ceramics.

Interphase layer on polycarbonate

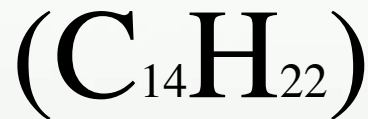
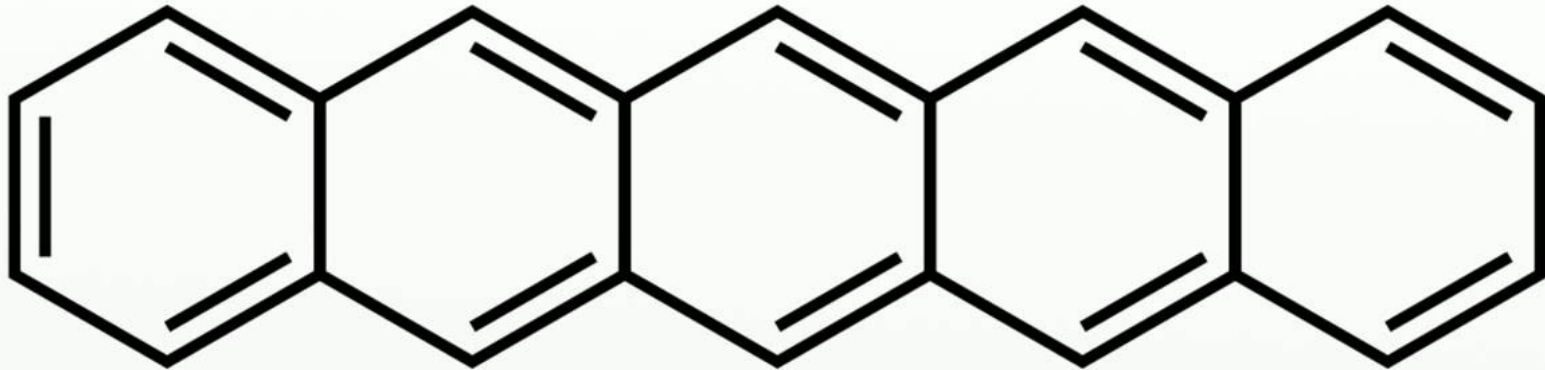


Plasma effects generally:

- a) cleaning
- b) etching
- c) cross linking
- d) functionalization

- (i) plasma pretreatment (cross linked polymer)
- (ii) mixed polymer-nitride material

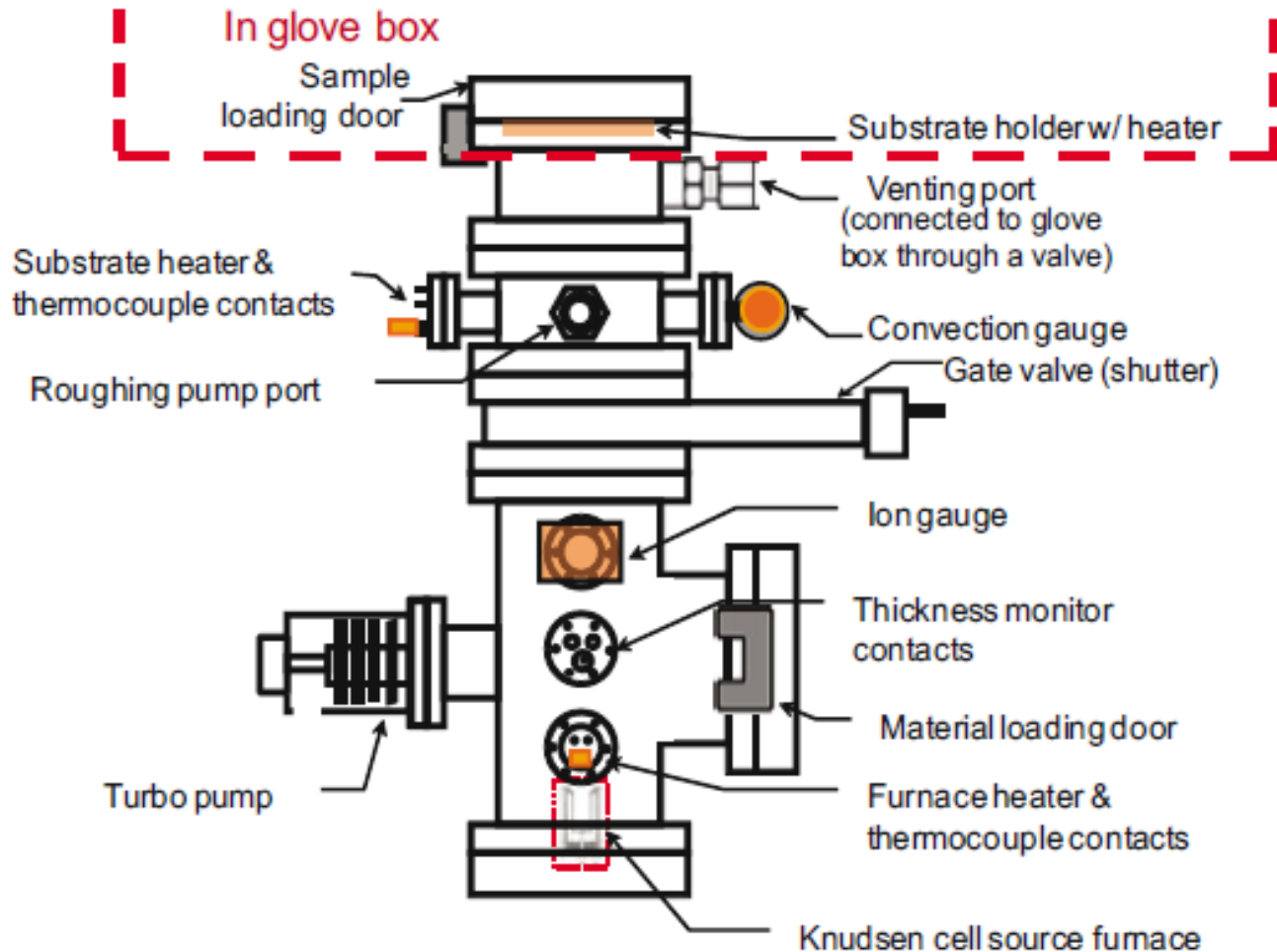
Pentacene



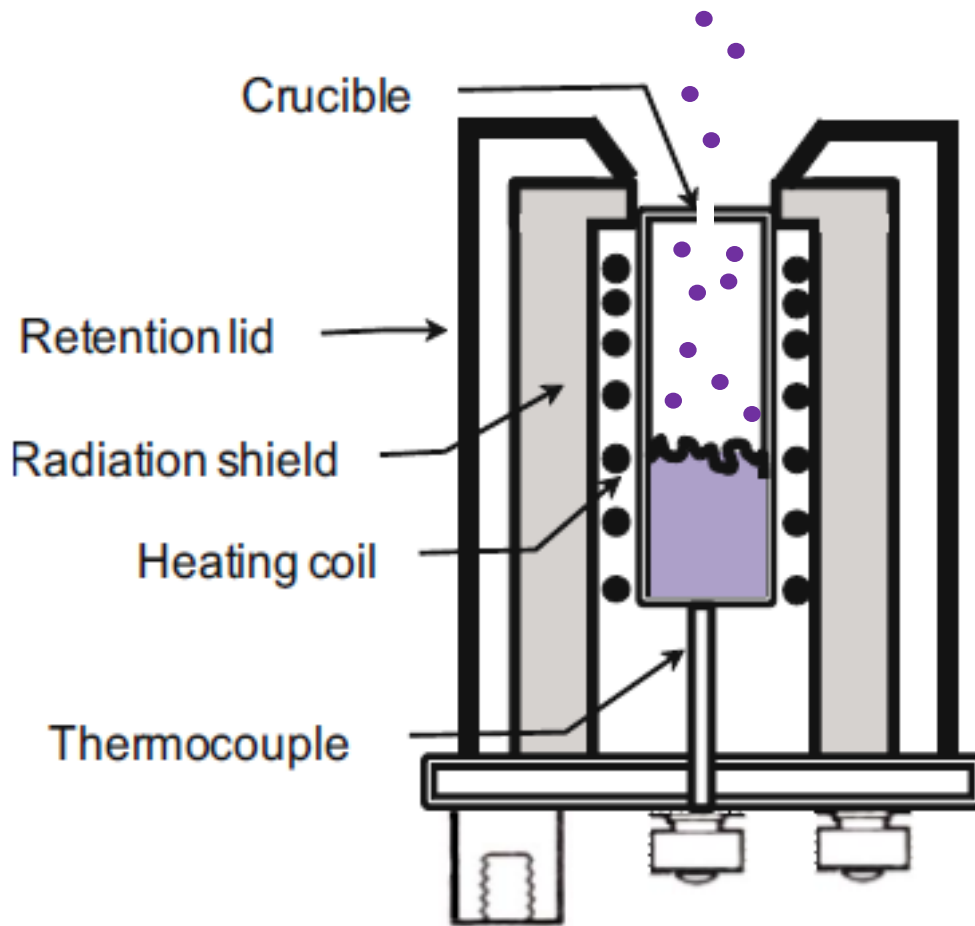
<https://en.wikipedia.org/wiki/File:Pentacene.svg>

Active channel material in
polymer electronics

Evaporator for pentacene



Knudsen cell for pentacene



Knudsen cell is an isothermal enclosure with a small orifice (whereas thermal evaporator has open crucible).

Vapor emerges in a thermal equilibrium process.

Pentacene TFT process



Deposit polyimide

(A)



Lithography
Gold evaporation & lift-off

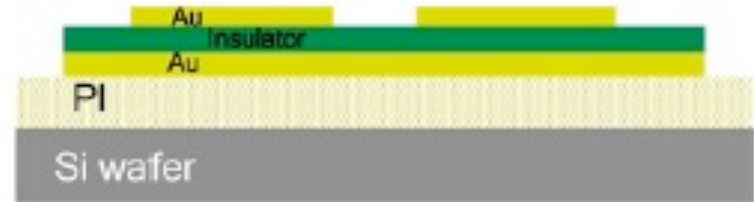
(B)



PECVD oxide (C)



(D) Lithography
Gold evaporation

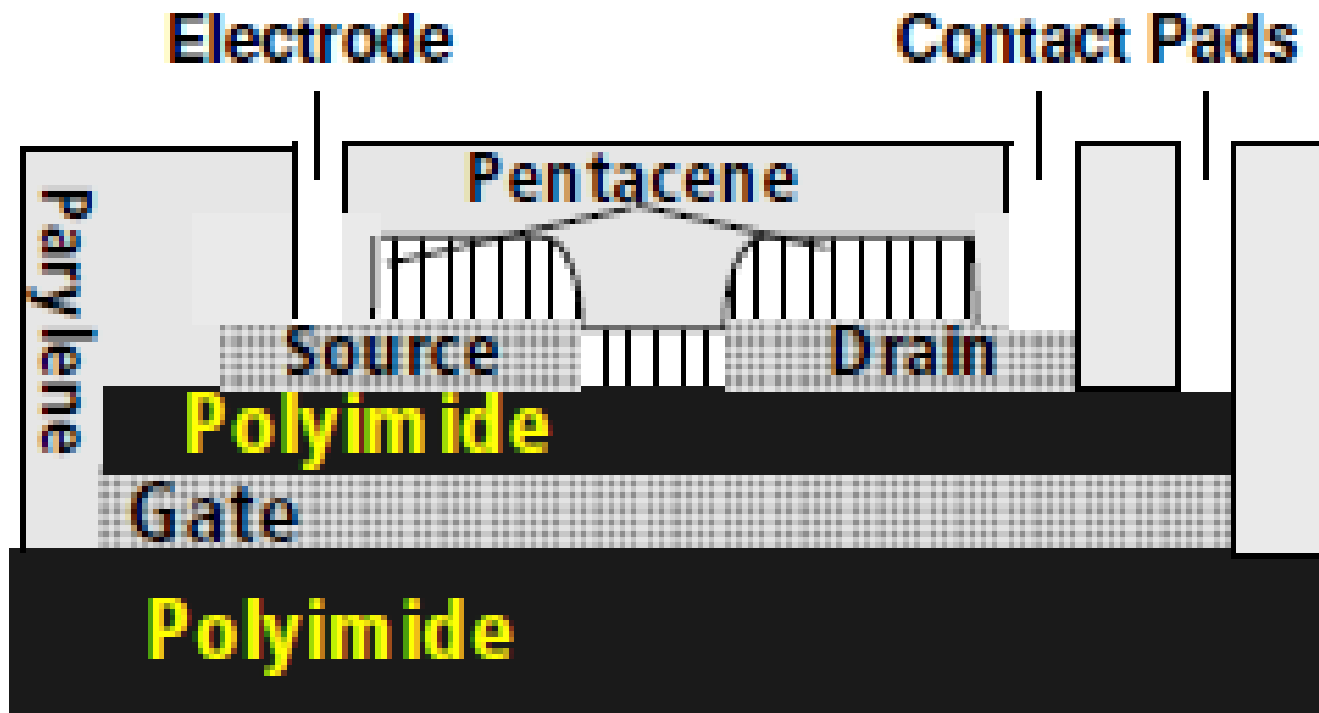


(E) Lift-off

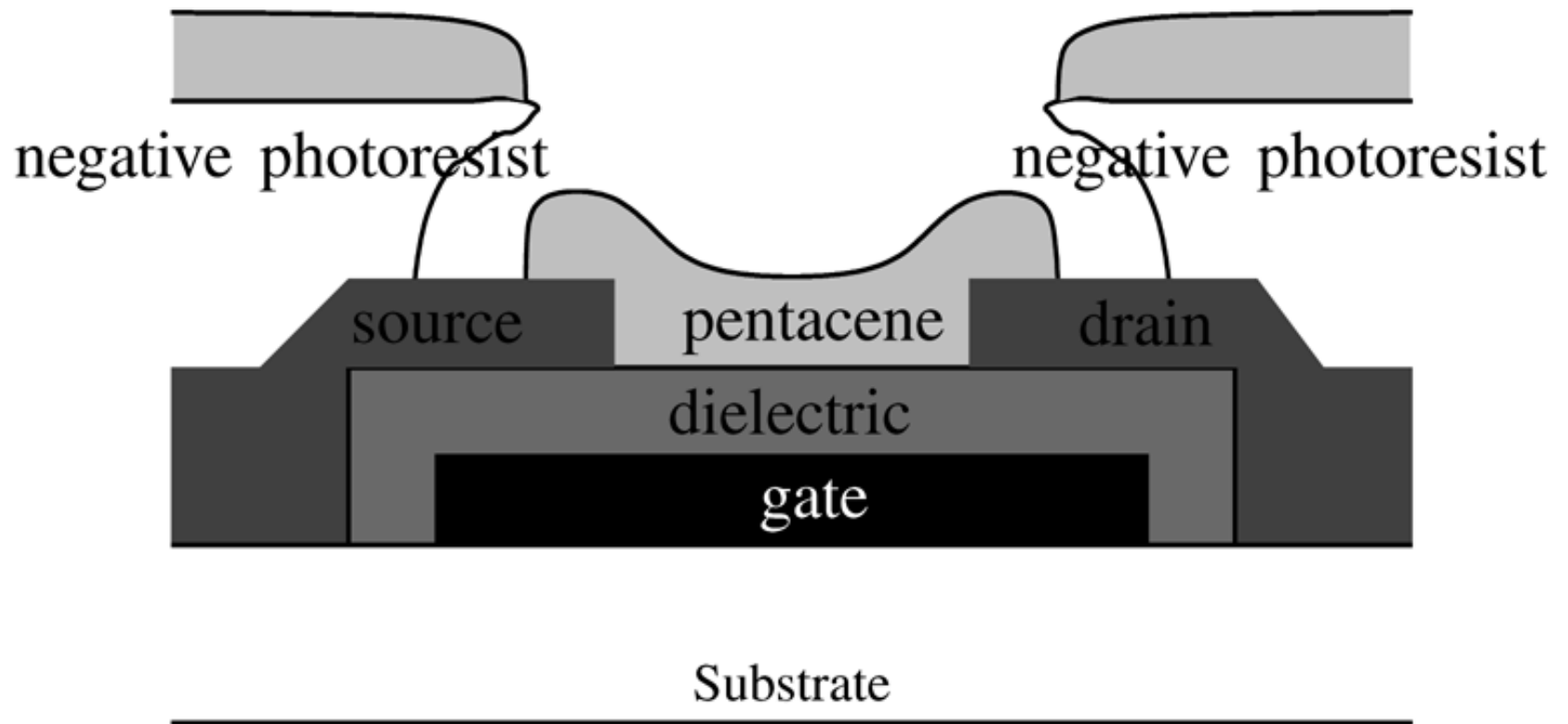


(F) Lithography
Pentacene evaporation
Lift-off

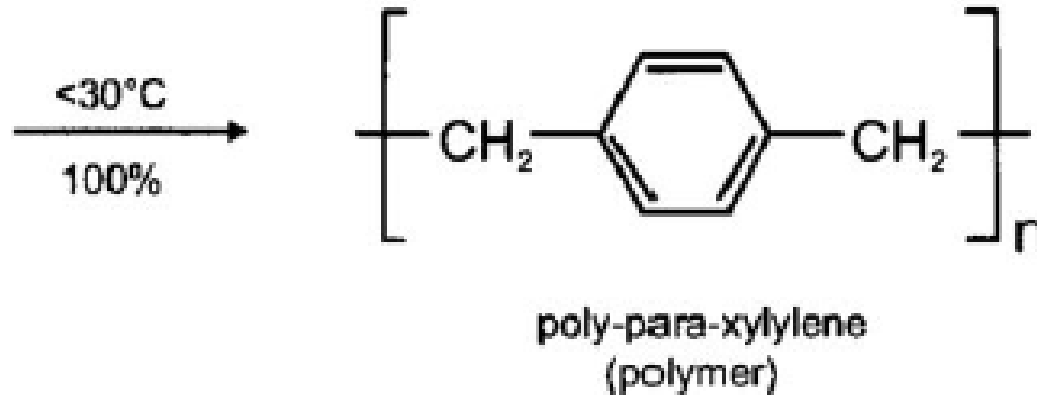
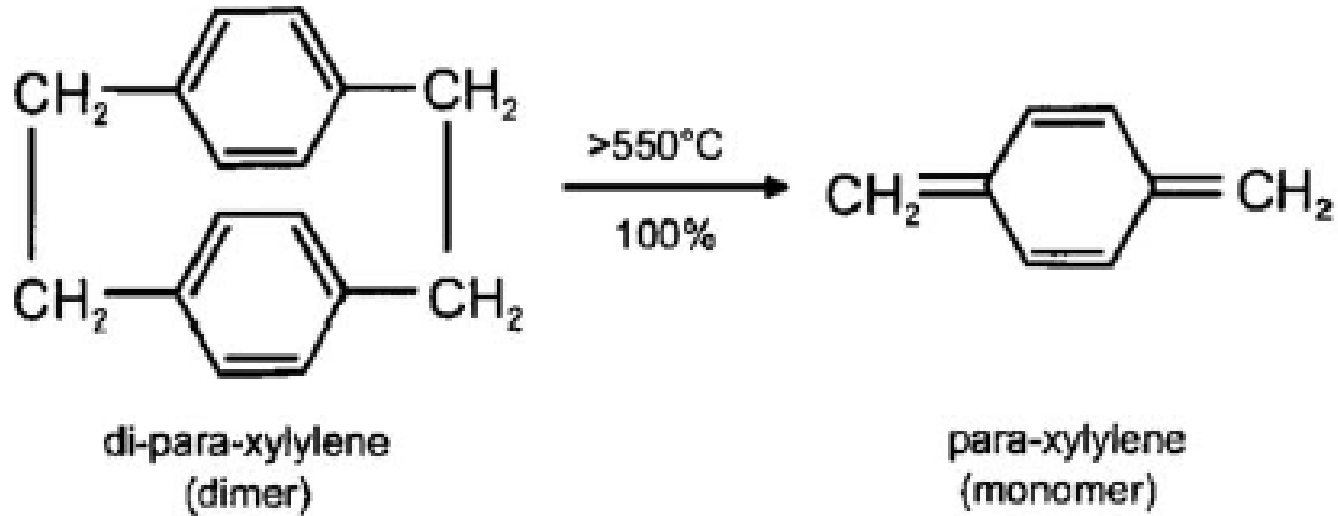
Flexible TFT: parylene passivation, silicon substrate detachment

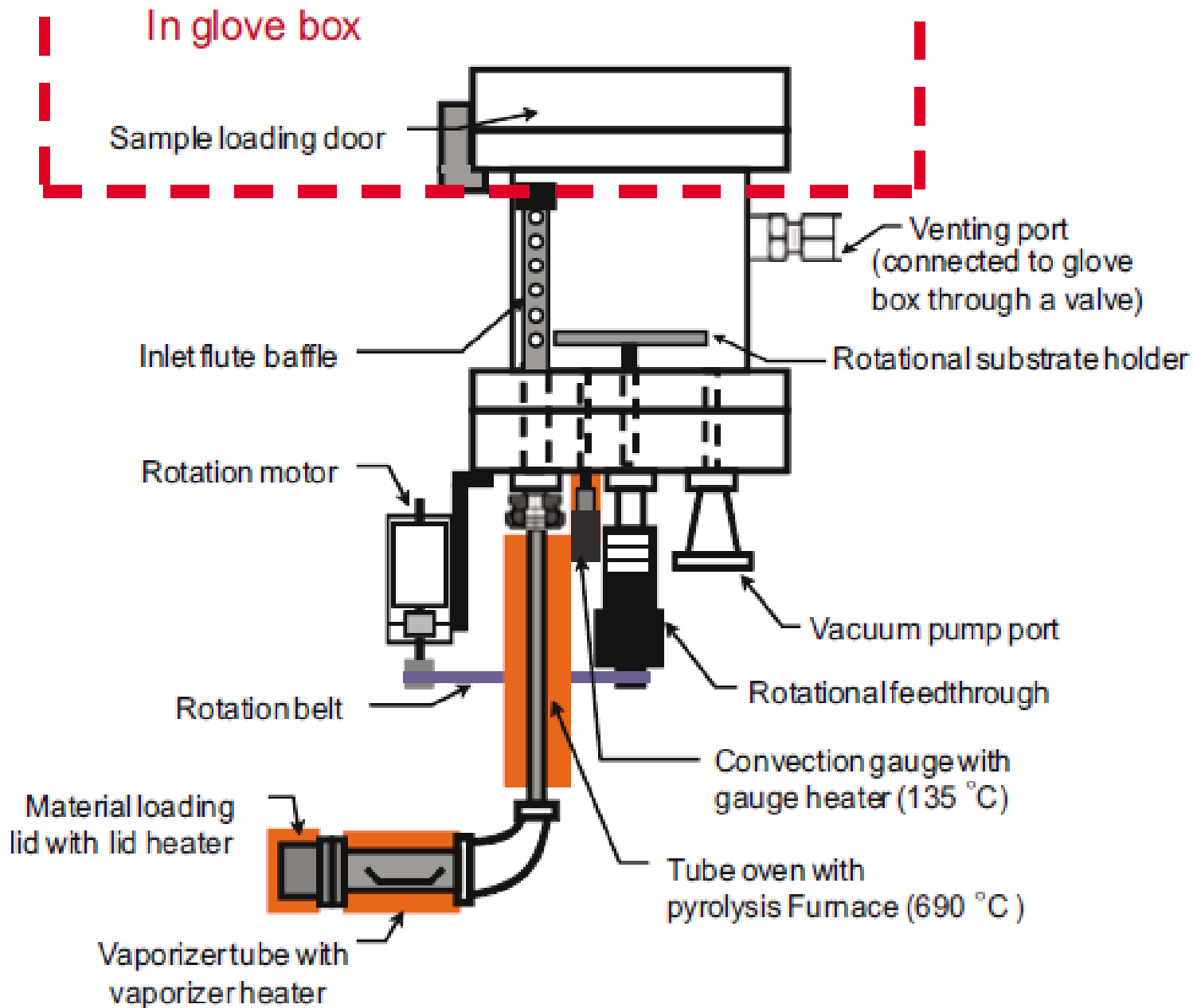


Evaporation good for lift-off



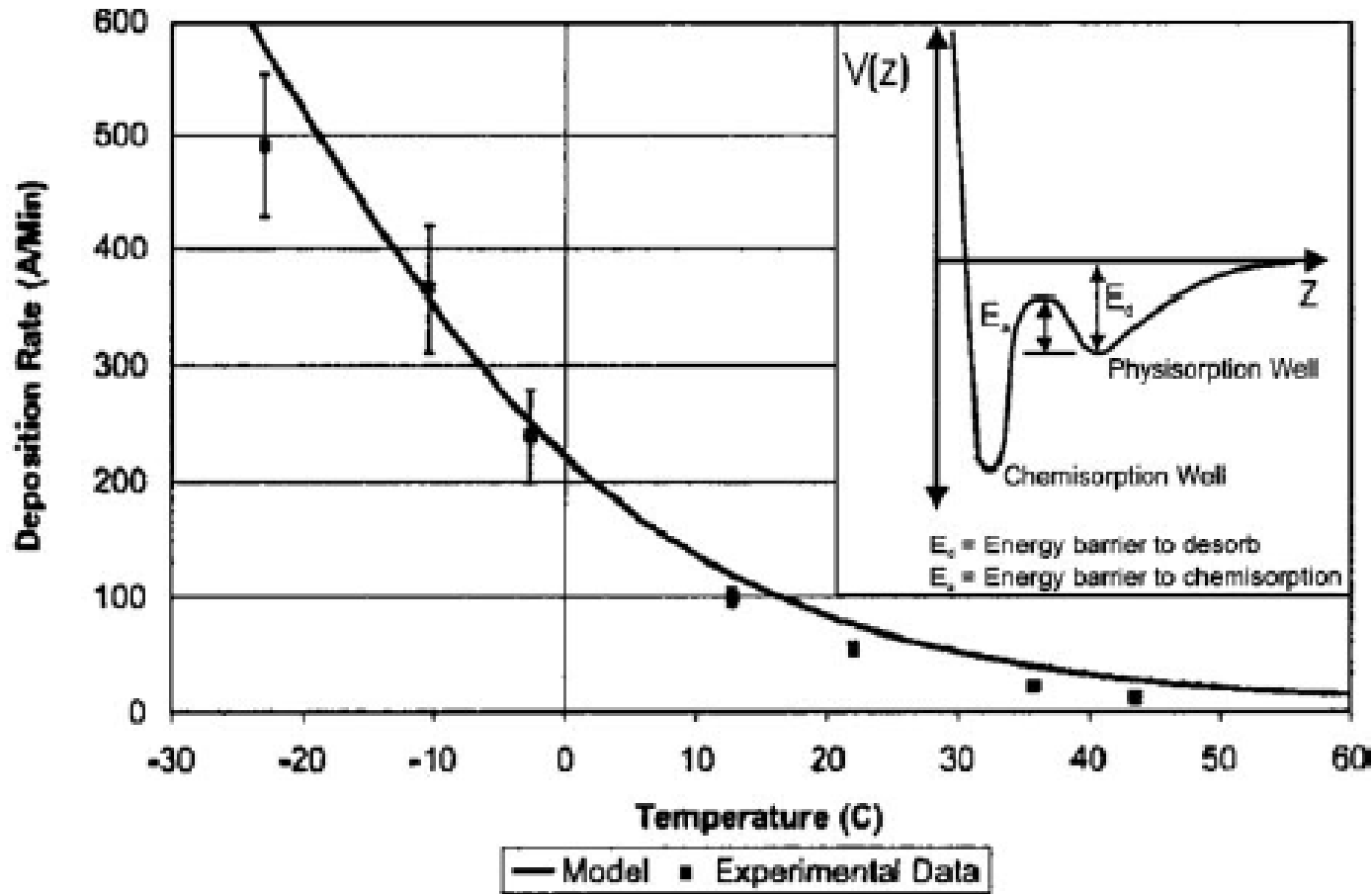
Parylene CVD





Jia *et al.*: Laboratory pentacene and parylene evaporation systems

Parylene CVD: rate up when temperature down ! Not Arrhenius!



Jia *et al.*: Laboratory pentacene and parylene evaporation systems

Rate limiting step

This apparent negative activation energy is the signature that surface adsorption of a reactive species is the rate-limiting step.

In the adsorption-limited regime, increased substrate temperature reduces adsorption onto the surface, leading to lower deposition rates, but often thickness uniformity is improved.

Sticking coefficient

Reactive sticking coefficient (g), is defined as the probability of a precursor species adsorbing/reacting each time it strikes the surface.

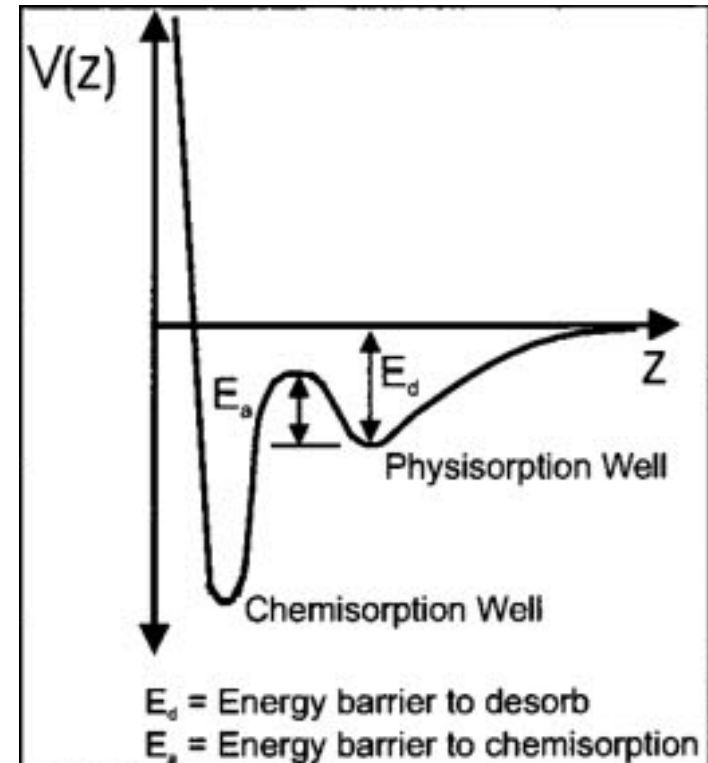
As g increases, species increasingly stick to the surface on impact, leading to a faster deposition at the trench opening and poor step coverage.

Conversely, low values of g lead to multiple collisions before sticking, allowing for deposition deep inside high aspect ratio features.

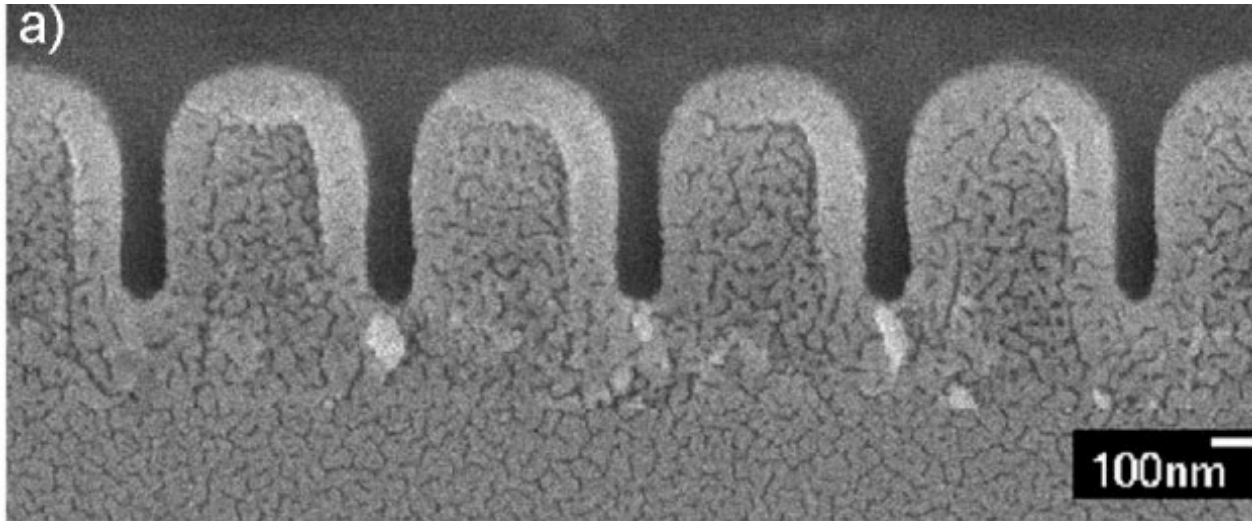
Parylene step coverage: excellent

Monomer first physisorbs and chemisorbs only after overcoming an energy barrier.

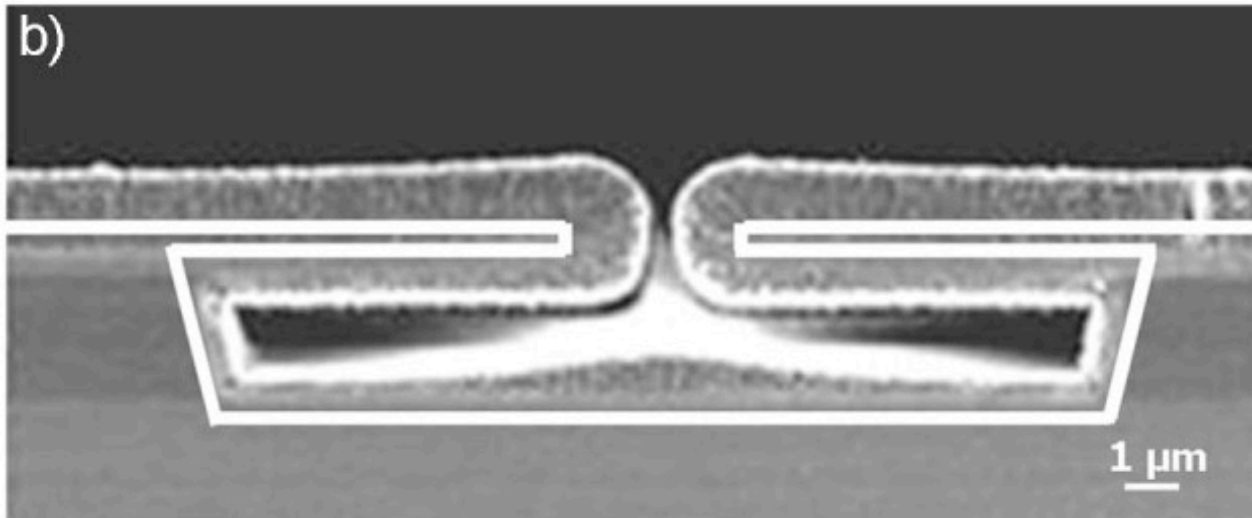
For the chemisorbed monomer, sticking coefficient was $2.0 \cdot 10^{-5}$ at 60°C and increased to $1.4 \cdot 10^{-3}$ at -60°C .



CVD polymer step coverage



300nm deep trench
conformally coated with
poly(p-xylylene)
(parlyene)



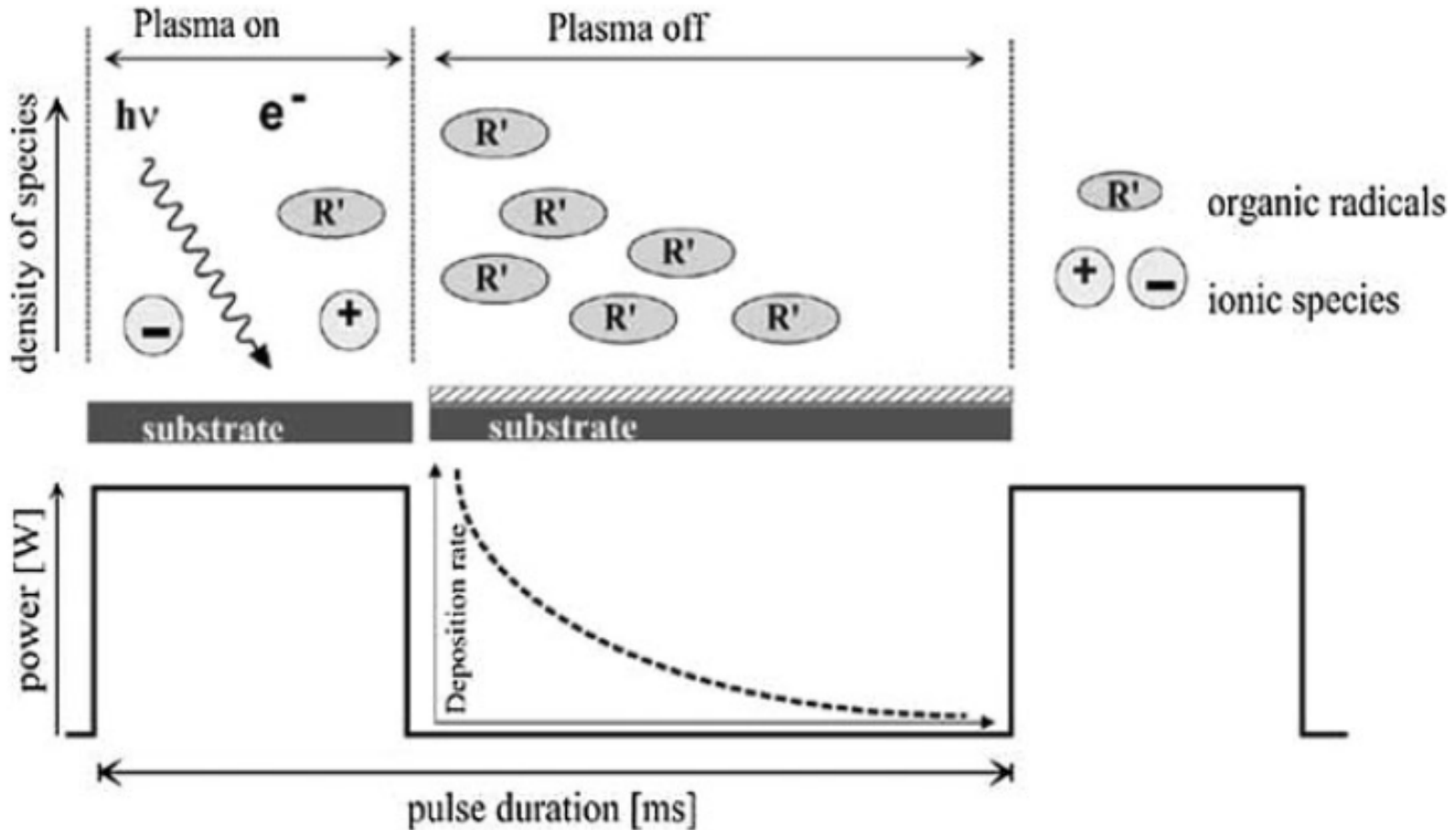
iCVD
poly(tetrafluoroethylene)
(PTFE)

Polymer surface activation

- Organic substrates can be chemically activated using a plasma glow discharge.
- This activation generates free-radical species on the substrate that can initiate polymerization when contacted with gas-phase polymer precursors.
- Alternatively, inorganic substrates can be chemically activated using a piranha solution or oxygen plasma pretreatment to create a high density of surface hydroxyl groups.

PECVD

- In PECVD, plasma excitation of the vapor phase creates the radical species.[11]
- However, the degree to which organic functionality is preserved often improves by decreasing the plasma power through strategies such as
 - pulsing the plasma excitation[12–20] or
 - performing the deposition downstream of the active plasma region



Too long and/or high energy pulses destroy polymer functionality

Hydrogels by PECVD

Hydrogel poly(2-hydroxyethyl methacrylate) (PHEMA) was deposited by pulsed PECVD

while preserving the functionality and biocompatibility of the film.

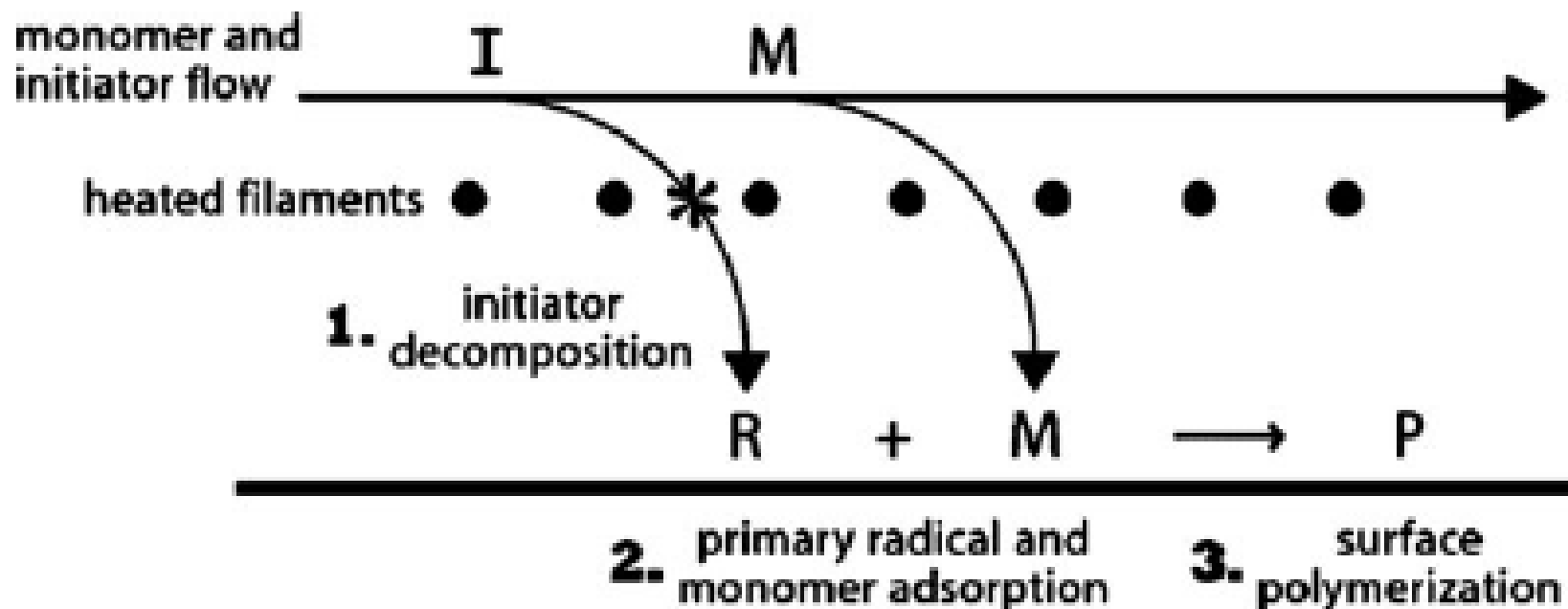
Approximately 80% retention of the surface hydroxyl groups, resulting in a sessile drop contact angle of 17°

at a deposition rate of 13.4nm/min

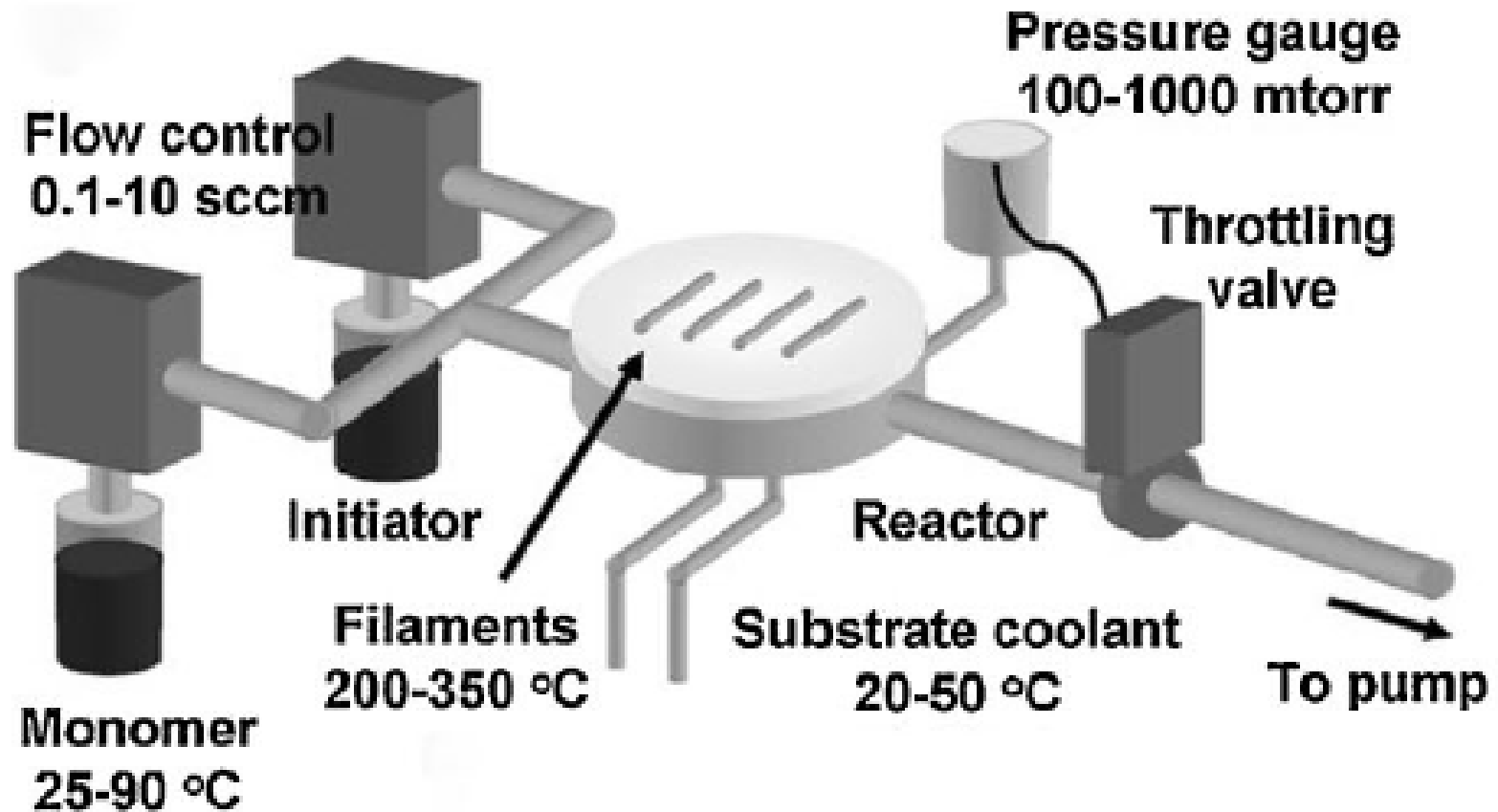
Dangling bonds

- if these species are not fully reacted during CVD growth, the resultant polymer film contains so-called dangling bond defects.
- Once exposed to the air, these defects can further react with oxygen and water, altering the film properties from their as-deposited state.

iCVD (initiator CVD)



iCVD reactor



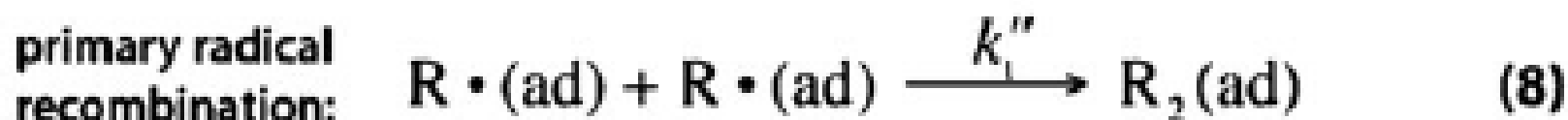
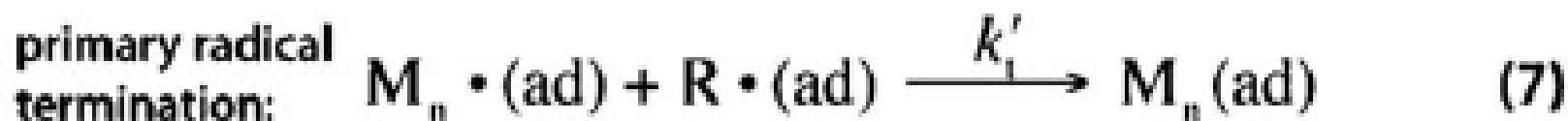
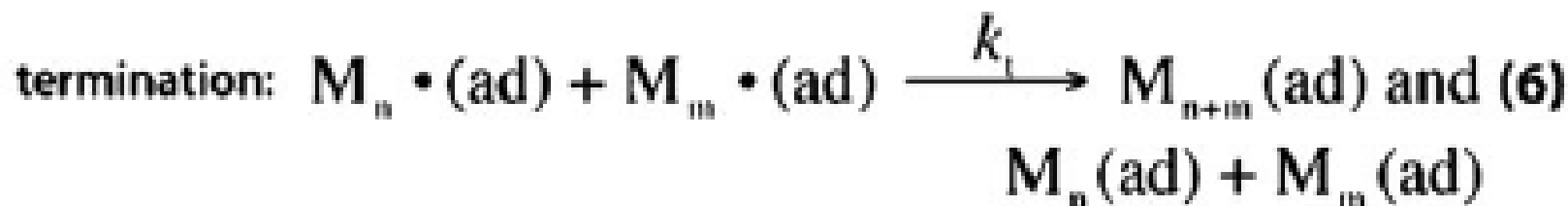
gas phase reactions



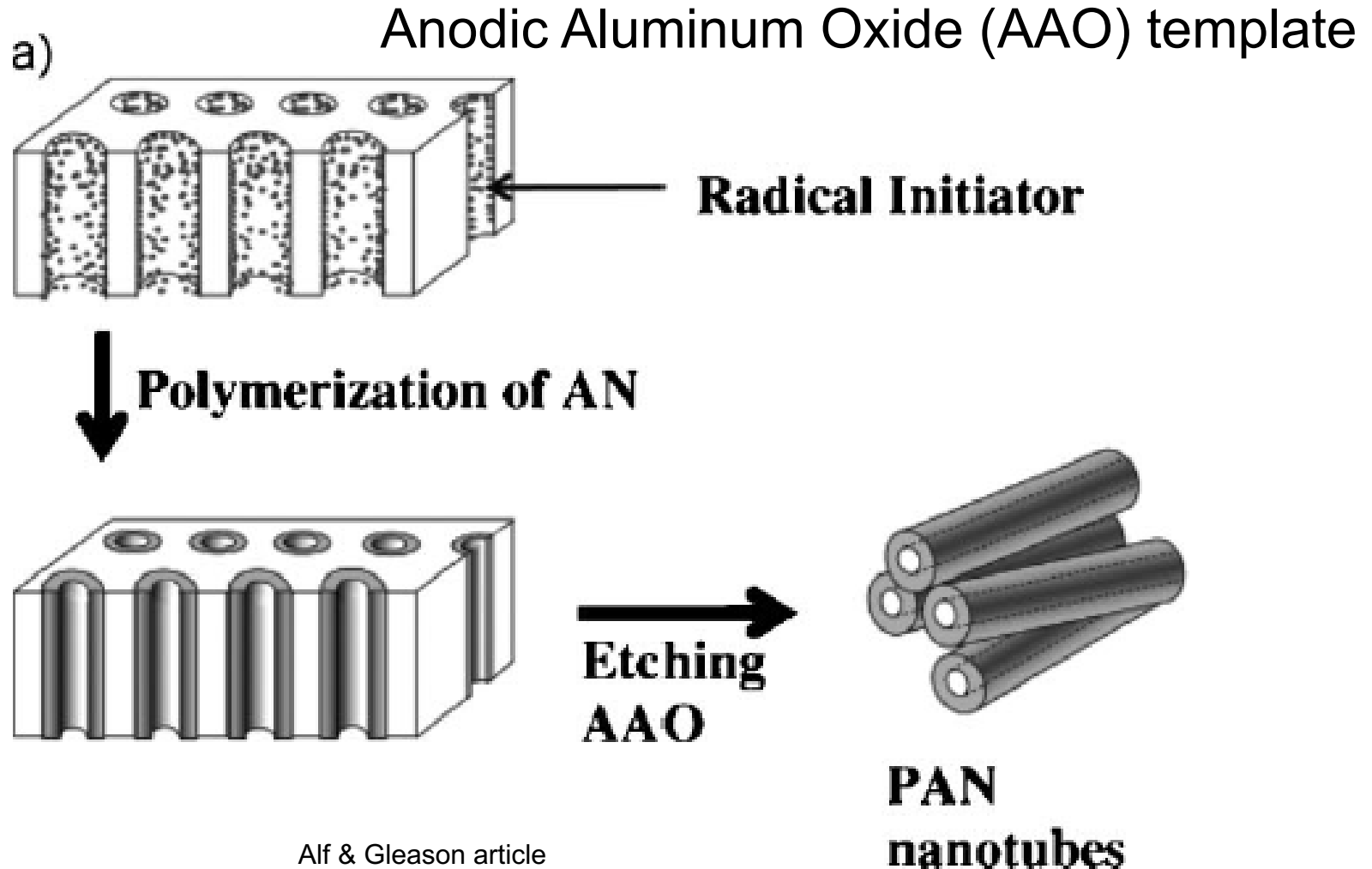
gas-to-surface processes



surface reactions



PAN nanotubes



Rate limiting step iCVD

Filament temperature strongly influences deposition rate.

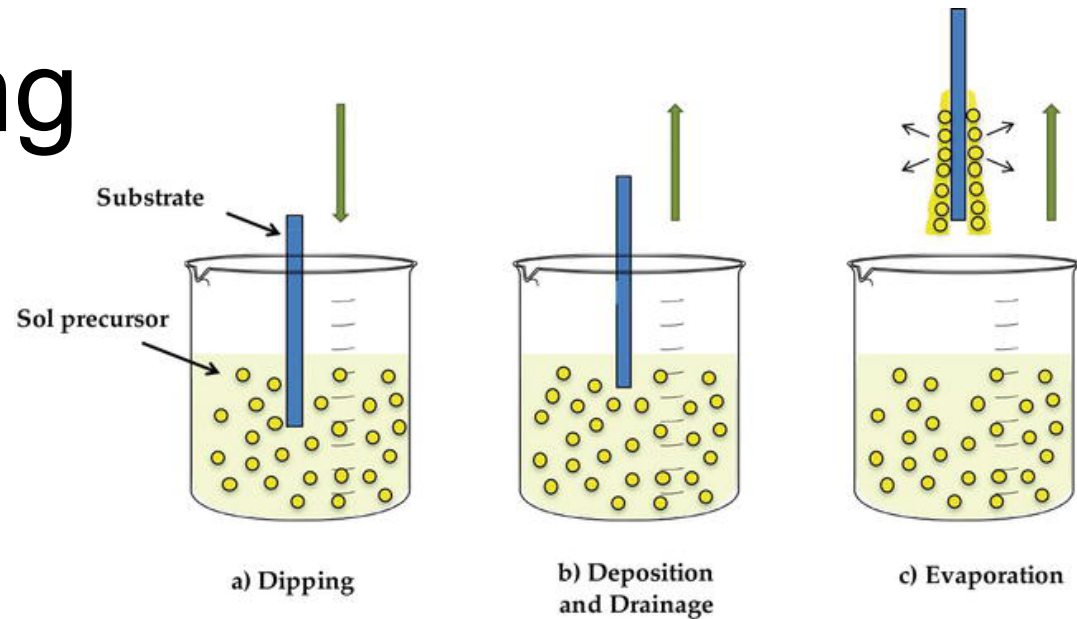
At low filament temperatures, the radical formation from the initiator is the rate-limiting step.

At higher filament temperatures, there is a weaker dependence between decomposition rate and filament temperature, suggesting that mass transport of the radical species to the surface becomes the rate-limiting mechanism.

Organic thin films: wet deposition techniques

- Dip coating
- Langmuir-Blodgett films
- layer-by-layer assembly
- spin coating

Dip coating

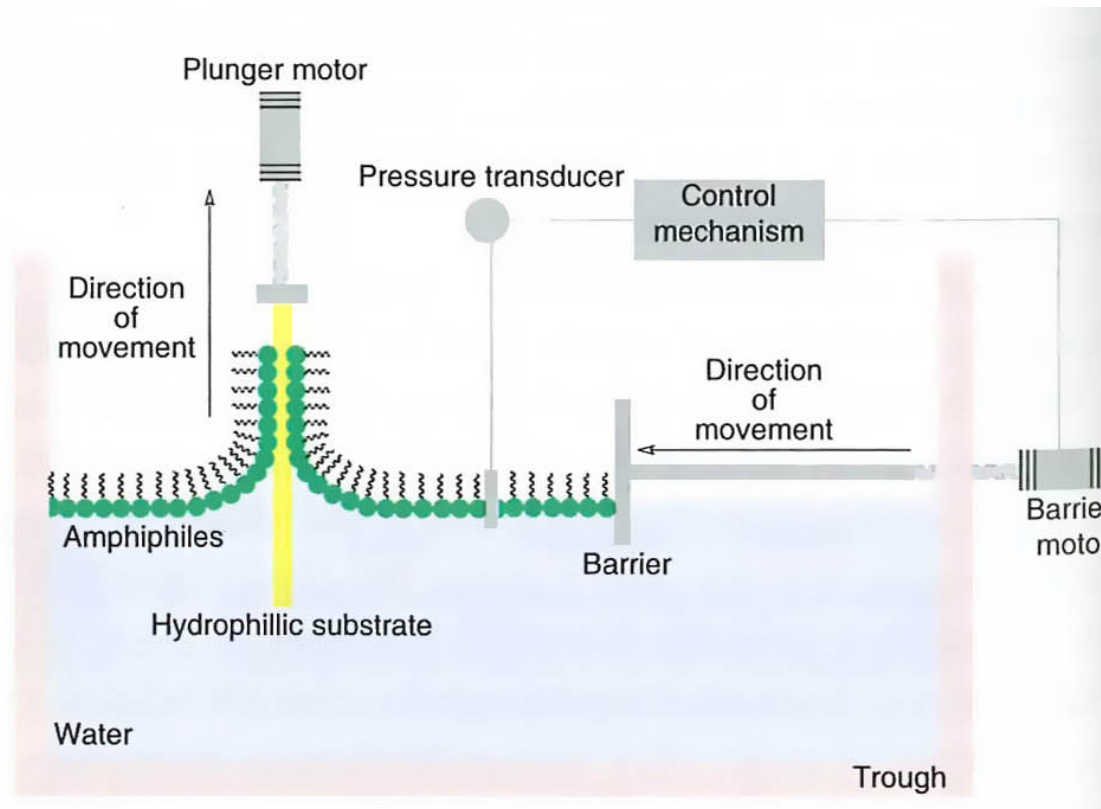


- Dippings of the substrates (glass, silica wafer etc) into liquid that contains organic molecules or sol-precursors
 - One dipping: one layer
 - More dippings: more layers
- Two-dimensional nanometer thickness films

Ana Isabel Gómez Varela et al:

Sol-Gel Glass Coating Synthesis for Different Applications: Active Gradient-Index Materials, Microlens Arrays and Biocompatible Channels, Intech Open 2017

Langmuir-Blodgett: advanced dip coating



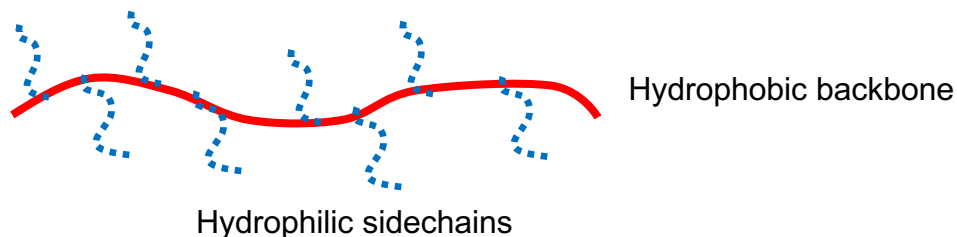
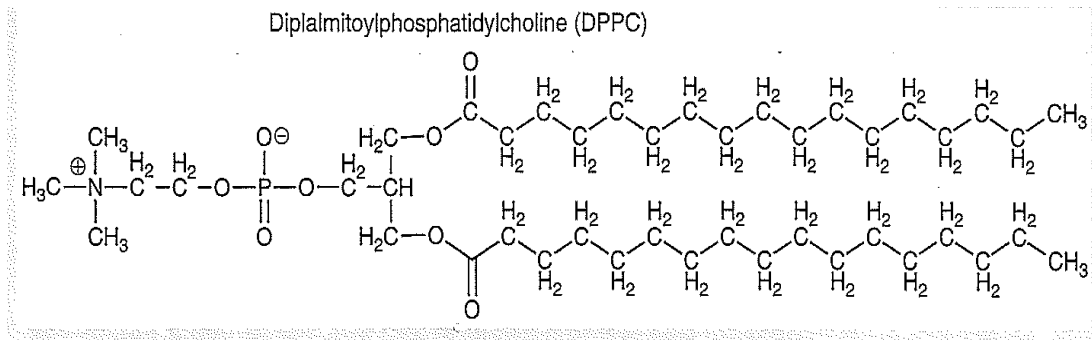
Amphiphilic molecules organize at water-air interface.

Pressure control.

Motorized lowering and raising.

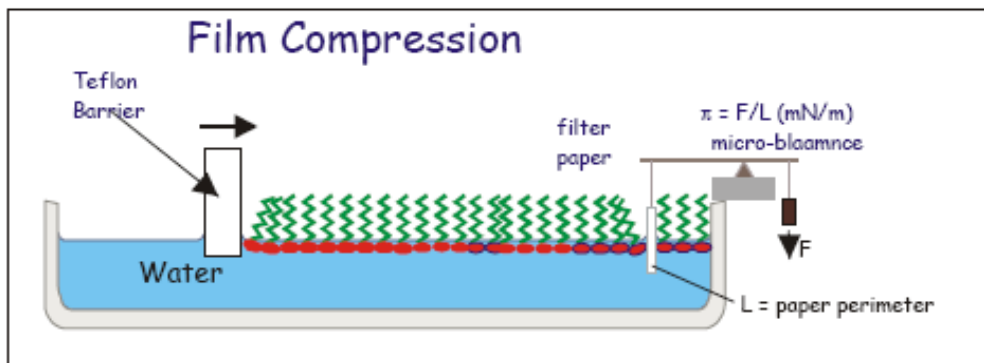
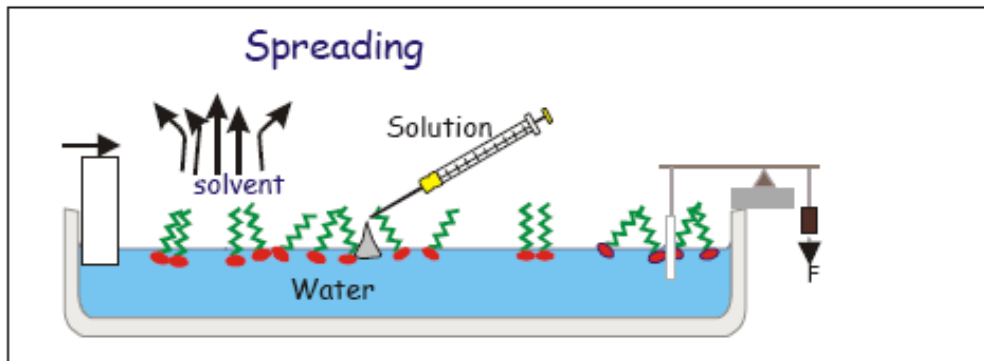
LB films (2)

- To form the film on the water surface, the molecules need to be surface active, i.e. they have both hydrophobic and hydrophilic parts
- For example hydrophobic polymers to have hydrophilic side chains etc.

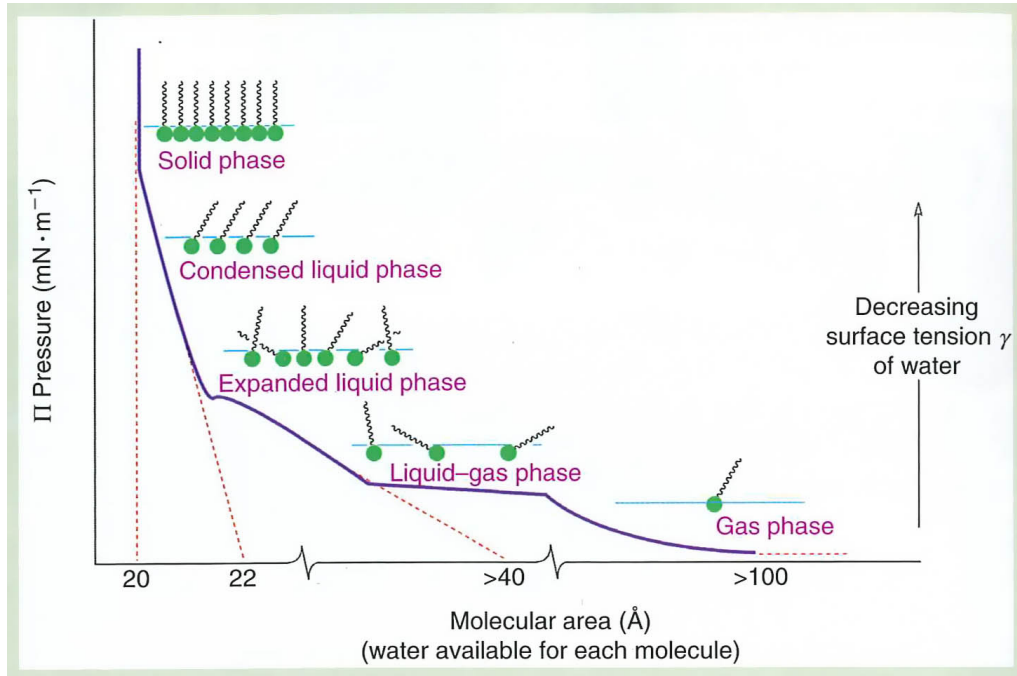


Langmuir-Blodgett through

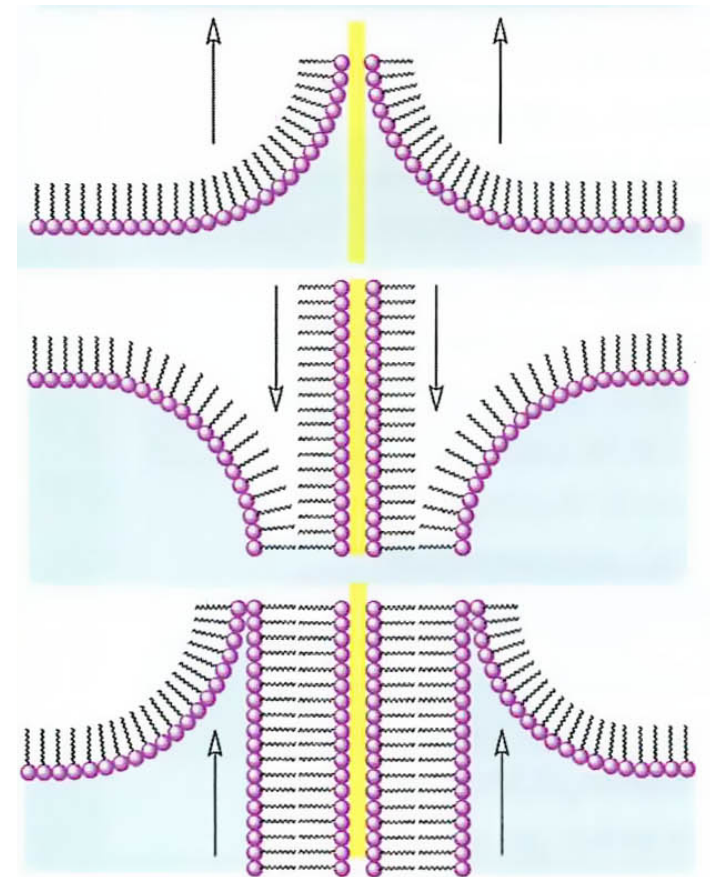
- Langmuir-Blodgett technique is based on formation of "floating" film on water, its compaction by "squeezing" to make densified 2-dimensional solid-like film on water surface, and its transfer on a substrate



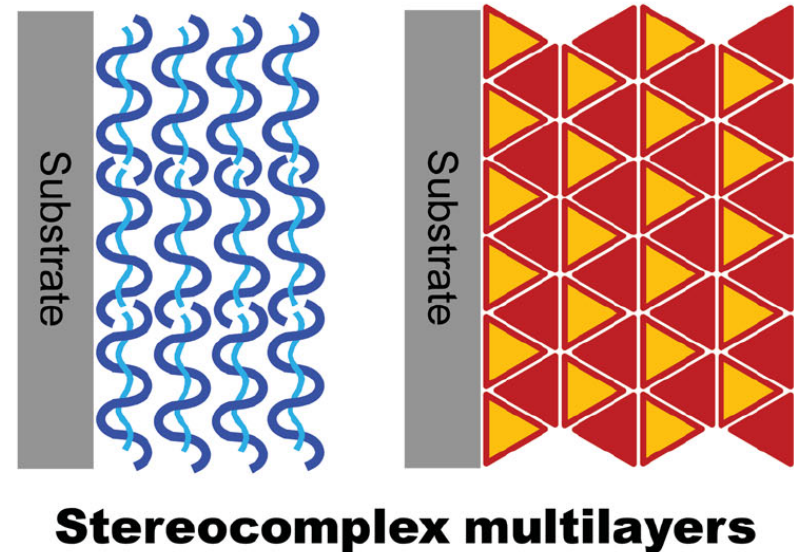
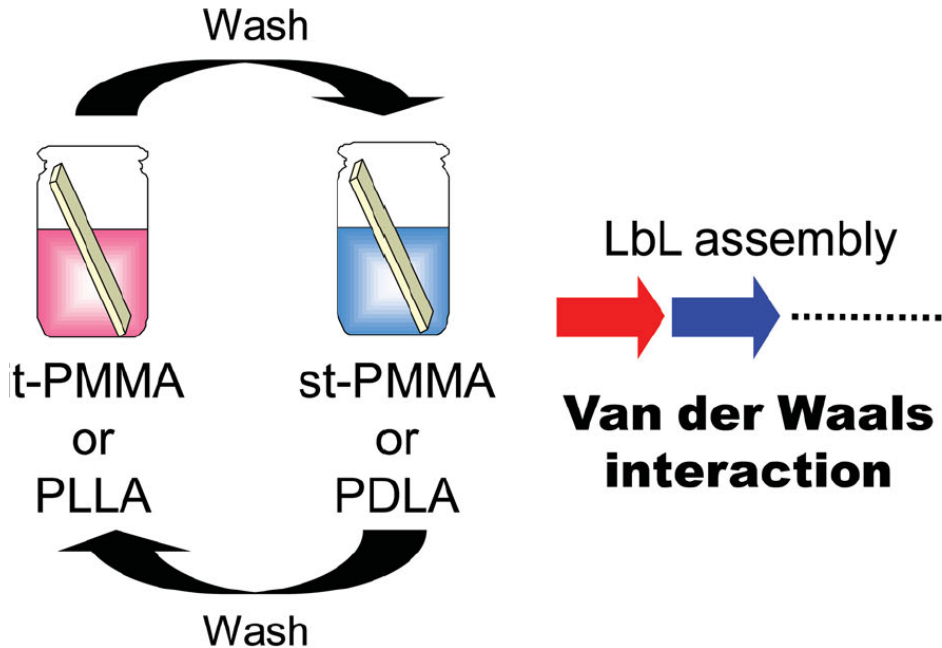
LB: Pressurization curve



Multiple layers

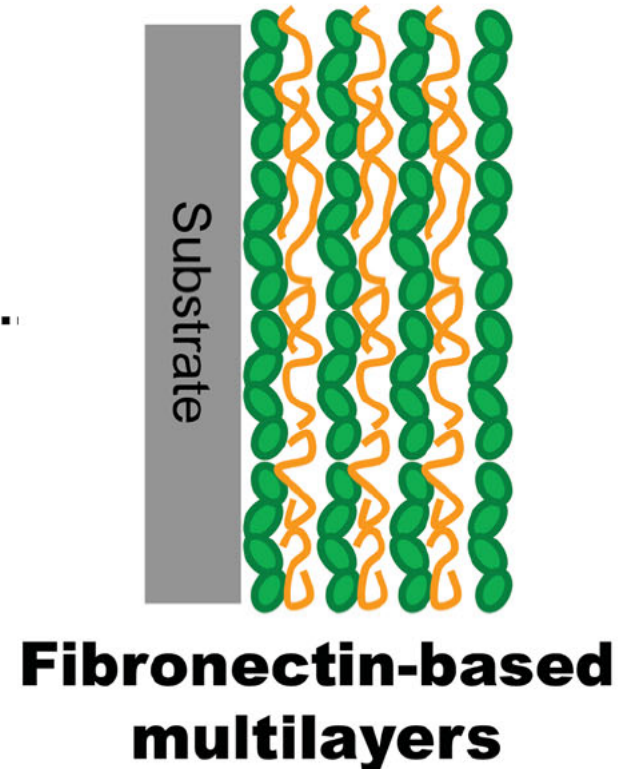
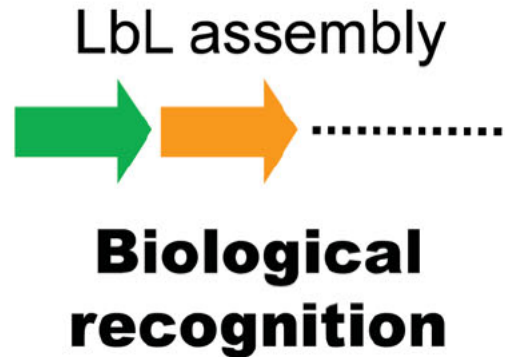
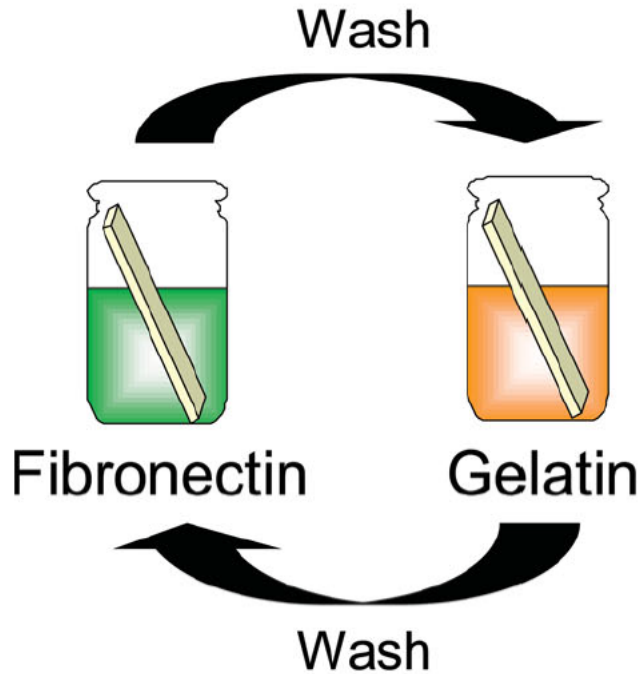


Polyelectrolytes/Layer-by-layer

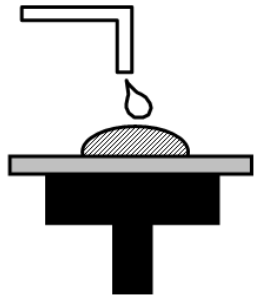


These films are random,
while LB films are highly
organized.

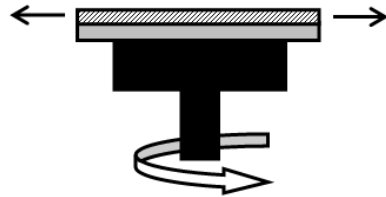
Polyelectrolytes (LbL 2)



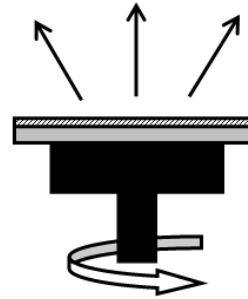
Spin coating



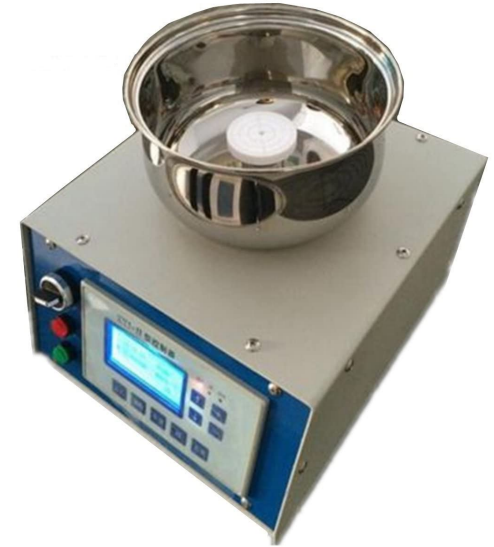
Polymer dispensing
(a few milliliters)



Acceleration
(liquid expelled)



Final spinning 5000 rpm
(partial drying via evaporation)



Film thickness is largely a balance between the force applied to shear the fluid towards the edge of the substrate and the drying rate which affects the solids content and thus viscosity.

As the film dries, the viscosity increases until the radial force of the spin process can no longer appreciably move the liquid over the surface.

Thickness in spin coating

The two main factors affecting film thickness are:

- viscosity η (which depends on solid content and solvent)
- spinning speed ω (faster \rightarrow thinner)

$$t \propto \sqrt{\frac{\eta}{\omega}}$$

Spin speed can be used to tailor thickness over one decade, e.g. 0.5-5 μm , but beyond that a new formulation with different viscosity must be used.

Viscosity is dependent on solid content (which can vary from 20-80%) and temperature.

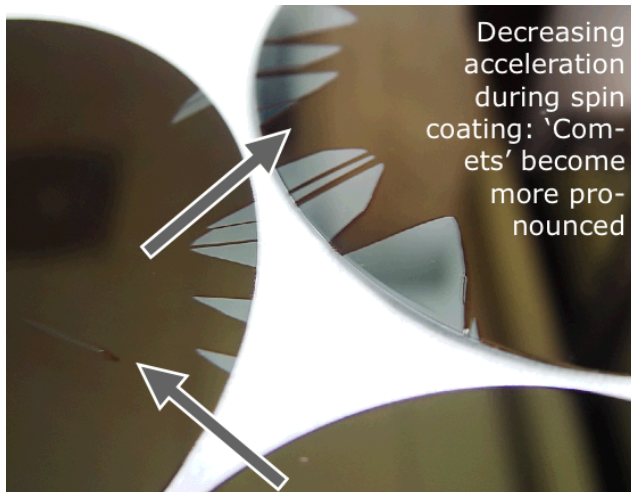
Solvent evaporation rate depends on ambient environment, and a closed spinner bowl with saturated solvent vapor and adjustable exhaust from spinner bowl can both be used to control evaporation.

Spin coating pros and cons

- short coating time (< 1 min)
- reliable
- cheap
- uniform film thickness in case of Newtonian liquids (=viscosity remains constant with shear rate)
- Various film thicknesses possible (0.1 μm to 500 μm)
- always requires baking step afterwards



Topography on surface \rightarrow non-uniform film thickness because liquid-like resist partly conforms and partly tries to flatten out.



Particles can become “sources” of defects: liquid does not spread evenly behind an obstacle.