Vékonyrétegek előállítása és alkalmazásai

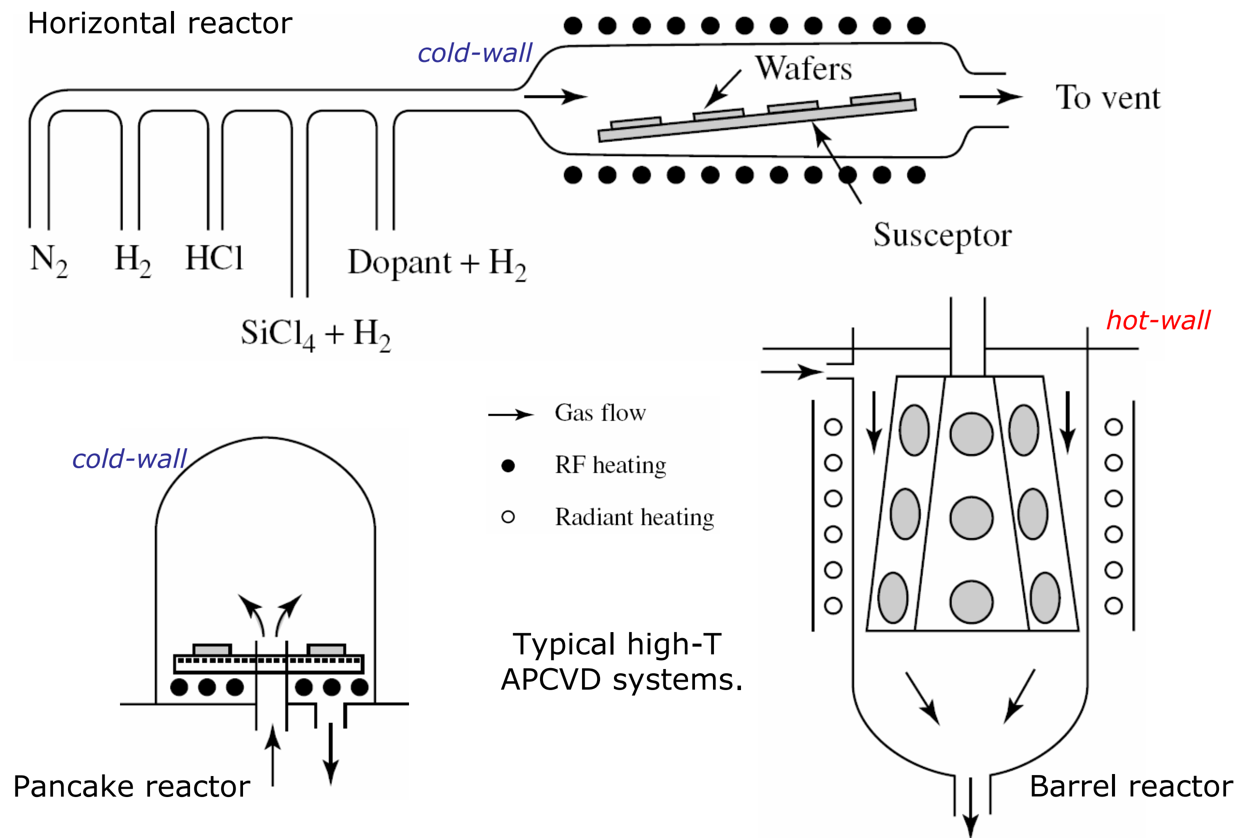
2010. november 22.

Dr. Geretovszky Zsolt

Major types of CVD

- *Atmospheric Pressure CVD* (APCVD)
- *Low Pressure CVD* (LPCVD)
- *Plasma Assisted/Enhanced CVD* (PACVD, PECVD)
- *PhotoChemical Vapor Deposition* (PCVD)
- *Laser assisted/enhanced CVD* (LCVD)
- *MetalOrganic Chemical Vapor Deposition* (MOCVD)

Thermal CVD reactors



LPCVD

Significant development in semiconductor device processing.
P<1 atm

In order to compensate for reduced pressure the concentration of reactants is enriched.

D and δ depends on pressure. An order of magnitude increase in J is typical.

Benefits of LPCVD over cheaper APCVD:

- Improved film thickness uniformity
- Better step coverage
- Better control over stoichiometry and contamination
- Lower particle density
- Fewer pinhole defects
- Higher throughput (more densely packed wafers)
- Higher deposition rates

1-100 torr	RPCVD (Reduced Pressure)
0.001-0.01 torr	LPCVD
10^{-7} torr	UHV CVD (Ultra-High Vacuum)

PECVD

In the PECVD process glow-discharge plasmas are sustained to assist the simultaneous vapor-phase chemical reactions and hence film deposition may proceed at lower temperatures.

Previously unfeasible high-T reactions can be made to occur on temperature sensitive substrates (e.g. TiC deposition from $TiCl_4$+CH_4: conventional CVD requires 1000ºC, while PECVD needs only 450ºC).

Seemingly different applications require such low-T processing, e.g. ULSI circuits, solar cells, flat-panel displays. -> PECVD is indispensable in these areas.

a-Si, B- or P-doped SiO_2, SiN, SiO_xN_y are the most typical materials deposited via PECVD (for further examples see next slide).

PECVD Films, Source Gases, and Deposition Temperatures

Film	Source gases	Deposition temperature (°C)
Elemental		
Al	$AlCl_3$–H_2	100–250
a-B	BCl_3–H_2	400
a-C	C_nH_m–H_2/Ar	25–250
a-Si	SiH_4–H_2	300
c-Si	SiH_4–H_2	400
Oxides		
Al_2O_3	$AlCl_3$–O_2	100–400
SiO_2	$SiCl_4$–O_2	100–400
TiO_2	$TiCl_4$–O_2	100–500
Nitrides		
AlN	$AlCl_3$–N_2	<1000
BN	B_2H_6–NH_3	300–700
	BCl_3–NH_3/Ar	300–700
Si_3N_4	SiH_4–NH_3–N_2	25–500
TiN	$TiCl_4$–N_2–H_2	100–500
Carbides		
B_4C	B_2H_6–CH_4	400
BCN	B_2H_6–CH_4–N_2	~25
	$C_8H_{18}BN$	250
SiC	SiH_4–C_nH_m	140–600
TiC	$TiCl_4$–CH_4–H_2	400–900
Borides		
TiB_2	$TiCl_4$–BCl_3–H_2	480–650

thermal CVD

Deposited material	Substrate	Input reactants	Deposition temperature (°C)	Crystallinity
Si	Single-crystal Si	$SiCl_2H_2$, $SiCl_3H$, or $SiCl_4+H_2$	1050–1200	E
Si		SiH_4+H_2	600–700	P
Ge	Single-crystal Ge	$GeCl_4$ or GeH_4+H_2	600–900	E
GaAs	Single-crystal GaAs	$(CH_3)_3Ga+AsH_3$	650–750	E
InP	Single-crystal InP	$(CH_3)_3In+PH_3$	725	E
SiC	Single-crystal Si	$SiCl_4$, toluene, H_2	1100	P
AlN	Sapphire	$AlCl_3$, NH_3, H_2	1000	E
In_2O_3:Sn	Glass	In-chelate, $(C_4H_9)_2Sn(OOCH_3)_2$, H_2O, O_2, H_2	500	A
ZnS	GaAs, GaP	Zn, H_2S, H_2	825	E
CdS	GaAs, sapphire	Cd, H_2S, H_2	690	E
Al_2O_3	Si, cemented carbide	$Al(CH_3)_3+O_2$, $AlCl_3$, CO_2, H_2	275–475 850–1100	A A
SiO_2	Si	SiH_4+O_2, $SiCl_2H_2+N_2O$	450	A
Si_3N_4	SiO_2	$SiCl_2H_2+NH_3$	750	A
TiO_2	Quartz	$Ti(OC_2H_5)_4+O_2$	450	A
TiC	Steel	$TiCl_4$, CH_4, H_2	1000	P
TiN	Steel	$TiCl_4$, N_2, H_2	1000	P
BN	Steel	BCl_3, NH_3, H_2	1000	P
TiB_2	Steel	$TiCl_4$, BCl_3, H_2	>800	P

Note: E = epitaxial; P = polycrystalline; A = amorphous.

Excitation:

- DC
  - It only works for conducting materials
  - Pressure is typically a few torr
- AC (dominates the market)
  - RF excitation (coupling is capacitive)
    - » Low frequency (100kHz-40MHz)
    - » Larger potential difference
    - » 6-6000Pa → e^- and ion densities: 10^9-10^{11} cm^{-3}, E_{e-}=1-10eV
  - Microwave excitation (coupling is inductive)
    - » High frequency (MHz - GHz)
    - » Low pressure (0.001-0.1Pa)
    - » High plasma density (approx. 10x that of RF)

Type of the process:

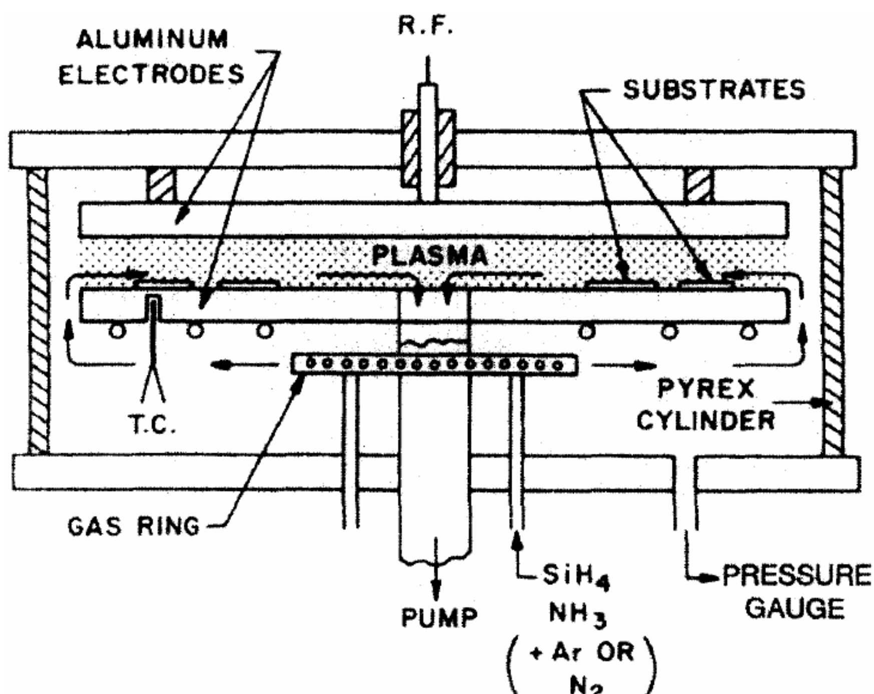
- Conventional or *Direct*:
  - reactant and product gases, plasma and substrates interact within the same space
- Remote or *Indirect*:
  - substrate lies outside the plasma generation zone (reduction of possible deposition and etching reaction pathways → better control of stoichiometry)

PECVD reactors 1.

Parallel-plate or Reinberg-type reactor

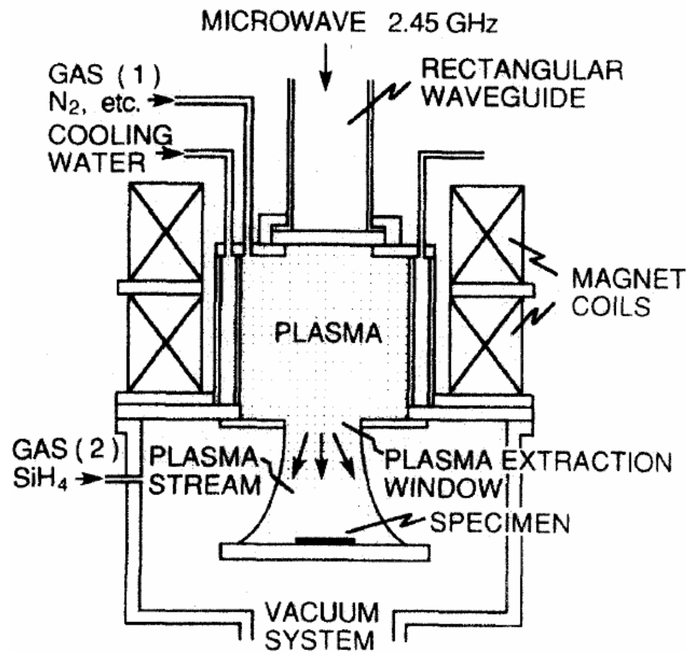
very popular reactor in industry

(low pressure, 300Å/min growth rate)



PECVD reactors 2.

HDP (High Density Plasma) reactor or ECR (Electron Cyclotron Reactor)



- Static magnetic field confines the plasma
- Typical pressure: 10^{-3} Pa– 0.1Pa
- Gas diffusion is more rapid relative to charge recombination -> 100-1000 times higher ionization
- SiO_2,Al_2O_3,SiN,Ta_2O_5
- Production of high-quality films at low substrate temperatures is a significant advantage

Pros and cons of PECVD

Advantage:

- Low-T (compared to CVD).
- Larger growth rate (compared to CVD).
- More sophisticated geometry.

Disadvantage:

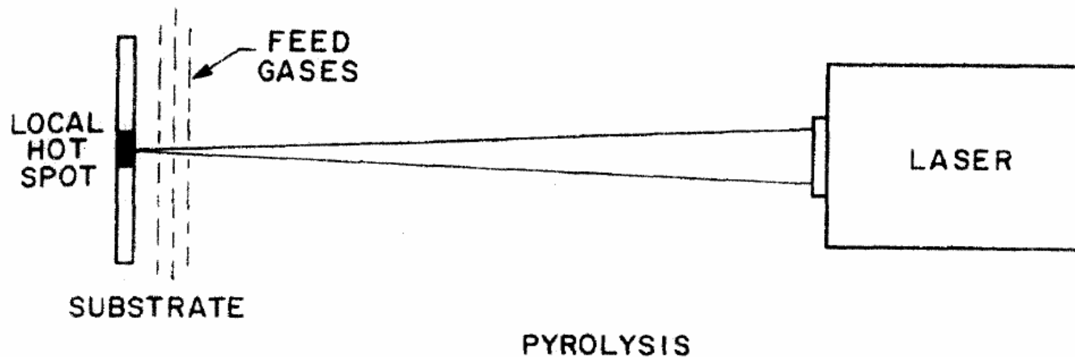
- Ionic bombardment (typical at high voltages) degrade the film.
- Consumes a lot of power.

LCVD

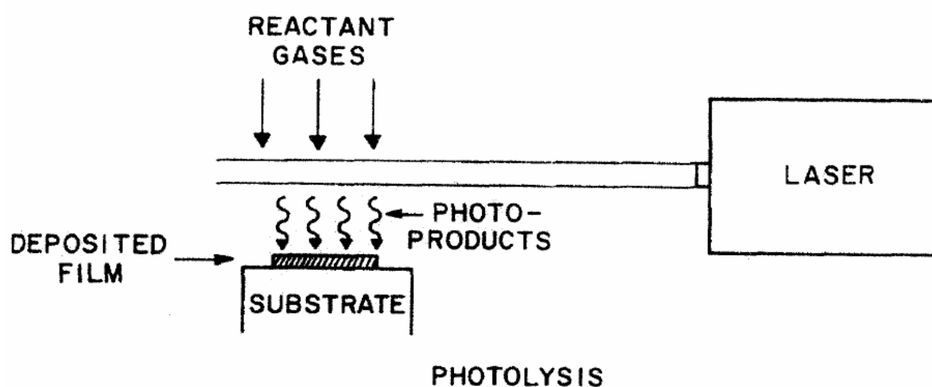
Laser- or (more generally photo-) assisted CVD involves the use of monochromatic light to enhance and control film deposition.

It may follow one of two distinct mechanisms:

In the **pyrolytic route** the laser *locally* heats the substrate and the induced temperature rise decomposes the gas above the substrate and enhance the chemical reaction in the reaction zone.



In the ***photolytic route*** energetic photons induces direct dissociation of certain bonds. Typical precursor molecules (e.g. metal-organics, carbonyls and hydrides) require ultraviolet light sources to be used ($\lambda<250$nm) for cleaving the bonds.



Photolytically deposited metals are usually contaminated by carbon and exhibit poor conductivity. To overcome this problem pyrolytic processes are preferred for direct writing (-> open circuit defect repair and clear defects in lithographic masks).

LCVD processing enables selective deposition at relatively low temperatures.

Safety of CVD

CVD processes are typically dealing with toxic, flamable, pyrophoric or corrosive substances, many of which exhibit the combination of these hazards. Safe handling of gases employed in CVD systems is of paramount importance.

The safety problems are magnified in low-pressure processing where concentrated gases are used.

Since many reactor operate at high temperatures, the gases leaving the reactors are very hot and capable of reactions further downstream (i.e. in the pumping hardware).

The exhaust stream (waste gas) must be cleaned (combustion or wet scrubbers) from acids, oxidisers, unreacted molecules (halogens) AND abrasive particulates (silica or SiN powder).

Hazardous gases employed in CVD

Gas	Corrosive	Flammable	Pyrophoric	Toxic	Bodily hazard
Ammonia (NH_3)	x			x	Eye and respiratory irritation
Arsine (AsH_3)		x		x	Anemia, kidney damage, death
Boron trichloride (BCl_3)	x				
Boron trifluoride (BF_3)	x				
Chlorine (Cl_2)	x			x	Eye and respiratory irritation
Diborane (B_2H_6)		x	x	x	Respiratory irritation
Dichlorosilane (SiH_2Cl_2)	x	x			
Germane (GeH_4)		x		x	
Hydrogen chloride (HCl)	x				
Hydrogen fluoride (HF)	x				Severe burns
Hydrogen (H_2)		x			
Phosphine (PH_3)		x	x	x	Respiratory irritation, death
Phosphorus pentachloride (PCl_5)	x				
Silane (SiH_4)		x	x	x	
Silicon tetrachloride ($SiCl_4$)	x				
Stibine (SbH_3)		x		x	

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2010. november 23.

Dr. Geretovszky Zsolt

Atomic Layer Deposition

Atomic Layer Deposition or ALD is a thin film growth technique in which the layer growth can be controlled to a monolayer thickness. Its bases are closely routed to CVD with the following two distinctions:

- The ALD process has two distinct steps.
- The precursor molecules are kept separated during the process.

The ALD process is self-limiting and governed by the surface reaction of the precursors.

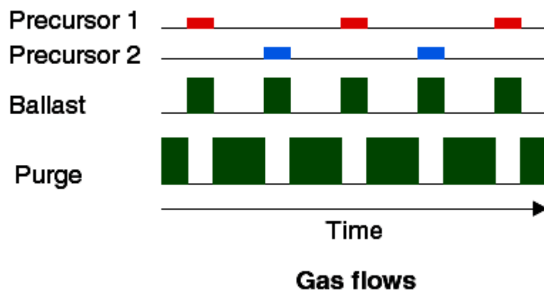
It was invented by Tuomo SUNTOLA in 1974 and found its first use for making ZnS layers for electroluminescent displays.

Today it is widely applied for making various films, including (high-k) dielectric layers.

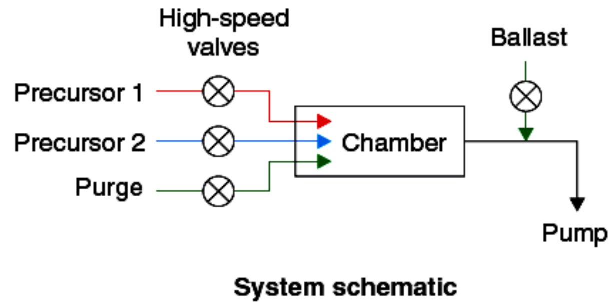
The process of ALD film growth

ALD is a sequential process, in which a monolayer of the film grows in every sequential step.

The first precursor forms a ML on the surface of the substrate and the second precursor reacts with this surface layer and transforms it to one monolayer of the aimed solid film. The key steps are saturative chemisorption and sequential surface reaction.



Gas flows



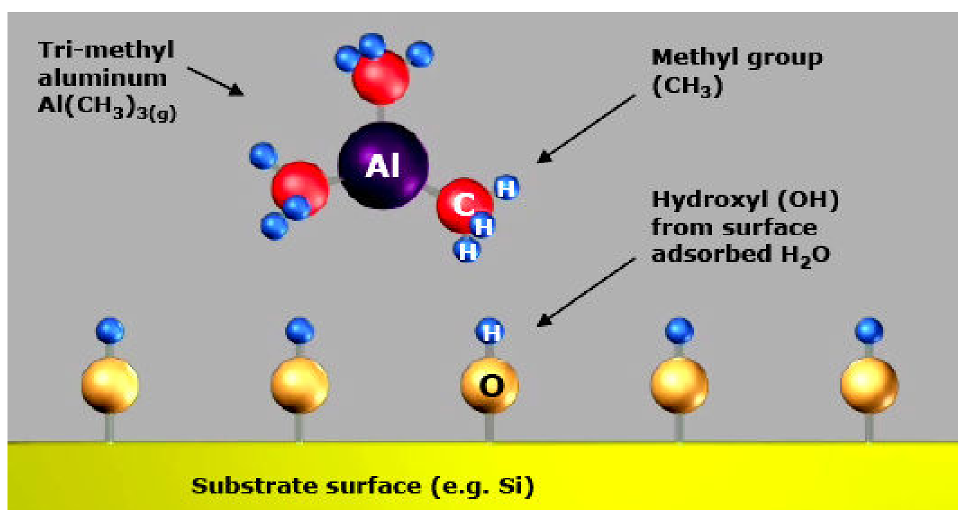
System schematic

Typical process parameteres

- pressure: 1-0,1 torr
- substarte temperature: 40-500°C

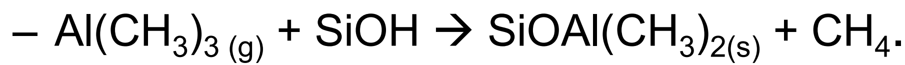
Referencia: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC. <www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf>.

- **Al_2O_3 réteg előállítása:**
  - Felületen jelenlévő vízgőz (SiOH).
  - Első prekurzor: Tri-metil alumínium (TMA).

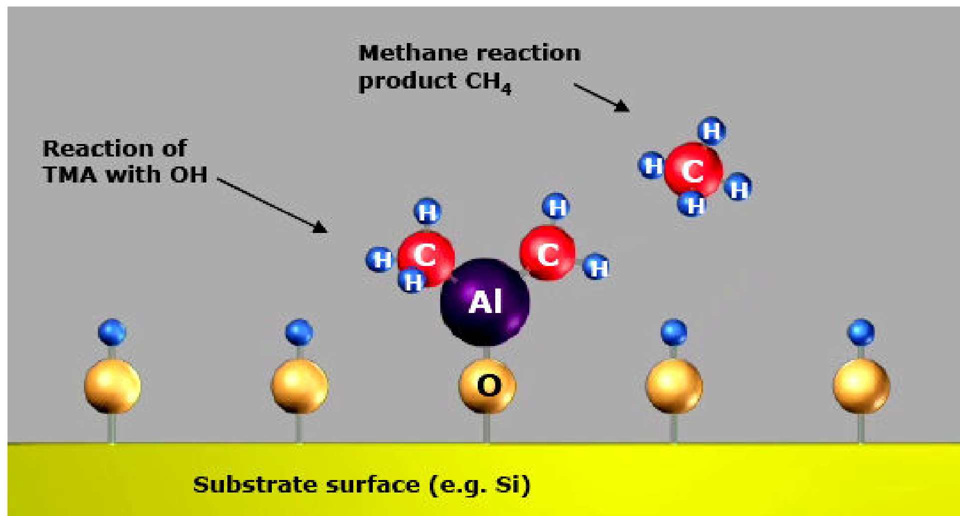


Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **Al_2O_3 réteg előállítása:**



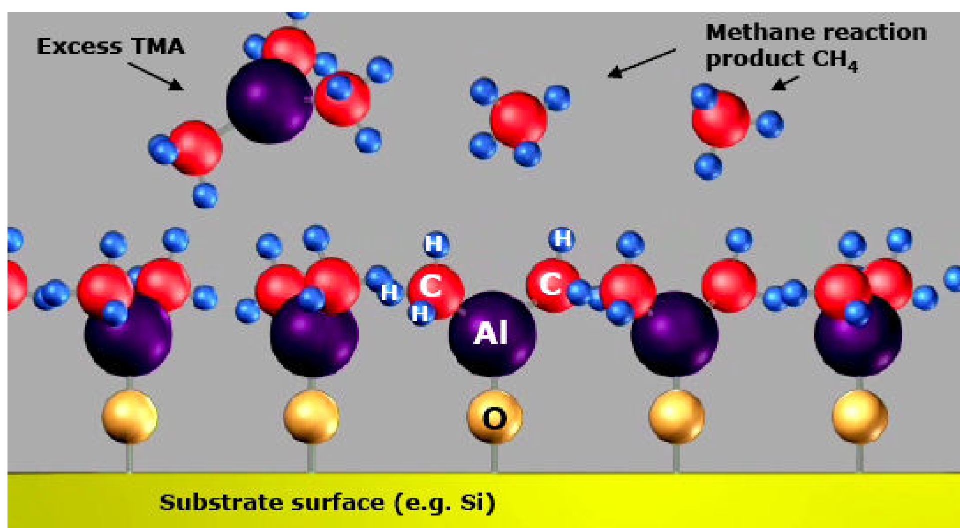
  - $Al(CH_3)_{3\,(g)} + SiOH \rightarrow SiOAl(CH_3)_{2(s)} + CH_4$.



Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

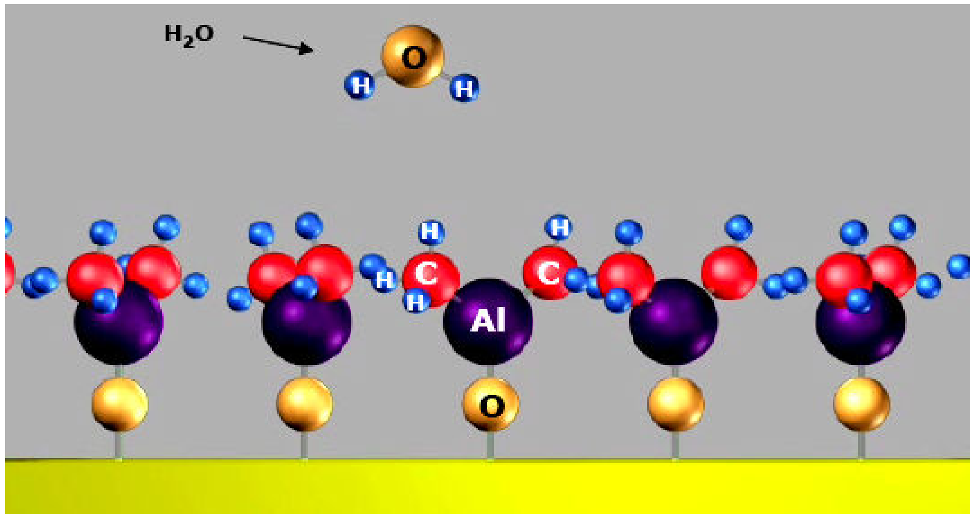
- **Al_2O_3 réteg előállítása:**

  - Telítődik a felszín.



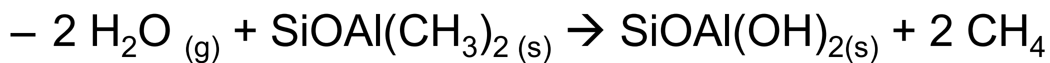
Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **Al_2O_3 réteg előállítása:**
  - Maradék TMA leszívása a reakciótérből.
  - Második prekurzor: H_2O (Vízgőz).

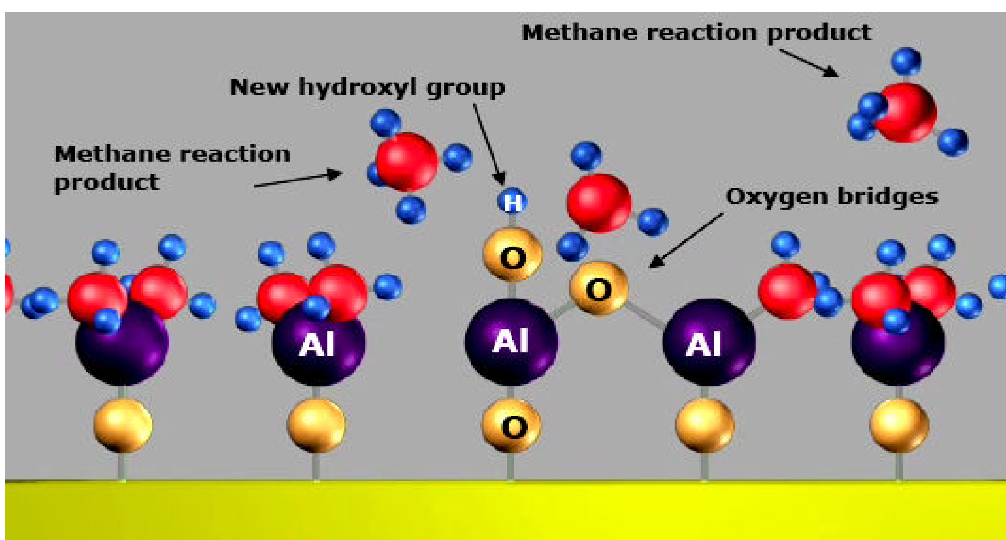


Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **Al_2O_3 réteg előállítása:**

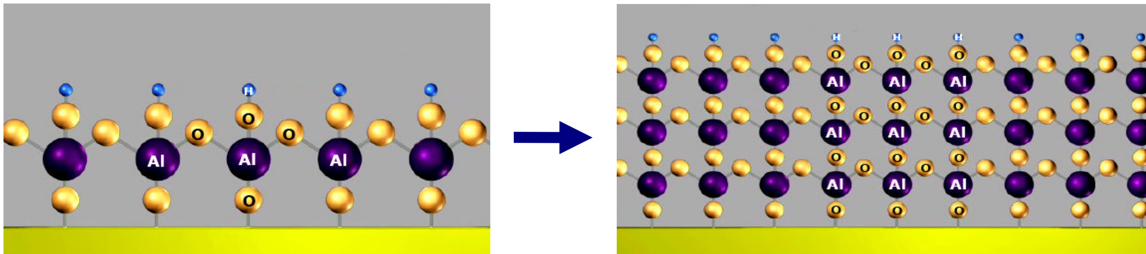


  - $2\,H_2O_{(g)} + SiOAl(CH_3)_{2\,(s)} \rightarrow SiOAl(OH)_{2(s)} + 2\,CH_4$



Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **Al_2O_3 réteg előállítása:**
  – Metán és maradék vízgőz leszívása.
  – A folyamat kezdődhet előről.

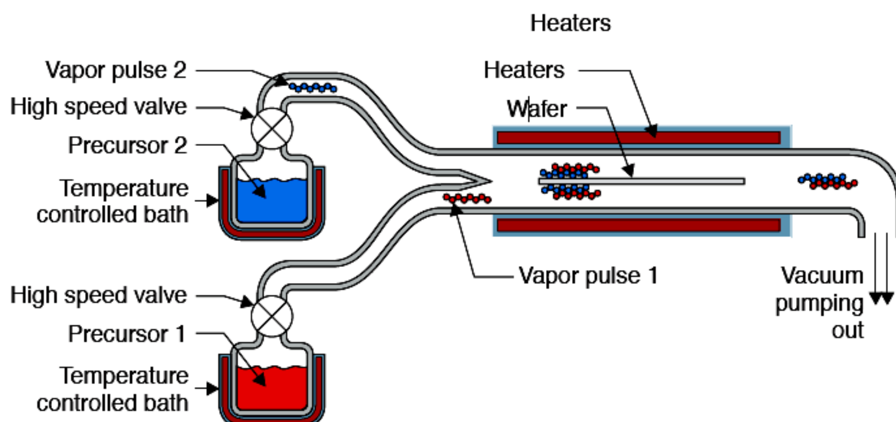


Növekedési sebesség:~ 1Angström / ciklus

T_{cilkus}: 3 perc

Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **ALD elrendezés:**
  – Zárt rendszerű reaktorkamrák (általánosan használt)
    - A kamra fala hatással van a prekurzorok transzportjára
  – Nyílt rendszerű kamrák
    - A kamra sokkal nagyobb a hordozó méretéhez képest
  – Vegyes rendszerek



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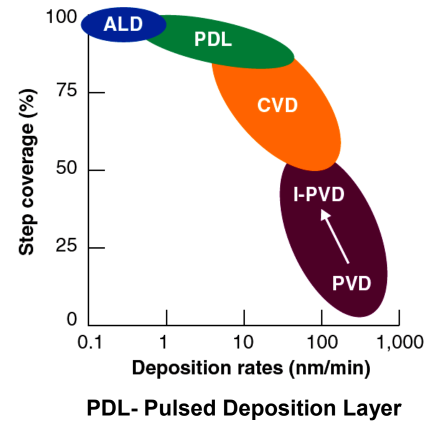
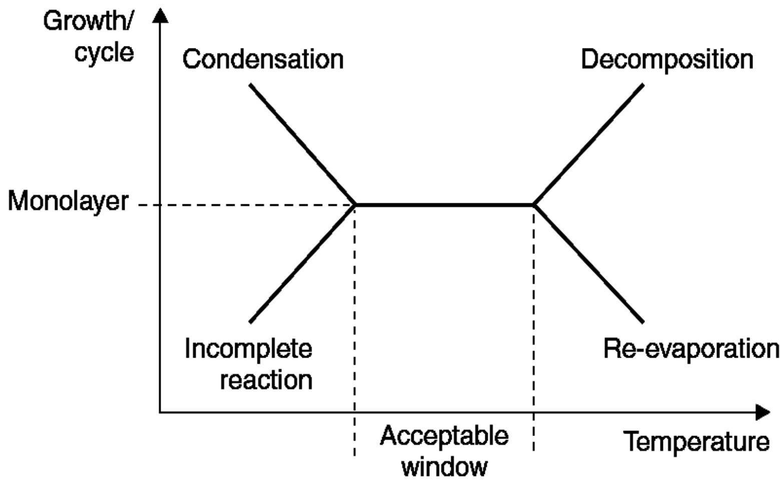
- **Folyamat paraméterei:**
  - Adott hőmérsékleti tartományban a rétegnövekedés független a közeg hőmérsékletétől.



PDL- Pulsed Deposition Layer



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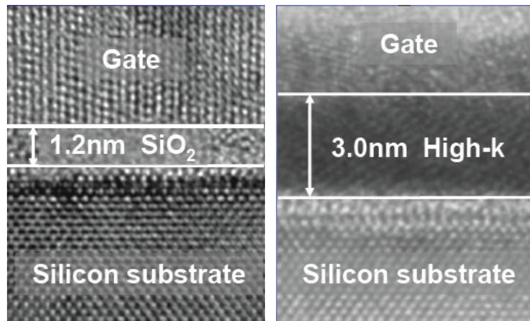
ALD precursors and target materials

Film	Precursors	Temperature °C	Application
Al_2O_3	$Al(CH)_3$, H_2O or O_3		High-k dielectric
AlN			
Cu	CuCl, $Cu(thd)_2$ or $Cu(acac)_2$ with H_2, $Cu(hfac)_2xH_2O$ with CH_3OH	360-410, 175-300, 250, 203-300	Interconnect
HfO_2	$HfCl_4$ or TEMAH, H_2O		High-k dielectric
Mo	MoF_6, $MoCl_5$ or $Mo(CO)_6$ with H_2	200-500, 500-1100, 200-600	
Ni	$Ni(acac)_2$, 2 step process NiO by O_3 reduced afterwards by H_2		
SiO_2	$SiCl_4$, H_2O		Dielectric
Ta	$TaCl_5$,		Barrier
TaN	TBTDET, NH_3	260	Barrier, deposited with plasma enhancement
TaO_2			
Ti	$TiCl_4$, H_2		Glue layer, deposited with plasma enhance-ment
TiN	$TiCl_4$ or TiI_4, NH_3	350 - 400	Barrier
TiO_2			High-k dielectric
TiSiN			
W	WF_6, B_2H_6 or Si_2H_6	300 - 350	Interconnect plug fill
WN			Barrier
WN_xC_y	WF_6, NH_3, TEB (triethylboron)	300 - 350	
ZrO_2	$ZrCl_4$, H_2O		High-k dielectric

Referencia: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC. <www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf>.

- **Alkalmazási területek:**
  - High-k dielektrikumok előállítása CMOS tranzisztorokhoz.

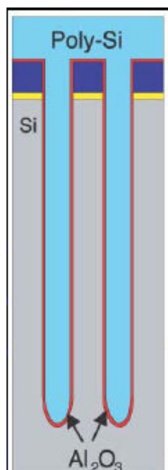


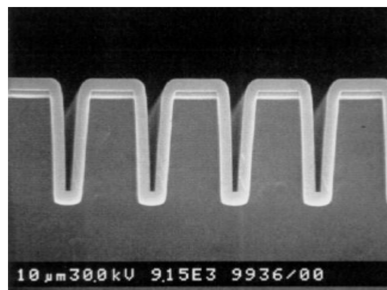
Film	Prekurzor
Al_2O_3	**$Al(CH)_3$, H_2O or O_3**
HfO_2	**$HfCl_4$, H_2O**
ZrO_2	**$ZrCl_4$, H_2O**

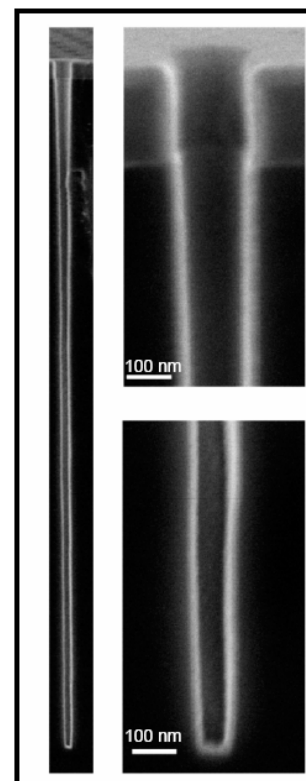
  - Szivárgási áram csökkentése
  - Kisebb fizikai kiterjedés
  - Gyorsabb kapcsolási sebesség

Referencia: "Atomic Layer Deposition," Cambridge NanoTech Inc. <http://www.cambridgenanotech.com/>.

- **Alkalmazási területek:**
  - DRAM-ok konformális bevonatának előállítása.
    - DRAM árkok
    - SAMSUNG által használt technika







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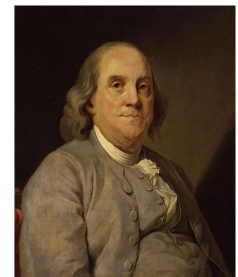
- **Előnyök, hátrányok:**
  - Előny:
    - Állandó sztöchiometria.
    - Precíz rétegvastagság szabályozás.
    - Alacsony hőmérsékleten is lehetséges filmépítés.
    - Konformális bevonatok.
  - Hátrány:
    - Lassú épülési sebesség (PEALD megoldás).
    - Bizonyos összetételű anyagokkal nem alkalmazható.

History of LB films


Benjamin_FRANKLIN
1706-1790

In 1774 Benjamin Franklin reported the following to the British Royal Society:

"At length at Clapman where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface ... the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leeside, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."

$$1\,acre = 43560\ feet^2 = 43560\,(0.3048m)^2 = 4046{,}8\ m^2$$

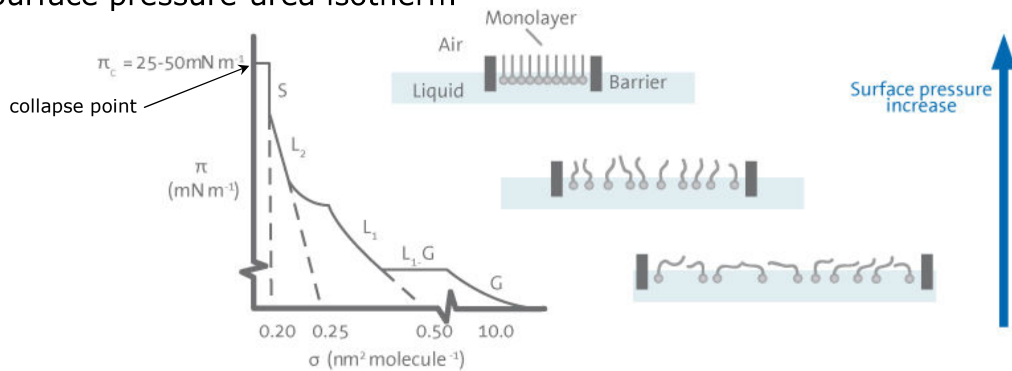
$$d = \frac{2ml}{2023{,}4m^2} = \frac{2\cdot 10^{-3}\,dm^3}{2023.4m^2} = \frac{2\cdot 10^{-3}\cdot 10^{-3}\,m^3}{2023{,}4m^2} = 9{,}88\cdot 10^{-10}\,m \approx 1nm$$

But Franklin had NOT made such a simple calculation!

Langmuir films

A Langmuir film can be defined as an insoluble monolayer of functional molecules, nanoparticles, nanowires or microparticles that reside at the gas-liquid or liquid-liquid interface.

Surface pressure-area isotherm



Orientation of the molecules in different "phases"

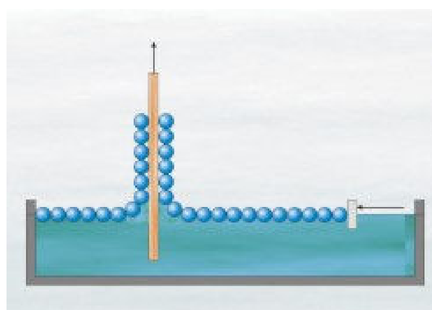
The LB deposition is usually carried out in the "solid" phase. The surface pressure is then high enough to ensure sufficient cohesion in the monolayer, e.g. the attraction between the molecules in the monolayer is high enough so that the monolayer does not fall apart during transfer to the solid substrate.

Langmuir-Blodgett technique

An insoluble spread monolayer of atoms or molecules floating at the gas/liquid interface and subsequently transferred onto a solid substrate. Lipids, polymers or other water insoluble atoms or molecules can form ultrathin and organized *monolayers,* i.e. *Langmuir films,* at the air/water interface. These films can be deposited on solid substrates to form highly organized regular *multilayer stacks called Langmuir-Blodgett films*. The LB films are prepared by successively dipping a solid substrate up and down through the monolayer at a constant molecular density or surface pressure. In this way multilayer structures of hundreds of a few nanometer thick monolayers can be produced.

1917

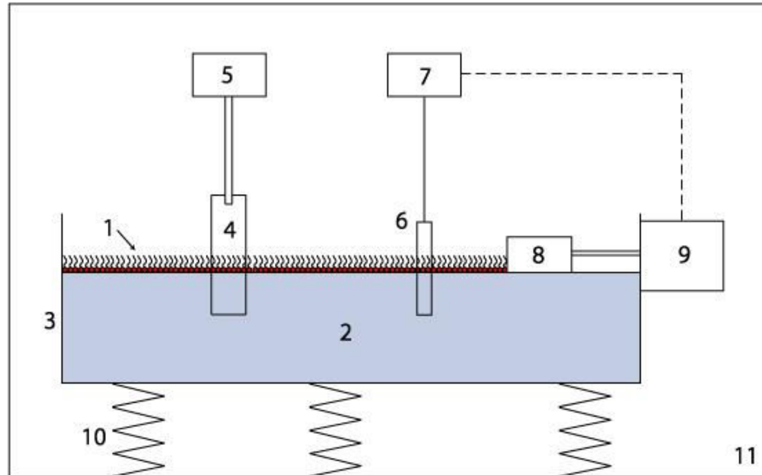
Irving LANGMUIR
1881–1957



1935

Katharine Burr BLODGETT
1898-1979

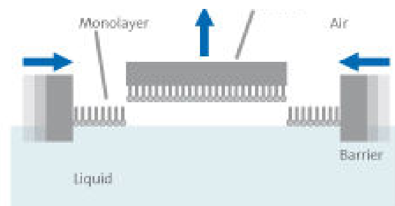
The Langmuir-Blodgett trough



1. Amphiphile monolayer
2. Liquid sub-phase
3. LB trough
4. Solid substrate
5. Dipping mechanism
6. Wilhelmy plate
7. Electrobalance
8. Barrier
9. Barrier mechanism
10. Vibration reduction system
11. Clean room enclosure

source: http://en.wikipedia.org/wiki/Langmuir-Blodgett_trough

c.f. Langmuir-Schaeffer technique



An alternative way to deposit the monolayer is the Langmuir-Schaeffer (LS) technique, in which the solid substrate is *horizontally* lowered.

http://www.ksvnima.com/langmuir-and-langmuir-blodgett-troughs
http://www.ksvnima.com/langmuir-blodgett-trough

The Langmuir-Blodgett films

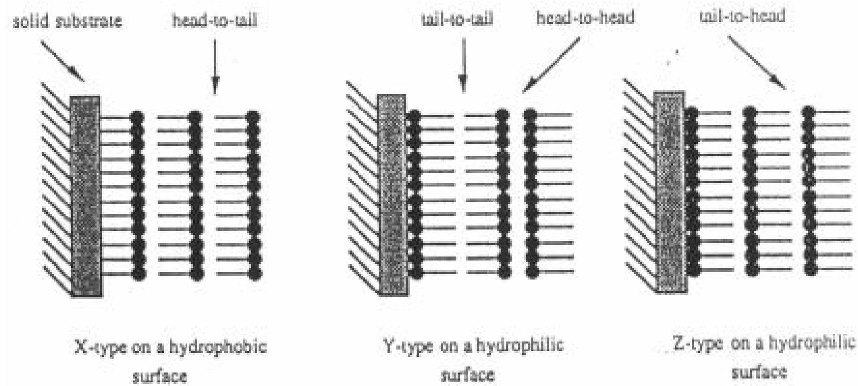
The LB technique also ensures the build up of homogeneous multilayers. The surface pressure value that gives the best results depends on the nature of the monolayer and is usually established empirically. However, amphiphiles can seldom be successfully deposited at surface pressures lower than 10 mN/m, and at surface pressures above 40 mN/m collapse and film rigidity often pose problems. When the solid ***substrate is***

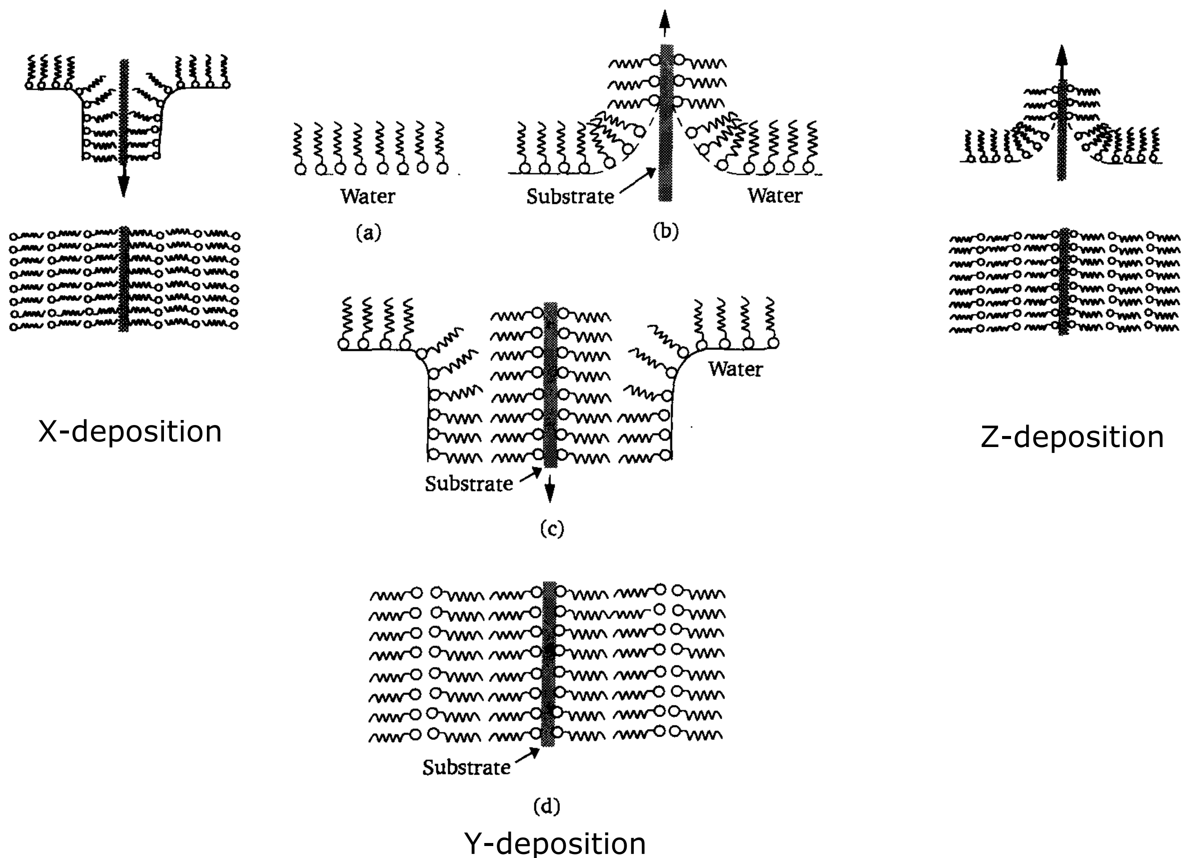
- ***hydrophilic*** (e.g. glass, SiO_2) *the first layer is deposited by raising* the solid substrate from the sub-phase through the monolayer,
- ***hydrophobic*** (e.g. HOPG, silanized SiO_2) *the first layer is deposited by lowering* the substrate into the sub-phase through the monolayer.

There are several parameters that affect on what type of LB film is produced. These are the nature of the spread film, the sub-phase composition and temperature, the surface pressure during the deposition and the deposition speed, the type and nature of the solid substrate and the time the solid substrate is stored in air or in the sub-phase between the deposition cycles.

The Langmuir-Blodgett films

Different kind of LB multilayers can be produced by successive deposition of monolayers on the same substrate.
The most common one is the **Y-type multilayer**, which is produced when the monolayer deposits to the solid substrate in *both up and down* directions.
When the monolayer deposits *only in the up or down* direction the multilayer structure is called either **Z-type or X-type**.
Intermediate structures are sometimes observed for some LB multilayers and they are often referred to be XY-type multilayers.





Mechanical film growth techniques

Mechanical methods:

- Liquid spraying
- Spinning
- Dipping and draining
- Flow coating
- Roller coating
- Pressure-curtain coating
- Brushing
- Off-set printing

Technique	Thickness	Advantages	Limitations	Applications
Spin	10 nm–5 μm	Uniformity, reproducibility, excellent thickness control, low cost	Requires flat substrate, high material loss	Photoresists, dielectric layers, flat panel displays
Dip	20 nm–50 μm	Complex and irregular shapes can be coated, can be a continuous process, very simple	Thickness variations, voids, and pin holes	Insulating polymer layers, electronic parts, and assemblies
Spray	2 nm–20 μm	Fast and adaptable to complex shapes and sizes, conformal step coverage, high efficiency	Expensive, low-viscosity coating solution	Electrical insulation, circuit board housing
Stamping; microcontact printing	50 nm–1.5 μm	Direct development of patterned film	Lateral resolution	Waveguides, capacitors, diffraction gratings, lab-on-a-chip structures

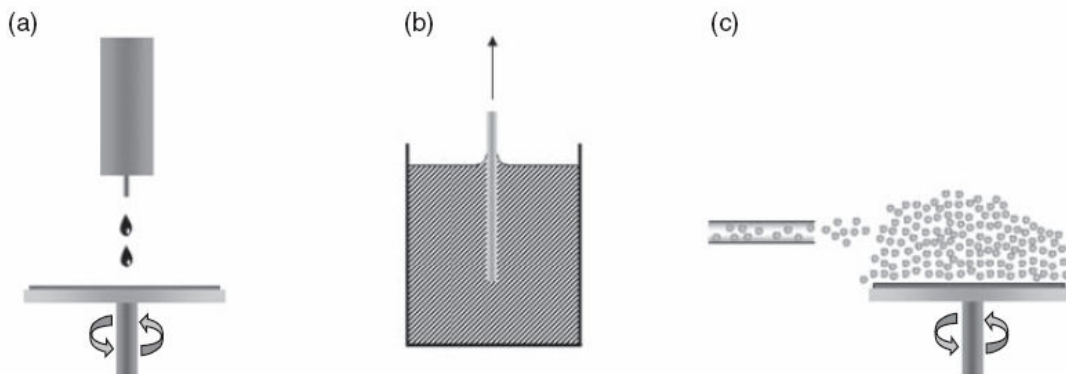


Figure 2.7. Schematic diagrams of (a) spin, (b) dip, and (c) spray coating. [Adapted with permission from Ref. 8: R. W. Schwartz et al., *C. R. Chemie*, **7**, 433 (2004).]

Spin coating

Spin coating has been used to deposit ultrathin to relatively thick coatings on flat substrates for several decades. Various materials, including resin, epoxy, polymers, and sol-gel stock solutions, have been successfully coated on metal, glass, ceramic, plastic, paper and semiconductor substrates. This technique normally uses the material to be coated in its liquid form or dissolved in a liquid solvent. Typically the substrate to be coated is held in place using a motor-driven vacuum chuck and the coating solution is dispensed on the substrate either manually or by an automated robotic arm. The substrate is then accelerated to very high angular velocities (approx. 300 to 10,000 rpm) during which the excess liquid is spun off from the substrate leaving a thin uniform coating.

The film thickness can be varied by controlling the spin speed and time, as well as the viscosity of the solution.

The major advantages of spin coating are reproducibility, uniformity, simplicity, ease of integration, ability to use different substrate materials, and low cost. The main disadvantage of the method is that a smooth, flat substrate should be used. Step coverage can prove difficult, and complex structures cannot be coated using this technique.

Dip coating

Dip coating is another low-cost solution deposition technique that is commonly used in the semiconductor industry, mainly to coat irregular and complex shapes. In this process the complex part or substrate is immersed into the coating solution and the film is formed by either removing the substrate vertically from the solution or draining the solution from the reservoir at a constant rate.

The physics behind film formation in the dip–coating process involves a balance among the viscous drag, gravitational forces, and surface tension in the concavely shaped meniscus. Various factors affecting the thickness of the film formed the viscosity and density of the solution and by the withdrawal speed or rate.

Spray coating

The spray is mainly used for its ability to coat non-planar structures like steps, trenches and stacks on semiconductor chips. In this process, very fine droplets are formed from the coating solution using *atomizers or nebulizers*. Compared with spin and dip coating, the solution viscosity has to be greatly reduced to facilitate the nebulization process to form fine droplets. These fine droplets are then carried into the coating chamber with a carrier gas and deposited on the substrate by gravity or with an electrostatic field, where the negatively charged droplets are attracted to the electrically grounded substrate.

The advantages of electrostatic spray coating over traditional gravitational spray coating are high deposition rates and low material loss. Materials savings of 25% to 50% over traditional spraying techniques have been reported. The step coverage and conformal nature of the films deposited on non-planar surfaces by spray coating have also been studied. A thickness variation of <20% was observed on 400nm trenches with 200 nm thin films. The conformal coating quality is determined by the size of the droplet, which can be reduced by decreasing the viscosity of the solution and by increasing the atomizing pressure or using a Venturi nozzle.