UNIVERSITAS STVDIORVM CARALITANA

Deposition and Patterning Techniques for Organic Electronics

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Tecnologie e Dispositivi Elettronici Avanzati
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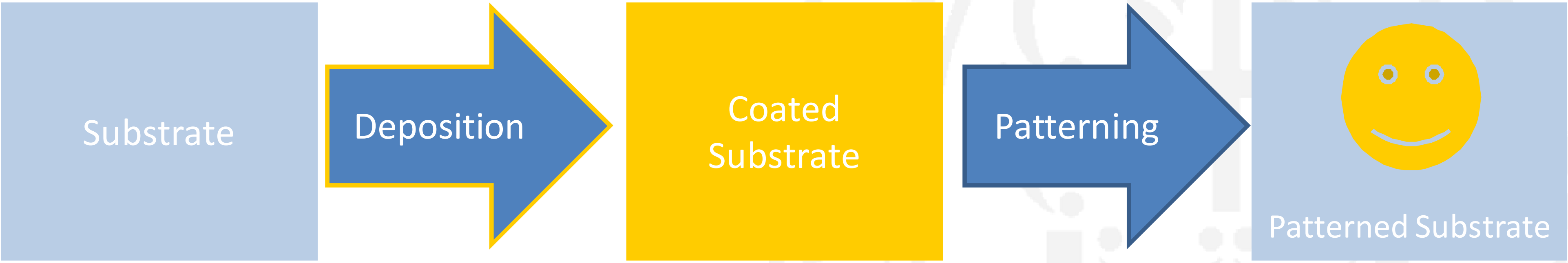
DEALAB

Summary

- Deposition vs. Patterning or Deposition + Patterning?
- Deposition techniques:
  - Physical Vapor Deposition;
  - Chemical Vapor Deposition;
  - ALD;
  - Deposition from Liquid Phase;
- Patterning: photolithographic techniques;
- Depositing a pattern: soft lithography

Deposition and Patterning



Substrate

Deposition

Coated Substrate

Patterning

Patterned Substrate

- Classically, deposition and patterning are two subsequent operations that allow obtaining a defined pattern onto the substrate;
- What about their combination?

Deposition and Patterning

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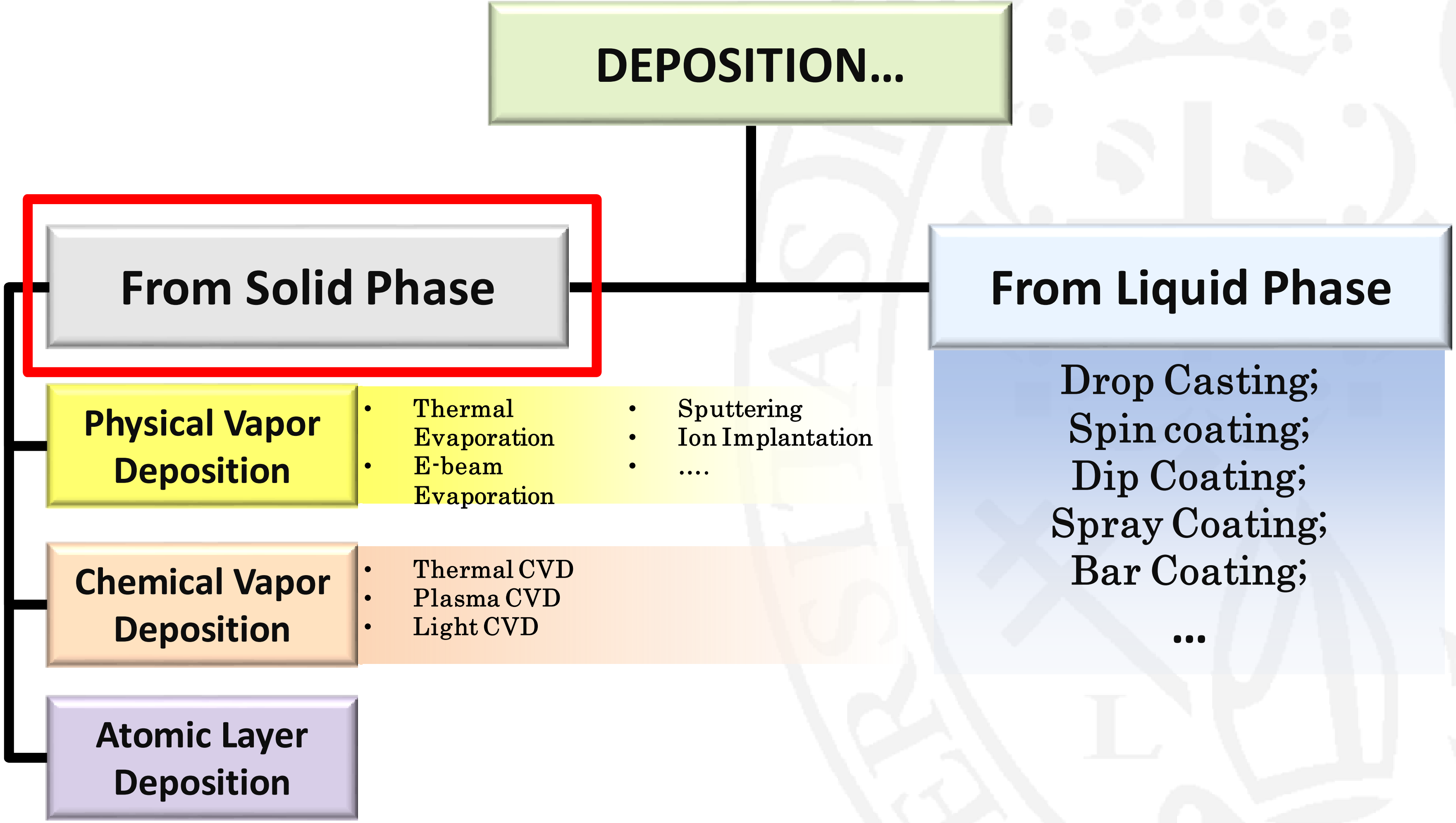
Deposition Techniques



DEPOSITION…

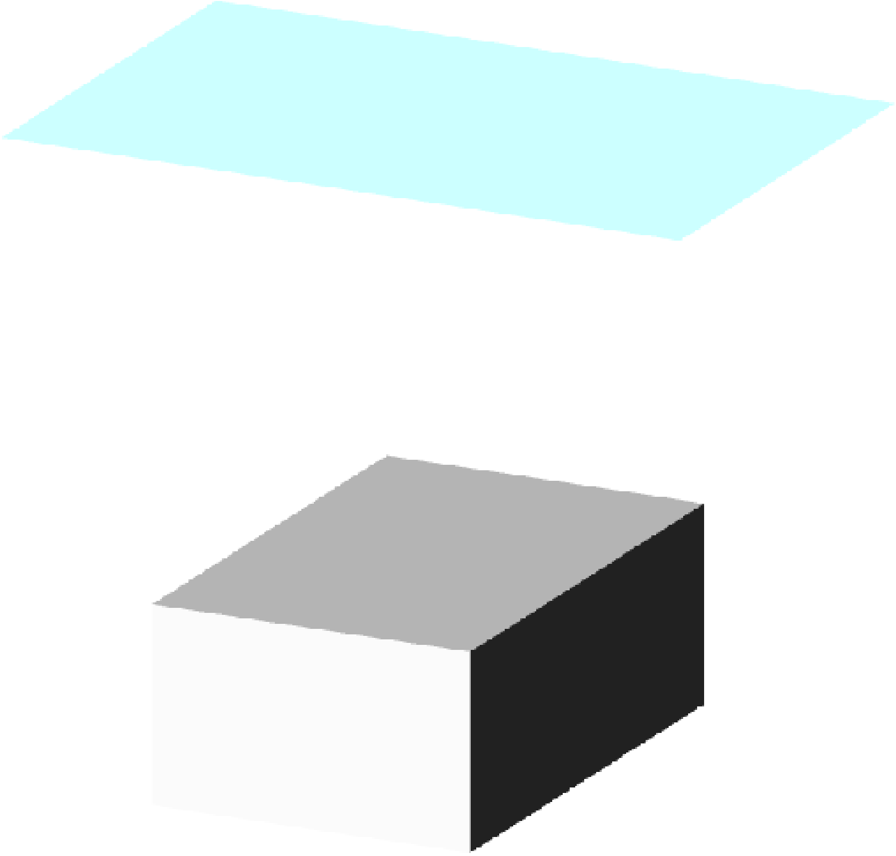
From Solid Phase

- **Physical Vapor Deposition**
  - Thermal Evaporation
  - E-beam Evaporation
  - Sputtering
  - Ion Implantation
  - ….
- **Chemical Vapor Deposition**
  - Thermal CVD
  - Plasma CVD
  - Light CVD
- **Atomic Layer Deposition**

From Liquid Phase

Drop Casting;
Spin coating;
Dip Coating;
Spray Coating;
Bar Coating;
…

Physical Vapor Deposition Techniques



- Allow depositing any kind of material (conductors, semiconductors, insulators) on every kind of substrate;
- The material is in its solid state, and make sublimate (passing to its vapor state)
- They can be categorized according to the mechanism adopted for obtaining sublimation
- **All PVD techniques are vacuum techniques!**

Why PVD in vacuum?

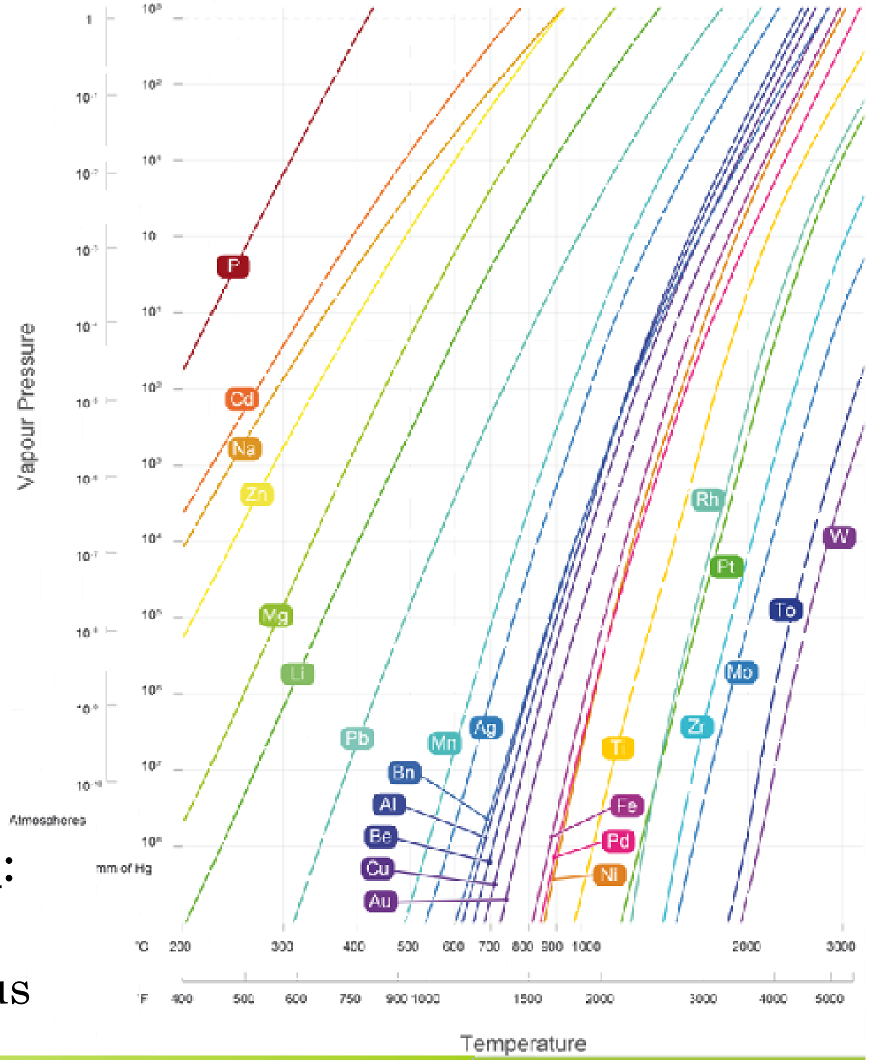
- Vacuum = absence of everything!
- ...but, how many kinds of vacuum conditions can be created?
  - Low (rough) Vacuum (LV): 25-760 Torr;
  - Medium Vacuum (MV): 10^{-3}-25 Torr;
  - High Vacuum (HV): 10^{-6}-10^{-3} Torr;
  - Very High Vacuum (VHV): 10^{-9}-10^{-6} Torr;
  - Ultra-High Vacuum (UHV): 10^{-9}-10^{-12} Torr;
  - Extreme-High Vacuum (EHV): $< 10^{-12}$ Torr

Why PVD in vacuum?

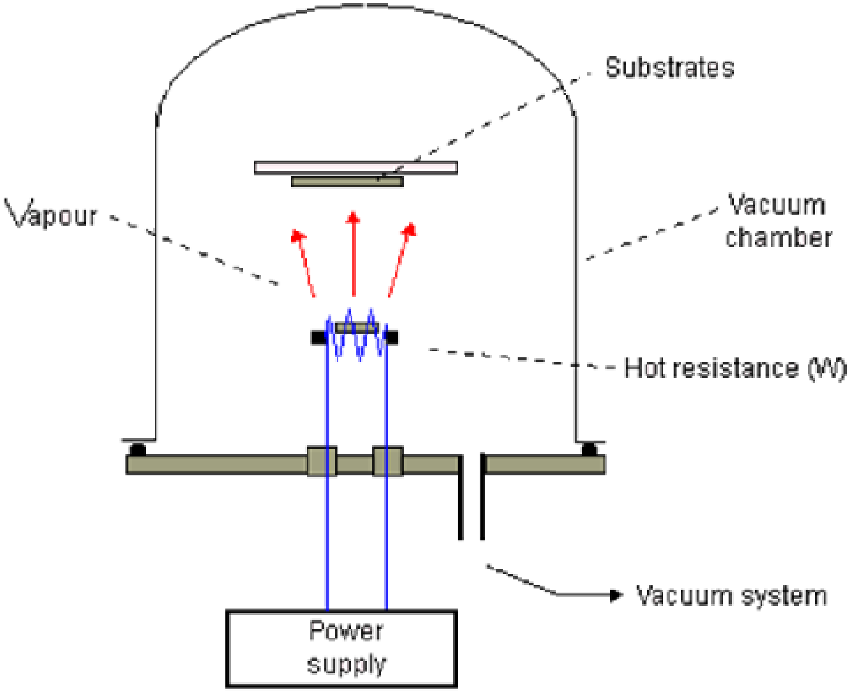
- In vacuum, contamination/ chemical reactions are prevented!
- In vacuum, materials can sublimate!
- In vacuum, molecules can reach the substrate without deflection!

$$\lambda = \frac{kT}{4\pi\sqrt{2}r^2 p}$$

Mean free path:
p=pressure
r=collision radius

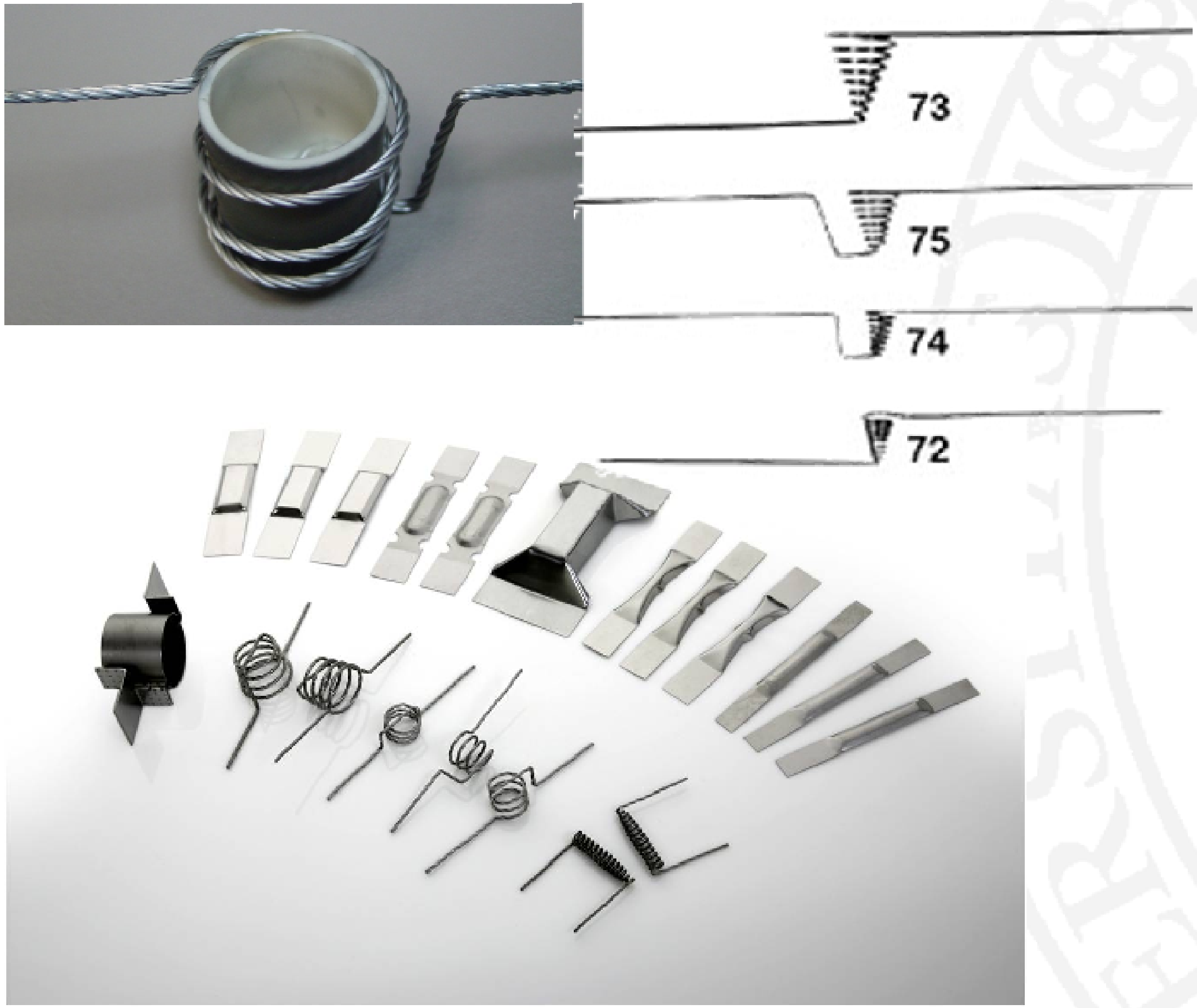


PVD: Thermal Evaporation



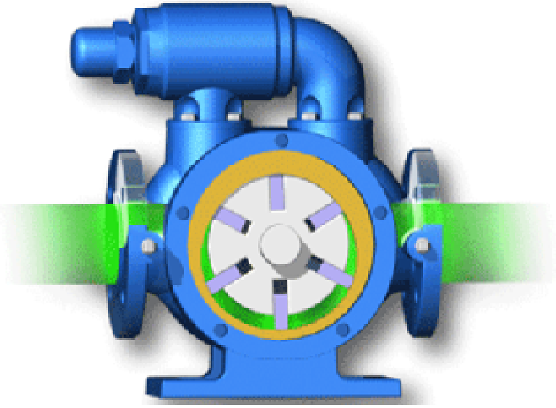
- Employed for the deposition of **metals** and **organic semiconductors** (in general, of **low-molecular weight materials**);
- Sublimation is obtained by **heating up** the material by means of **Joule effect**

PVD: Thermal Evaporation



- The material to be sublimated is put inside a crucible.
- There are different crucibles, with different shapes adapted to the material
- What is the crucible material?

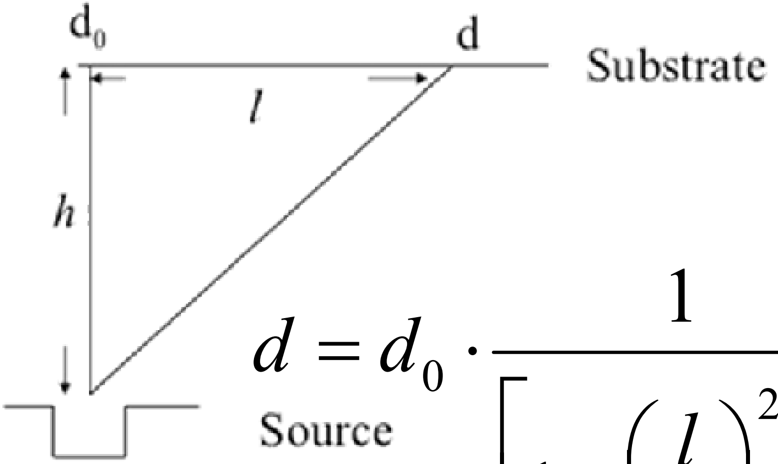
PVD: Thermal Evaporation



- The vacuum systems is generally composed by different pumps:
  - Rotary pump, to create rough vacuum conditions (necessary for a correct functionality of HV pumps;
  - Molecular pumps (diffusive, turbo), to create the high vacuum conditions

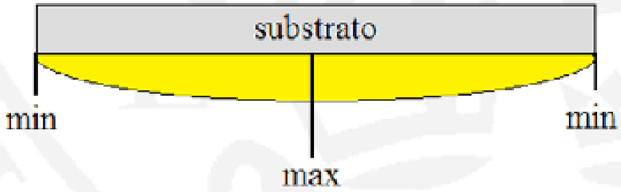
PVD: Thermal Evaporation

$$\Phi_e = c \cdot \frac{(P_e - P_h)}{\sqrt{T}}$$

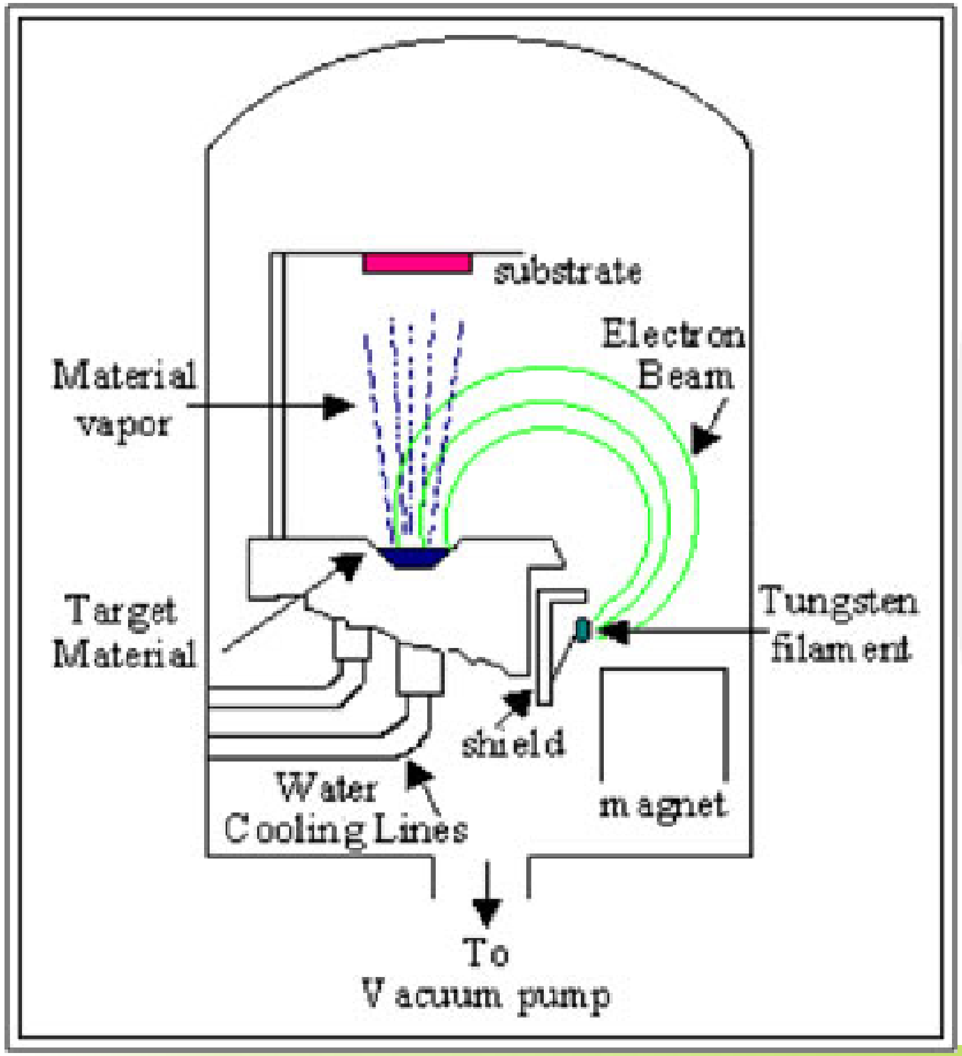


$$d = d_0 \cdot \frac{1}{\left[1 + \left(\frac{l}{h}\right)^2\right]^\alpha}$$

- The speed of evaporation is a function of temperature and pressure;
- The characteristic of the evaporated films can be modified according to the distance between crucible and substrate;
- The deposited film is NEVER uniform!

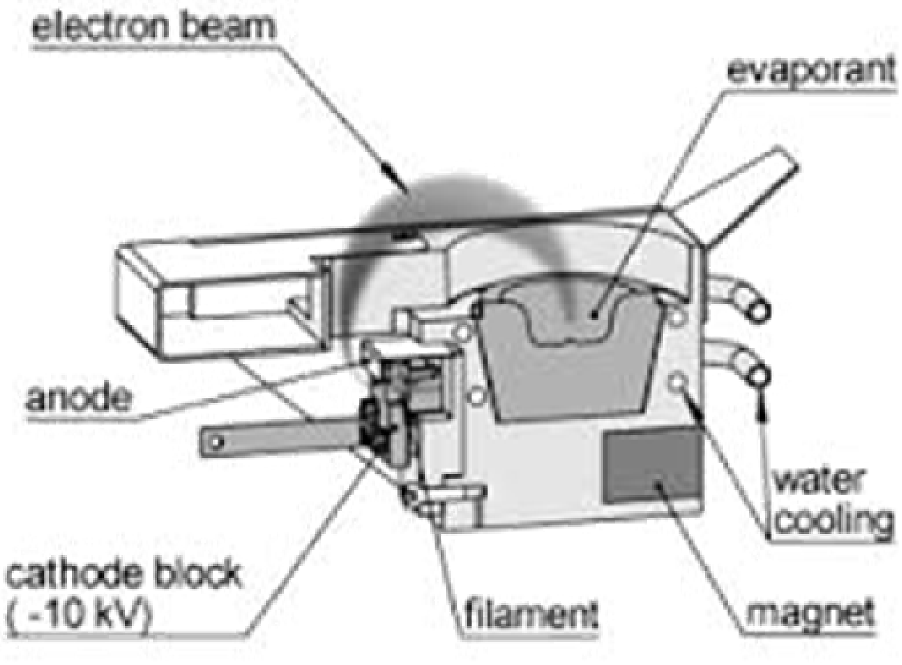


PVD: E-Beam Evaporation



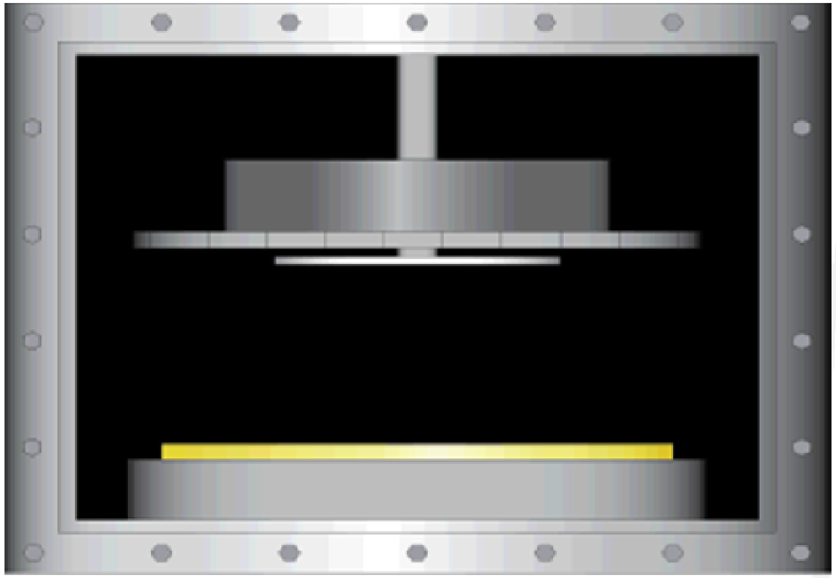
- Employed for the deposition of **metals** and **ceramics**;
- Sublimation is obtained **heating up** the materials (inside a crucible) using an **electron beam**;
- Temperature as high as 3500°C can be reached;
- High purity of the deposited materials

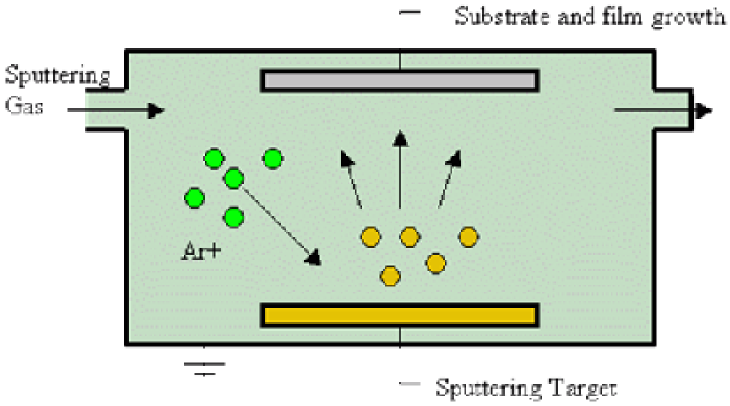
PVD: E-Beam Evaporation



- A filament is heated up.
- If the vacuum conditions are sufficiently high, it start to emit electrons by thermo-ionic effect
- Electrons are accelerated in the direction of the crucible using a magnetic field;
- The collision between electrons and the material heat up the latter, that sublimates.

PVD: Sputtering

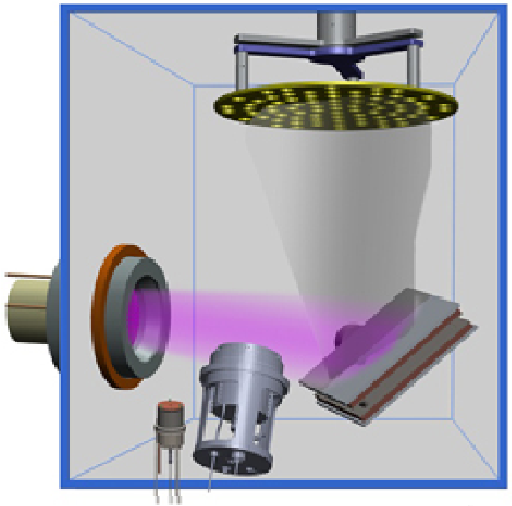


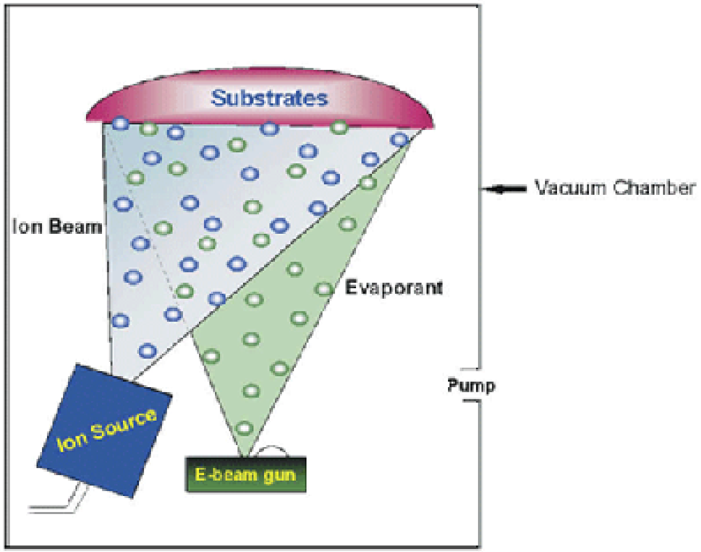


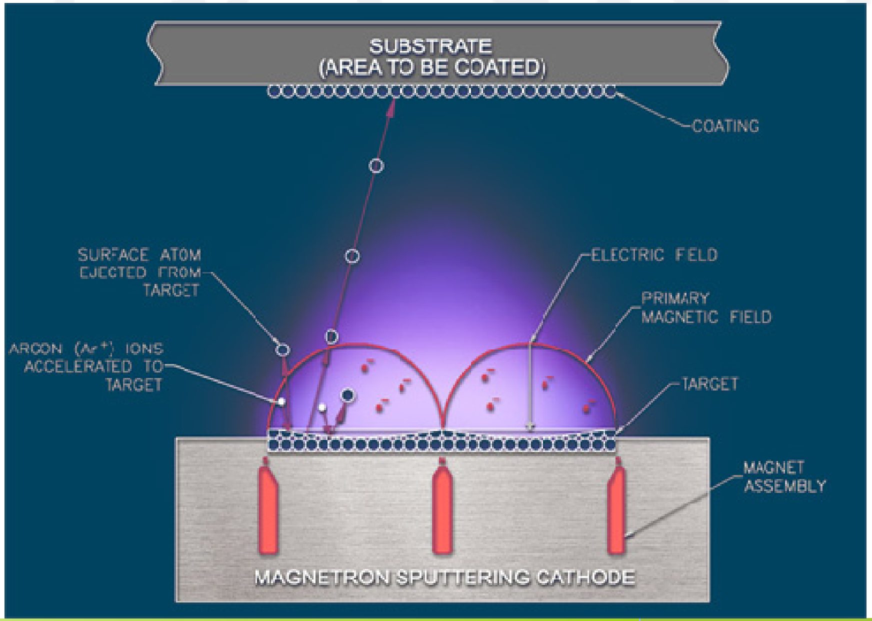
- In sputtering techniques, ions are accelerated towards a target made of the material to be deposited;
- Atoms are removed from the surface of the target, and transferred onto the substrate

PVD: Sputtering

- Ions acceleration towards the target can be made in different ways



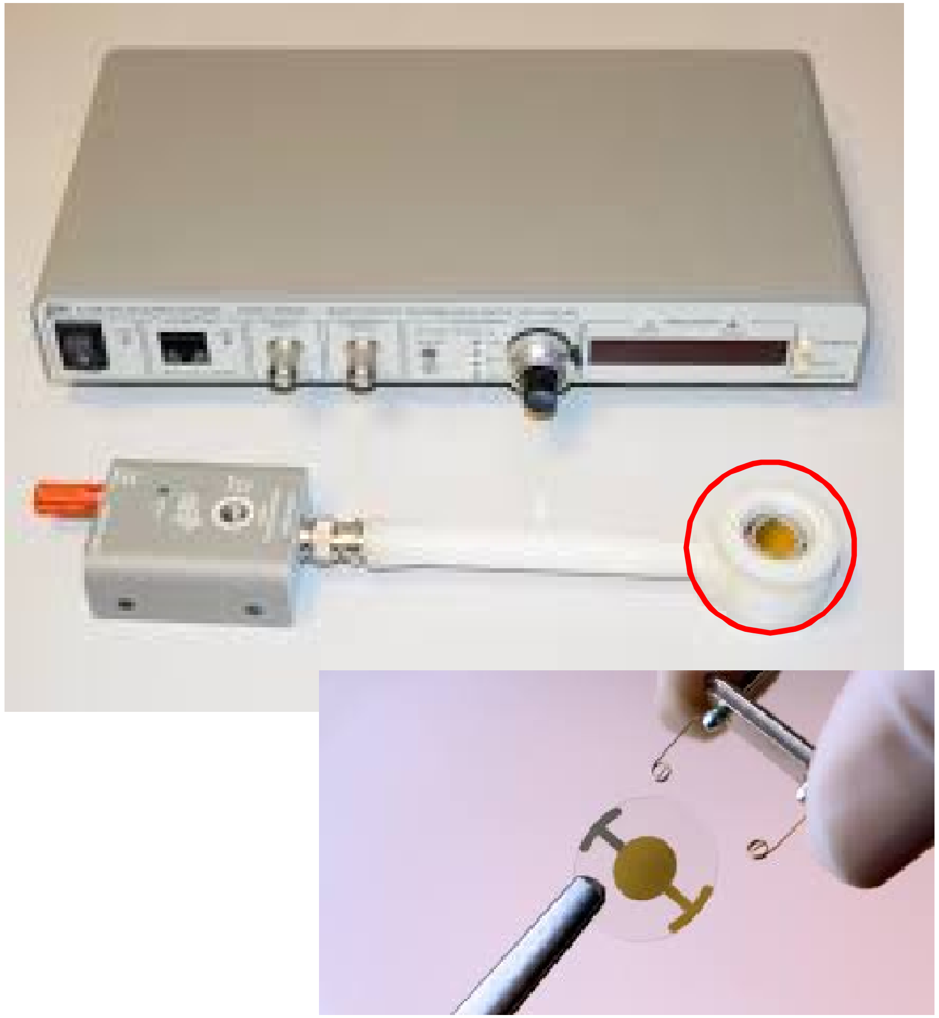




PVD: Controlling the film thickness

- In order to control the thickness of the deposited materials, a quartz crystal microbalance (QCM) is generally used.
- QCM takes advantage of the piezoelectric effect found in quartz crystals.
  - Application of an electric potential across the quartz crystal induces mechanical shear strain in the crystal.
  - Rapid oscillation of the electric potential polarity leads to vibrational motion of the quartz crystal.
  - Under the proper conditions, this vibration can induce an acoustic standing wave between the two crystal faces.
  - The frequency of the standing wave is proportional to the thickness of the quartz crystal.
- If additional material is uniformly deposited on the face of the crystal, the additional thickness will decrease the resonant frequency of the acoustic wave.

PVD: Controlling the film thickness



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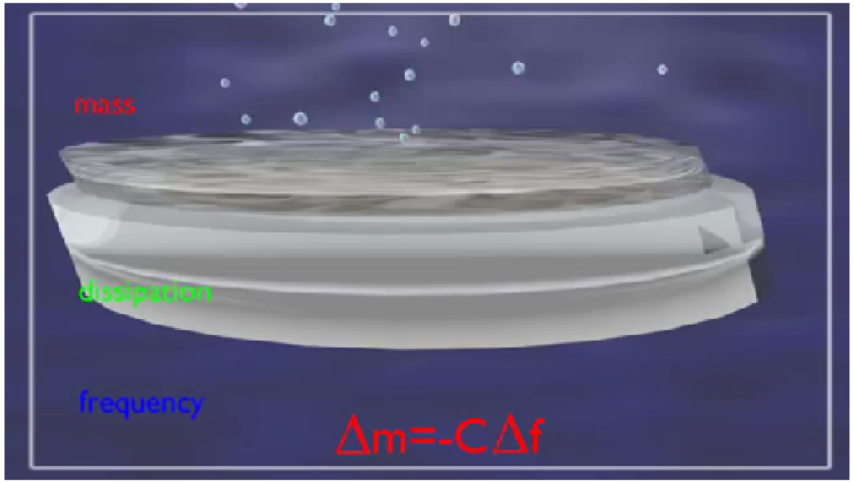
Quartz Crystal Microbalance



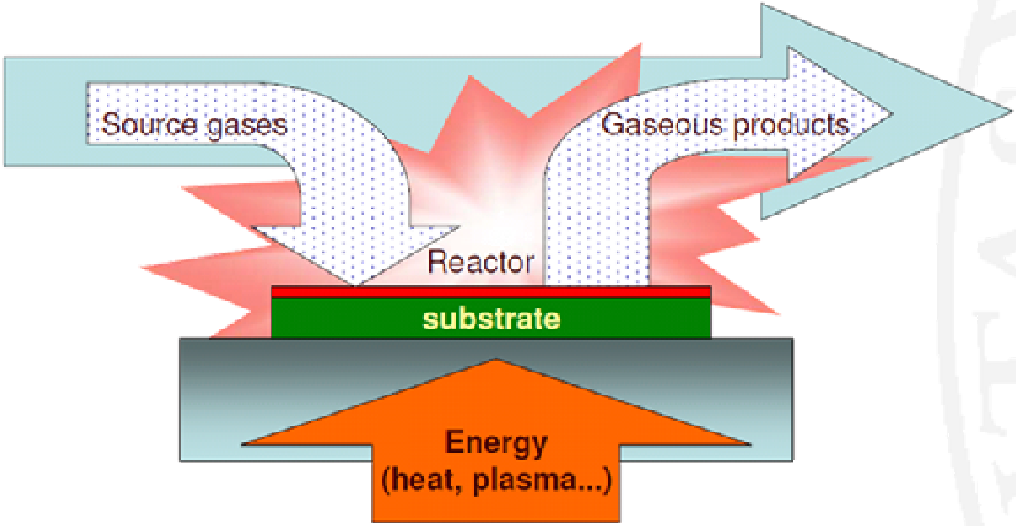
The frequency shift due to mass deposition may be correlated to the absolute mass deposited via the following equation:

$$\Delta m = \frac{\rho_q A_q N_q (F - F_q)}{F_q^2} = -C(F_q - F) = -C\Delta f$$

Where:

- ρ_q is the density of quartz,
- A_q is the area of resonance,
- N_q is a frequency constant for AT-cut quartz crystals
- (1.668 10^5 Hz cm),
- F_q is the frequency of quartz prior to deposition, and
- F is the frequency at any point during the deposition process.

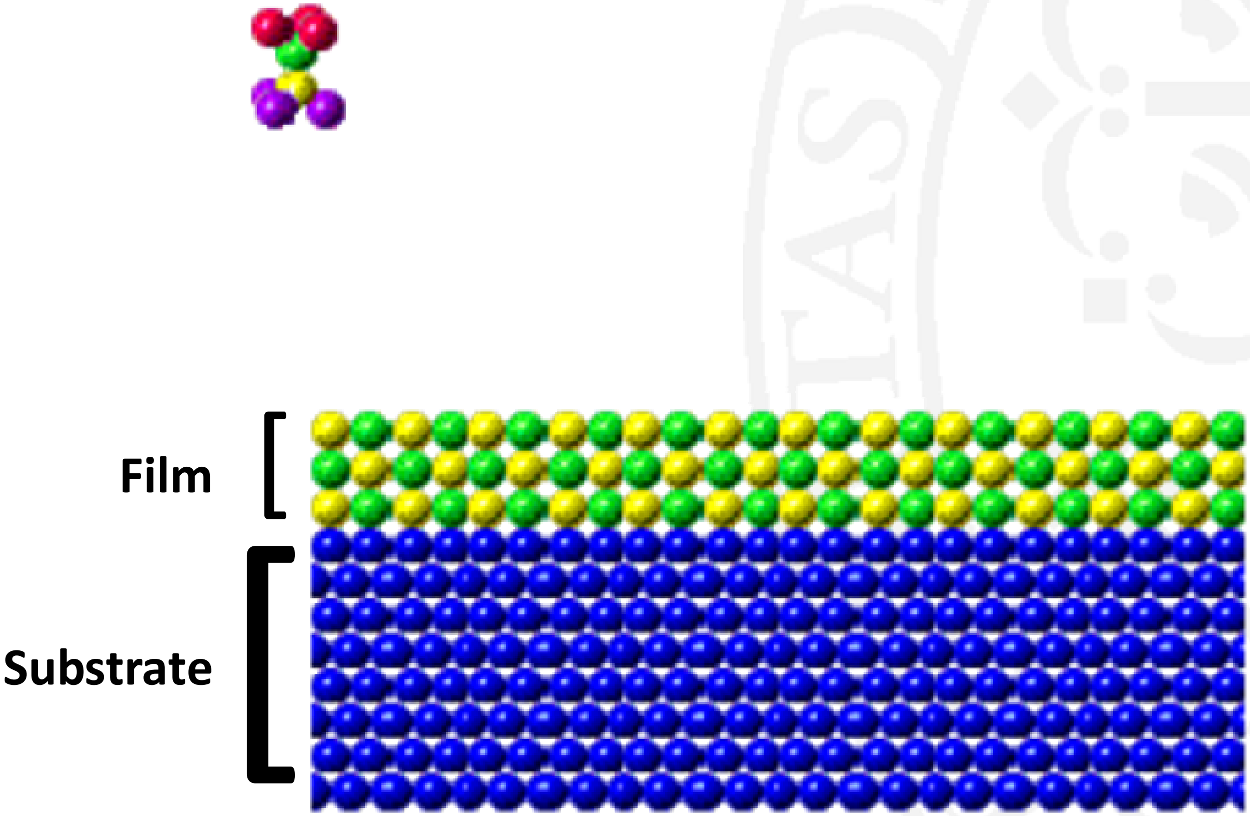
Chemical Vapor Deposition Techniques



- CVD : deposit film through chemical reaction and surface absorption.
- CVD steps:
  - Introduce reactive gases to the chamber.
  - Activate gases (decomposition) by heat or plasma.
  - Gas absorption by substrate surface .
  - Reaction take place on substrate surface, film firmed.
  - Transport of volatile byproducts away form substrate.
  - Exhaust waste.

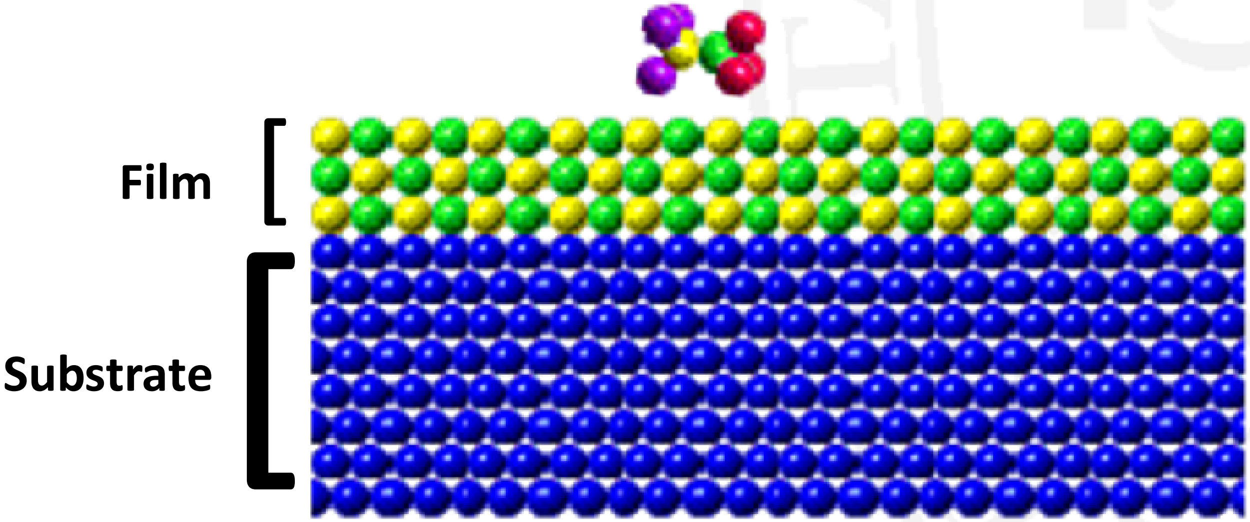
CVD: How it works

1.Vaporization and Transport;



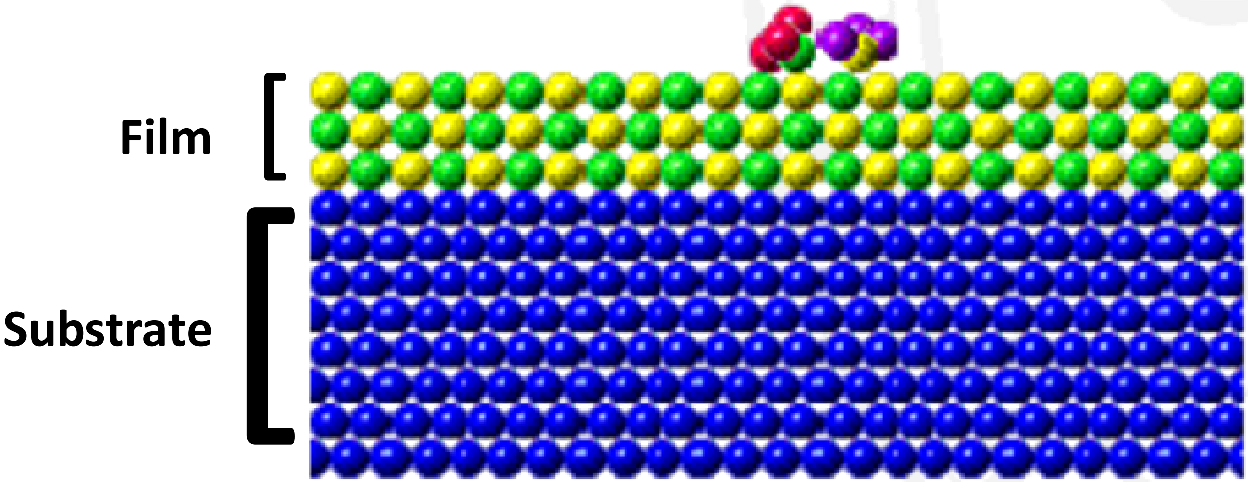
CVD: How it works

1. Vaporization and Transport;
2. Diffusion;



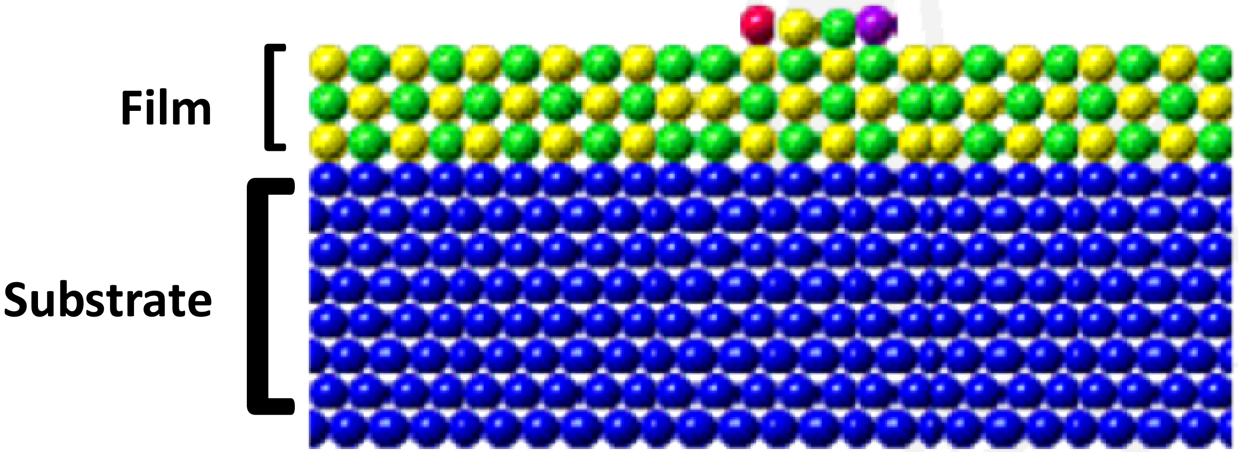
CVD: How it works

1.Vaporization and Transport;
2.Diffusion;
3.Absorption



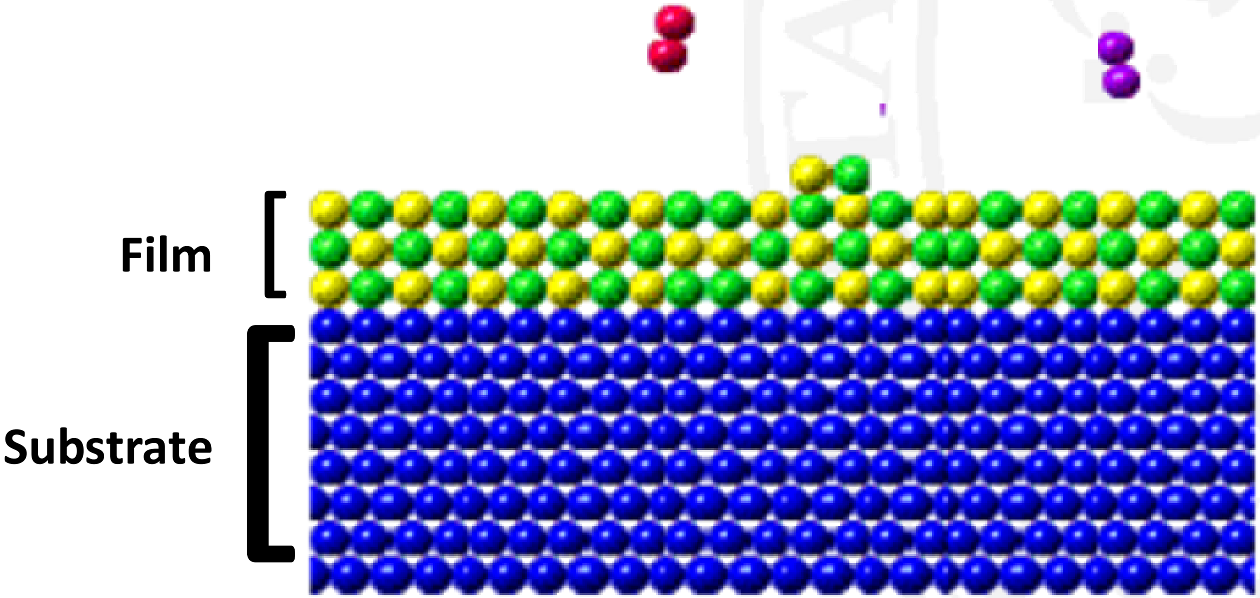
CVD: How it works

1.Vaporization and Transport;
2.Diffusion;
3.Absorption
4.Decomposition and incorporation on film



CVD: How it works

1. Vaporization and Transport;
2. Diffusion;
3. Absorption
4. Decomposition and incorporation on film
5. Expulsion of byproducts



CVD – Pros and Cons (as respect of PVD)

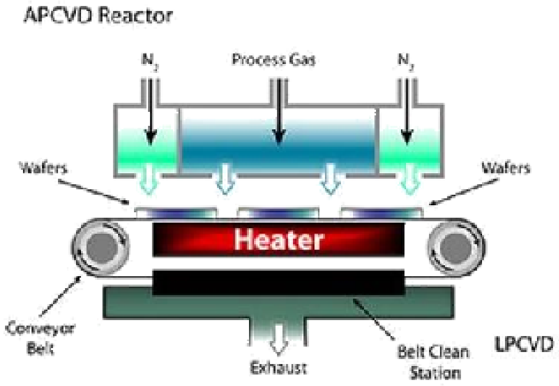
Advantages:

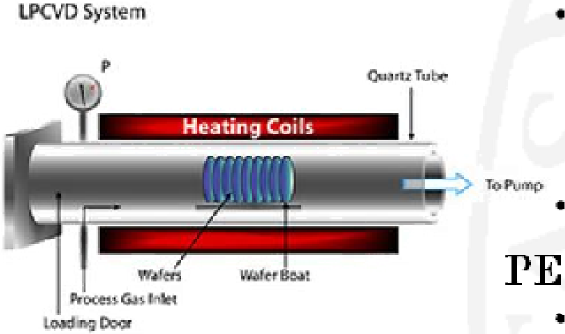
- High growth rates possible, good reproducibility.
- Can deposit materials which are hard to evaporate.
- Can grow epitaxial films. In this case also termed as "vapor phase epitaxy (VPE)". For instance, MOCVD (metal-organic CVD) is also called OMVPE (organo-metallic VPE).
- Generally better film quality, more conformal step coverage (see image below).

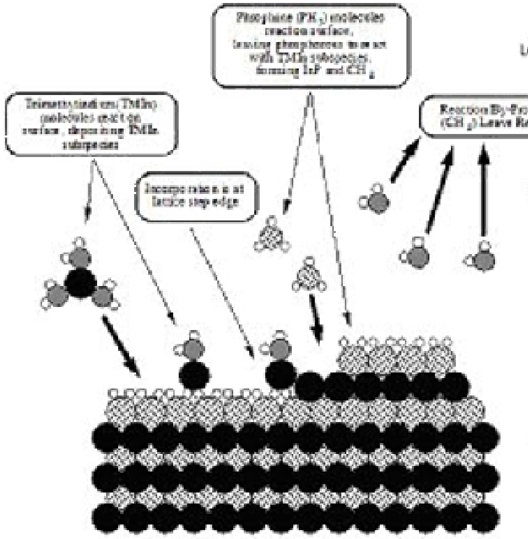
Disadvantages:

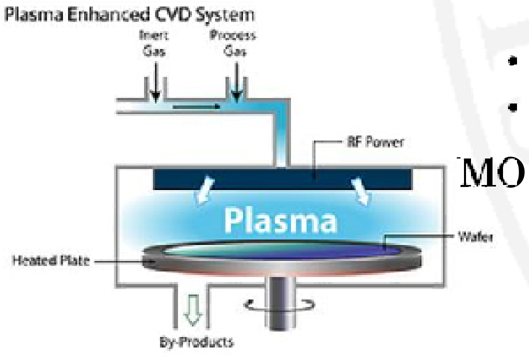
- High process temperatures.
- Complex processes, toxic and corrosive gasses.
- Film may not be pure (hydrogen incorporation…).

Types of CVD









APCVD (Atmospheric Pressure CVD),

- mass transport limited growth rate, leading to non-uniform film thickness.

LPCVD (Low Pressure CVD)

- Low deposition rate limited by surface reaction, so uniform film thickness (*many* Better film uniformity & step coverage and fewer defects
- Process temperature ≥500°C

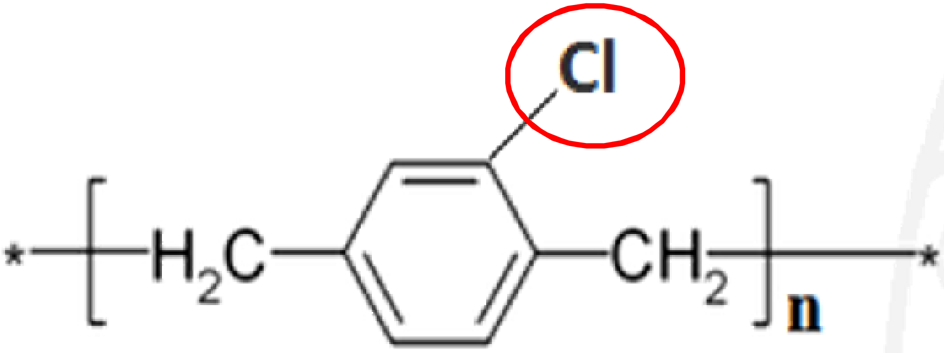
PECVD (Plasma Enhanced CVD)

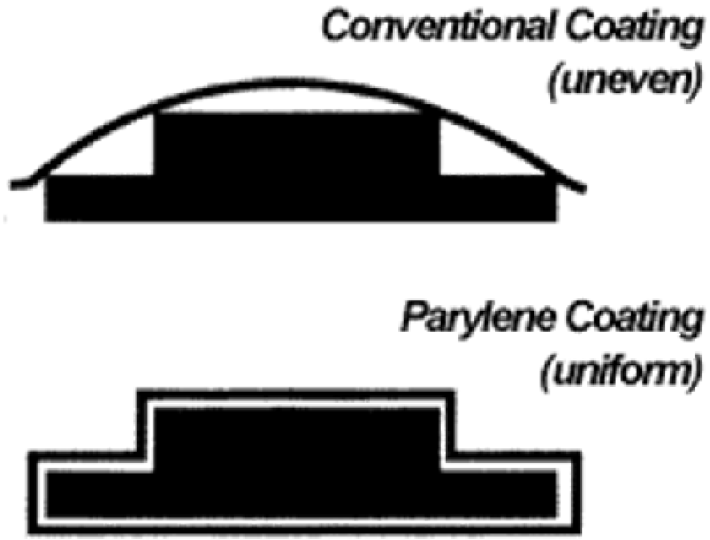
- Plasma helps to break up gas molecules: high reactivity, able to process at lower temperature and lower pressure (good for electronics on plastics).
- Film quality is poorer than LPCVD.
- Process temperature around 100 - 400°C.

MOCVD (Metal-organic CVD)

- epitaxial growth for many optoelectronic devices with III-V compounds for solar cells, lasers, LEDs, photo-cathodes and quantum wells.

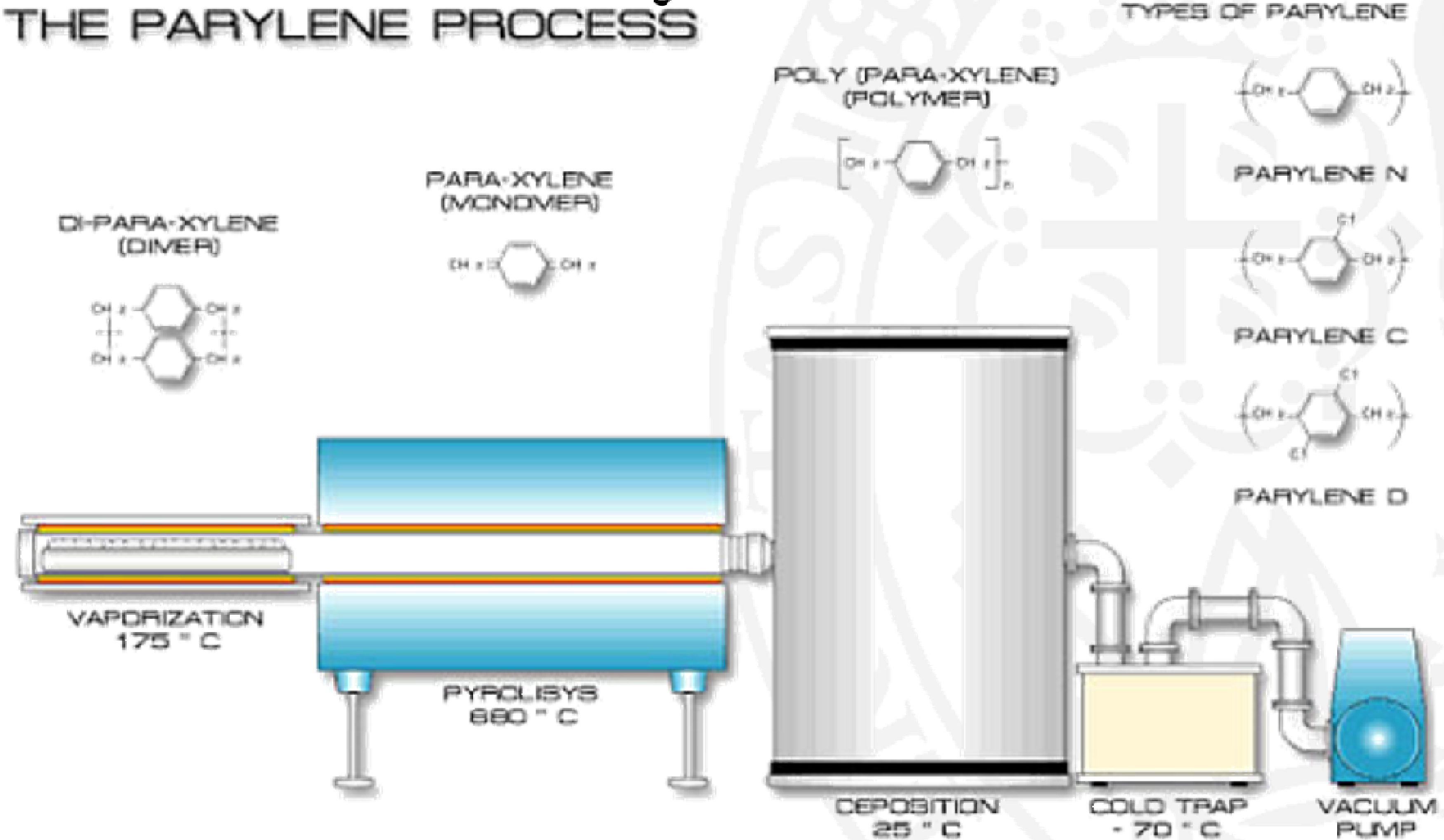
CVD for organic materials: Parylene C



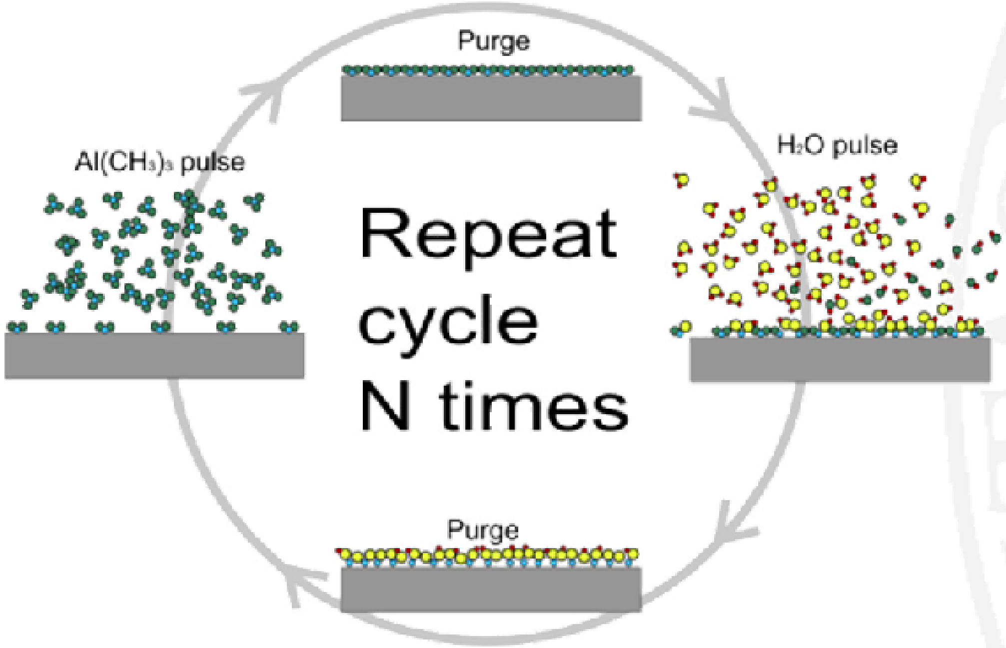


- Parylene is a common name for a class of molecules named poly(para xylylenes)
- There are many kind of Parylene; the most common for electronic applications in Parylene C

CVD for organic materials: Parylene C

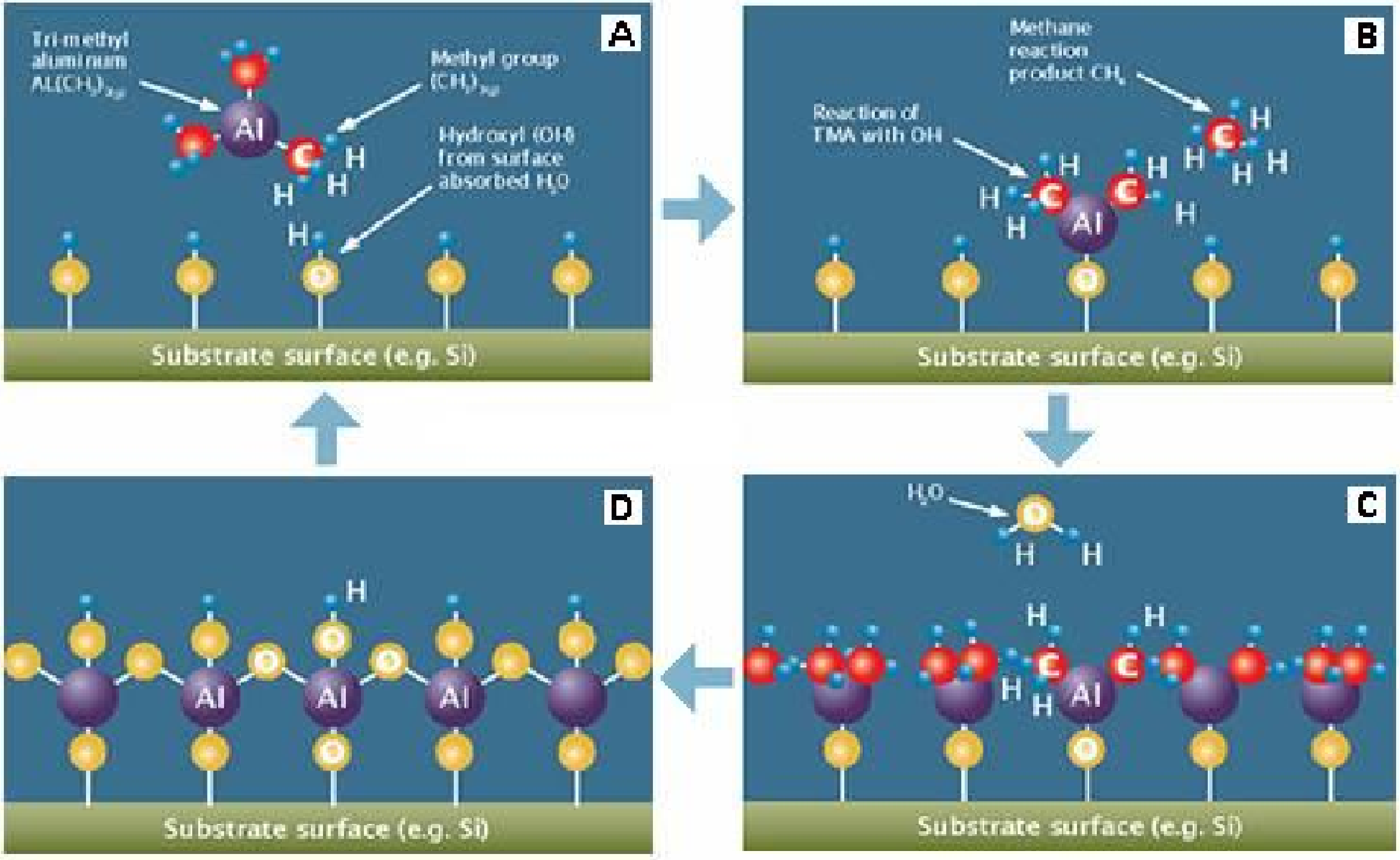


Atomic Layer Deposition (ALD)

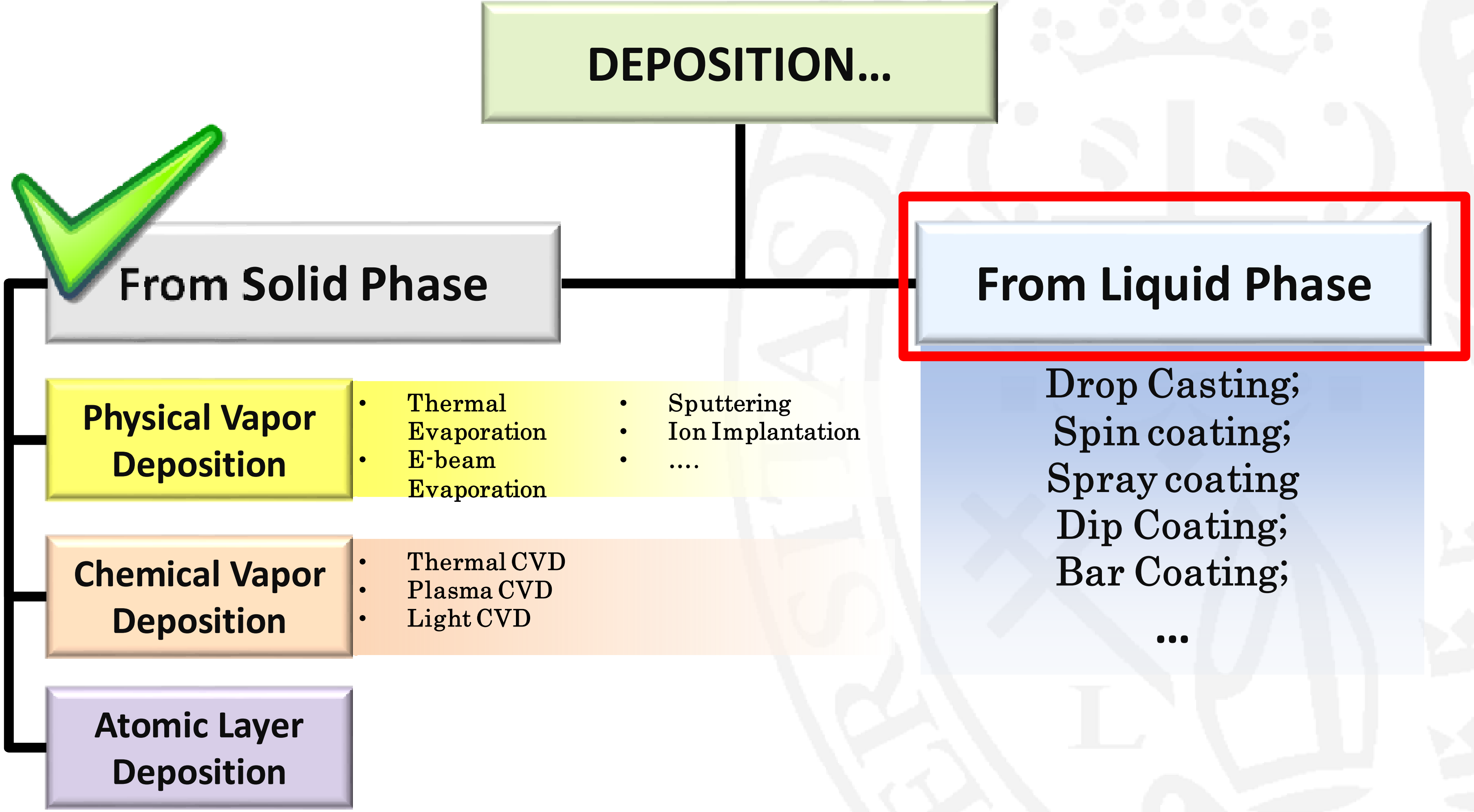


- ALD is a method of applying thin films to various substrates with **atomic scale precision**.
- Similar in chemistry to chemical vapor deposition (CVD), except that the **ALD reaction breaks the CVD reaction into two half-reactions**, keeping the **precursor materials separate** during the reaction.
- ALD film growth is **self-limited** and based on surface reactions, which makes achieving atomic scale deposition control possible.
- By keeping the precursors separate throughout the coating process, **atomic layer thickness control of film grown can be obtained as fine as atomic/molecular scale per monolayer.**

ALD: the example of Aluminum Oxide



Deposition Techniques (Reprise)

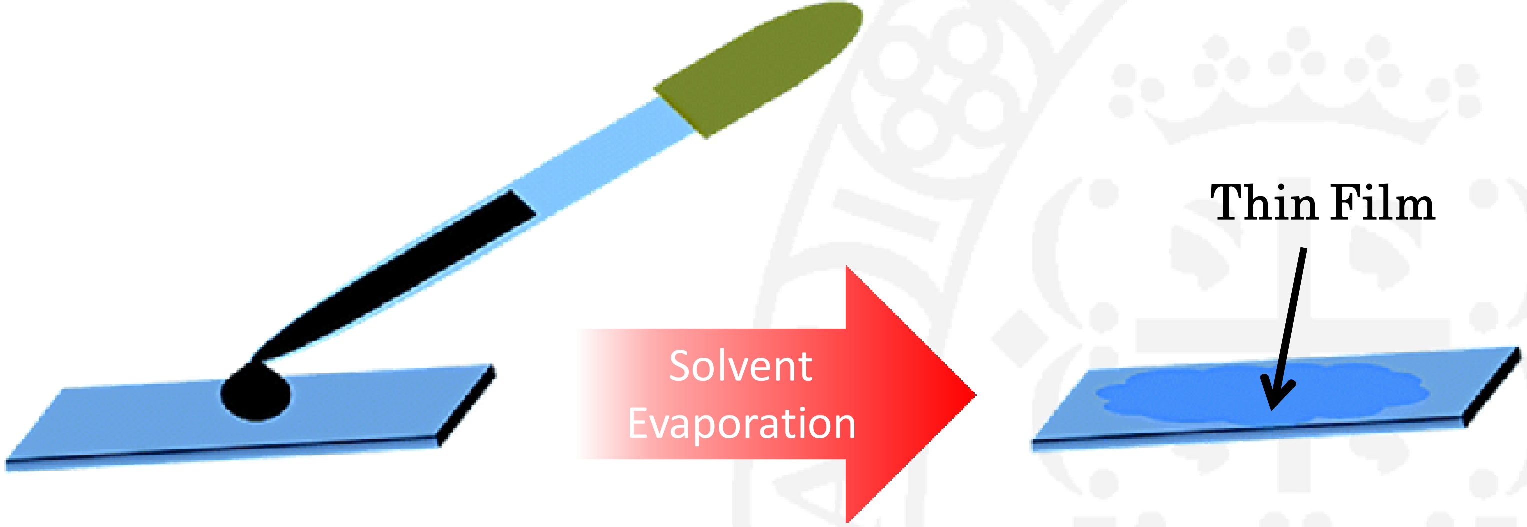


DEPOSITION…

- **From Solid Phase**
  - **Physical Vapor Deposition**
    - Thermal Evaporation
    - E-beam Evaporation
    - Sputtering
    - Ion Implantation
    - ….
  - **Chemical Vapor Deposition**
    - Thermal CVD
    - Plasma CVD
    - Light CVD
  - **Atomic Layer Deposition**
- **From Liquid Phase**

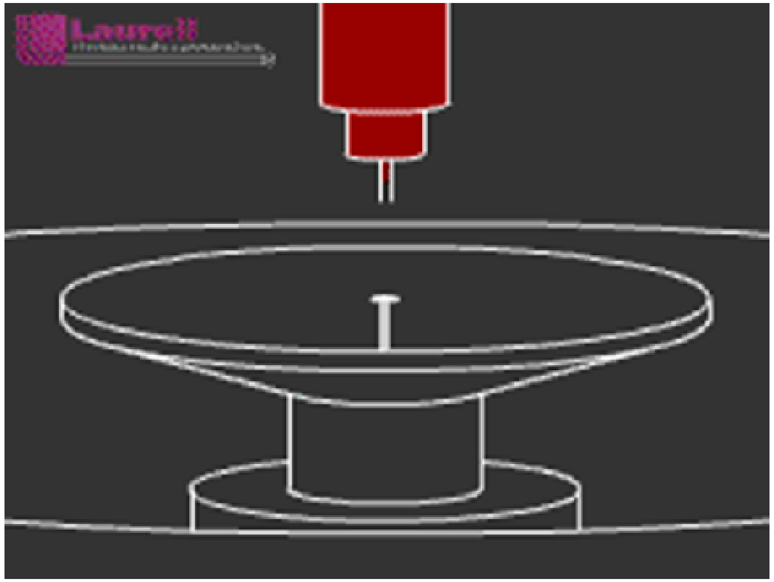
Drop Casting;
Spin coating;
Spray coating
Dip Coating;
Bar Coating;
…

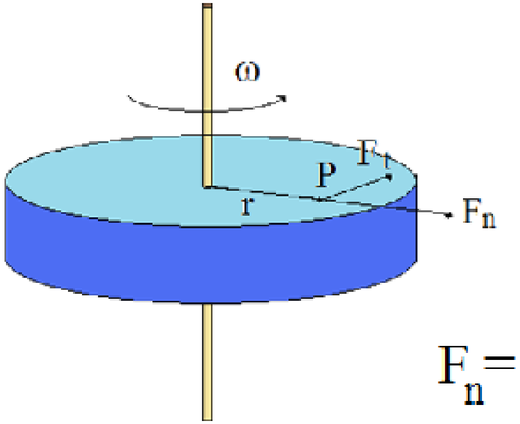
Drop casting



- The easiest technique ever!
- A certain amount of solution containing the material to be deposited (solute) is dropped onto the substrate (preferably a plane one);
- Solvent evaporates, thus bringing to the formation of the thin film.
- Although quite easy, it is the reference technique for the deposition of several kinds of materials (and in particular organic semiconductors) and the basics for further deposition methods by liquid phase
- Not easy to control film characteristics, they depends on the solution employed (kind of solvent, concentration of solute), on the surface energy of the substrates, on the temperature, …

Spin coating

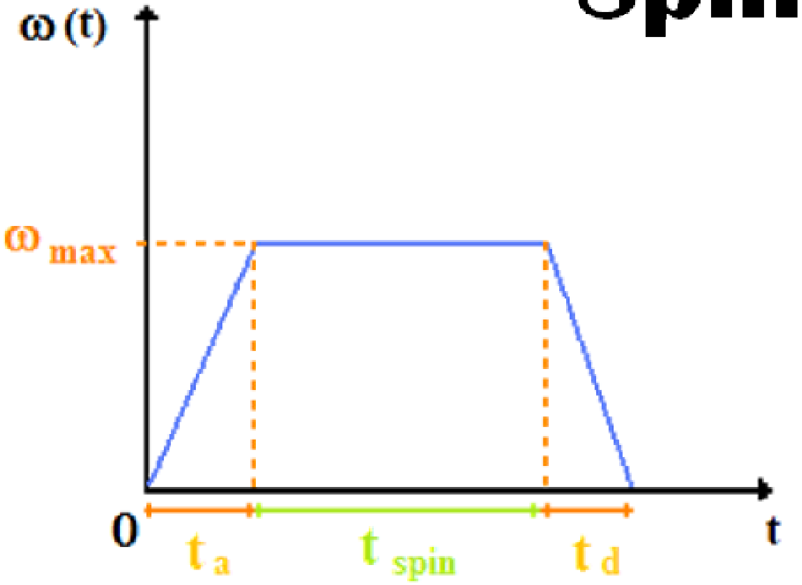


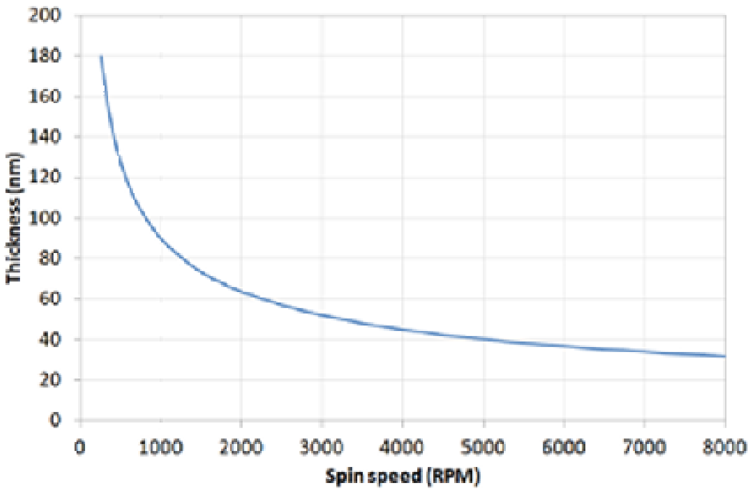


$$F_n = F_{cf} = -k\omega^2 r$$

- Used for obtaining uniform, thin films from liquid phase;
- Based on the principle of **centrifugal force**:
  - a certain amount of liquid is deposited in the center of the substrate, located over a rotating plate (spinner);
  - In each point of the substrates, the liquid is subjected to the centrifugal force, so it starts to move away from the center.
  - According to the amount of material initially deposited, to its chemical/physical properties, to the surface properties of the substrate and to the spinner settings, different film thicknesses can be obtained.

Spin coating

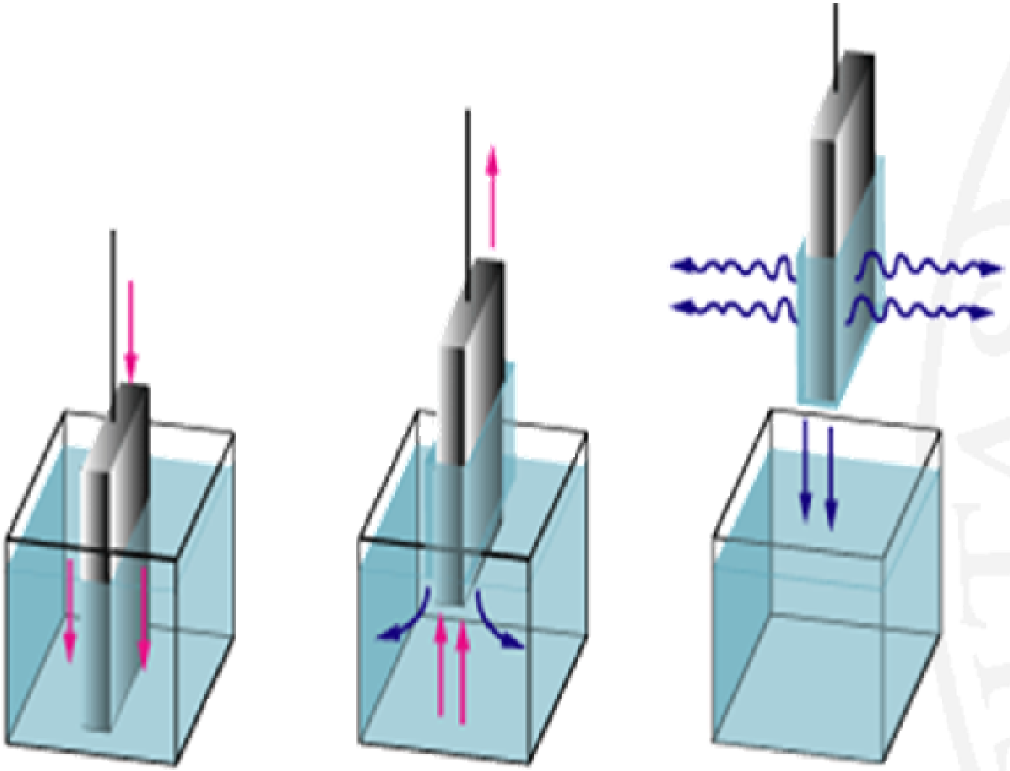




- Normally, several parameters can be set in spinners:
  - t_a = acceleration time;
  - t_{spin} = spinning time;
  - t_d = deceleration time;
  - ω_{max} = maximum angular speed.
- The film thickness is a function of spin speed according to the equation:

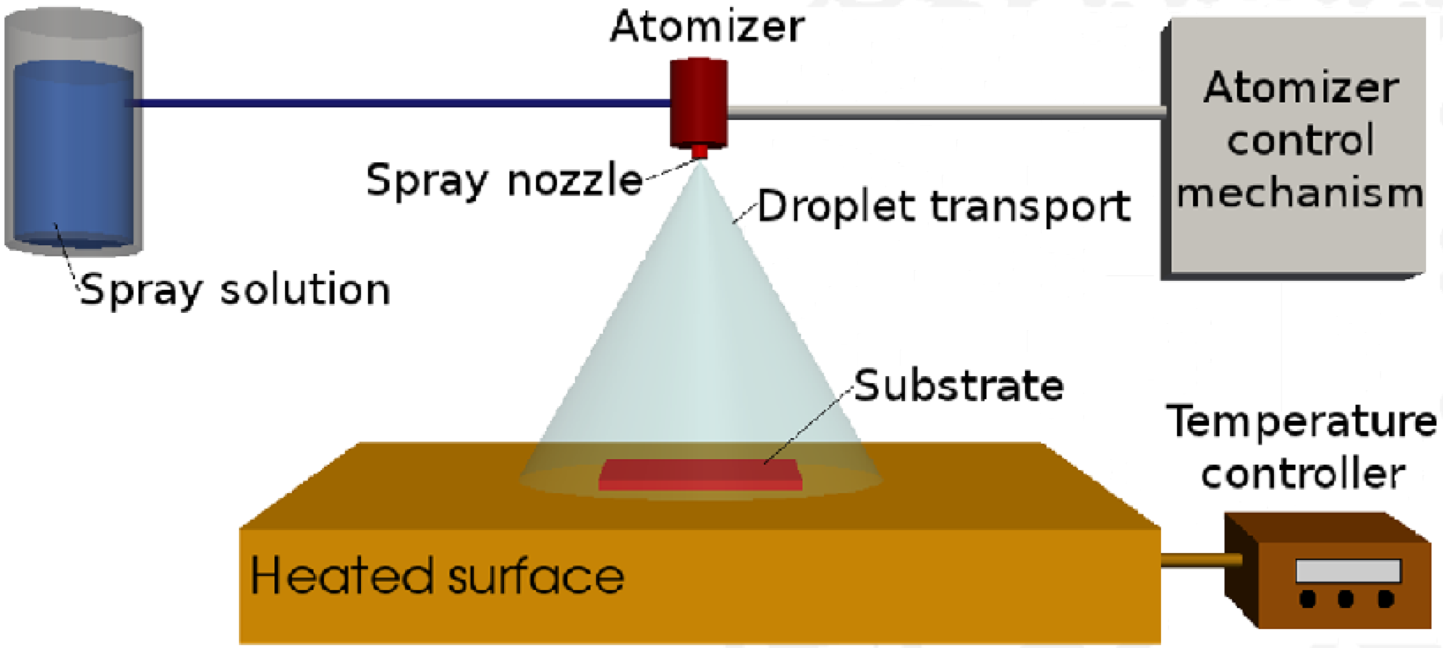
$$d(\omega) \propto \frac{1}{\sqrt{\omega}}$$

Dip Coating



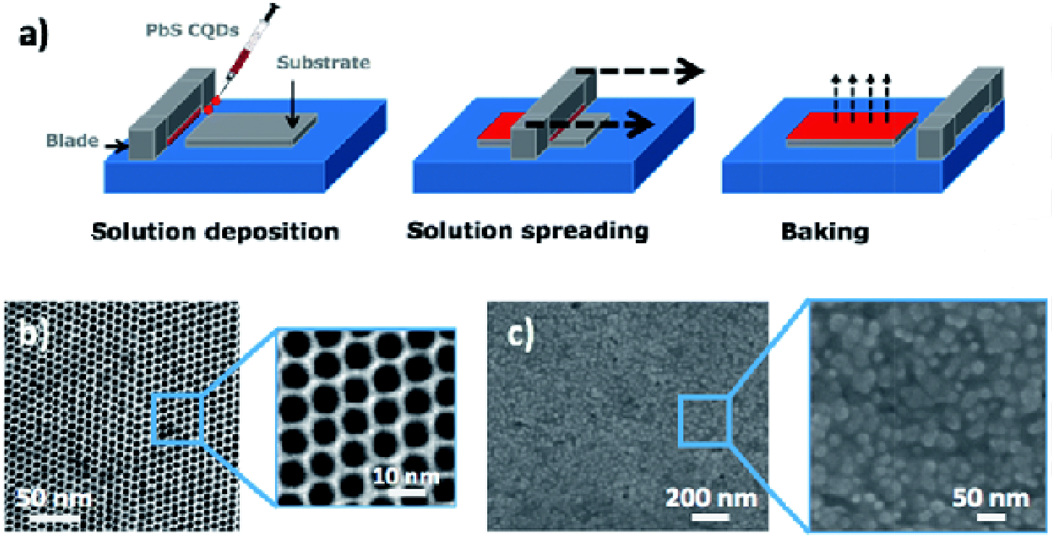
- It is an alternative technique to spin coating, in particular when a 3D coating would be realized and/or the substrate is not planar;
- Five stages:
  - **Immersion:** The substrate is immersed in the solution of the coating material at a constant speed (preferably jitter-free).
  - **Start-up:** The substrate has remained inside the solution for a while and is starting to be pulled up.
  - **Deposition:** The thin layer deposits itself on the substrate while it is pulled up. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating (faster withdrawal gives thicker coating material).
  - **Drainage:** Excess liquid will drain from the surface.
  - **Evaporation:** The solvent evaporates from the liquid, forming the thin layer.

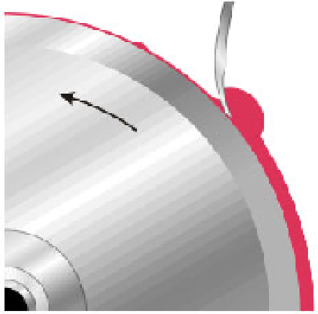
Spray Coating



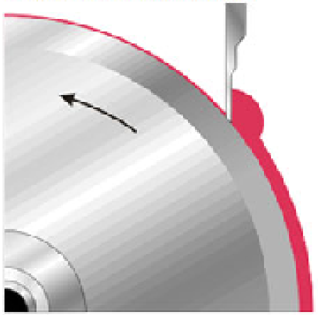
- Another coating technique, alternative to spin coating;
- It allows conformal coating

Blade coating





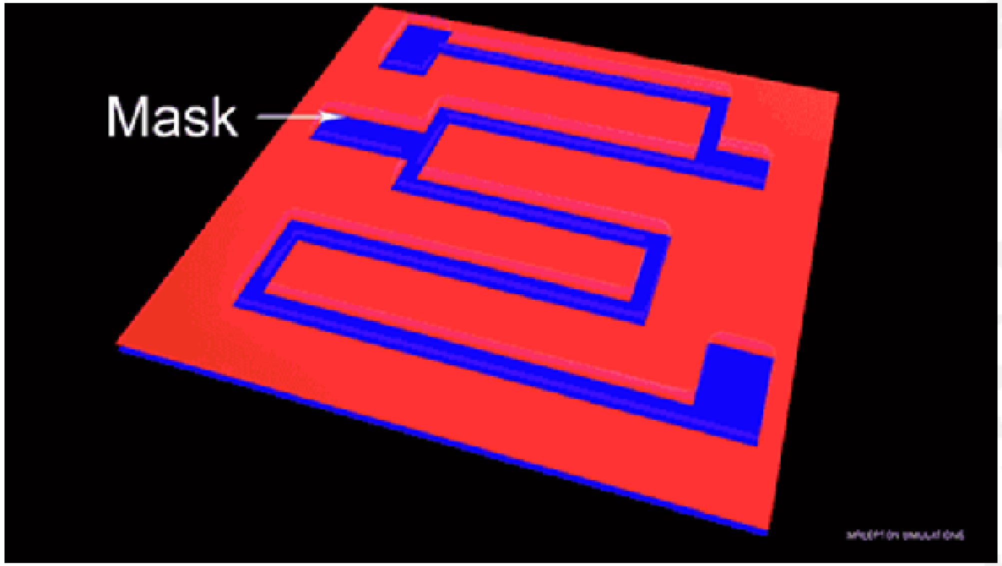
As the ink hydroplanes and builds up behind the blade, the blade starts to flex. This allows ink to drool under this portion of the blade and transfer to the plate and to the substrate.



By stiffening the base of the blade, the blade holds its position, allowing for a correct shearing (metering) of the ink. This results in minimal or no UV spitting.

- Blade coating, also known as knife coating or doctor blading, is a processing method for the fabrication of large area films on rigid or flexible substrates. The well-defined thickness is mainly controlled by the gap size of the blade to the surface.
- There are different kind of blade coating, according to the fact that substrates is fixed and blade is moving, or viceversa, or both are moving, on the fact that the substrate is planar or not,…

Patterning Techniques

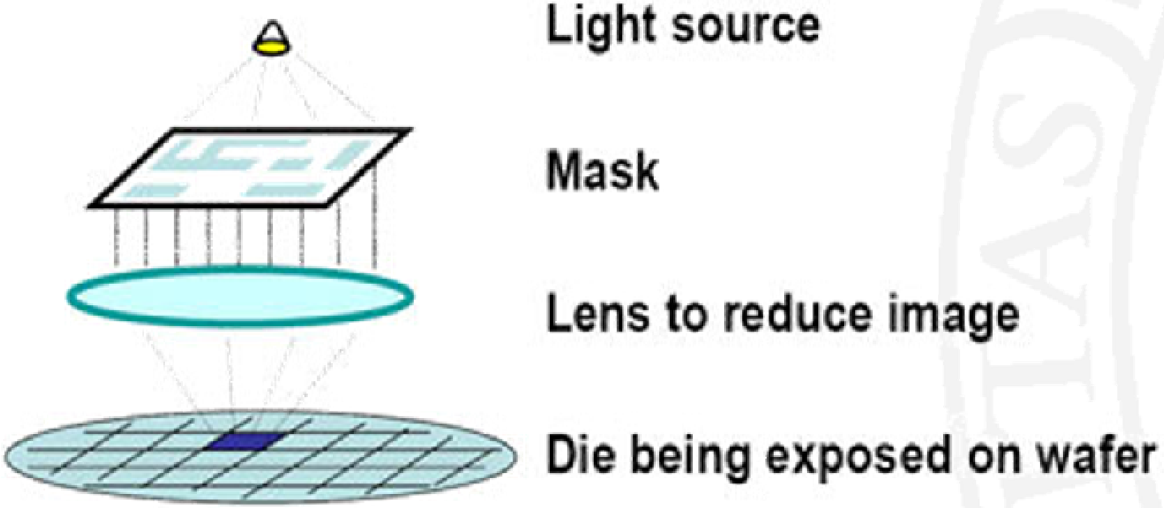


- Material patterning after deposition is a fundamental activity for obtaining the geometrical features of devices and circuits;
- Commonly, patterning techniques are **subtractive** methods, i.e. the patterns are obtained by removing an excess of material from the surface.
- The most common class of such techniques are **lithographic processes**

Lithographic processes

- Lithography means «stone-writing»
- It's a class of technique originally conceived for art, based on the different hydrophobicity of water and oil.

Photolithographic processes



- It is the most common class of lithographic processes;
- It is based on te employment of:
  - A photosensitive material (**photoresist**);
  - A **photomask**;
  - An **excitation source** (photonic)
- A **lens system** can be eventually used.

Photolithography: Photoresist

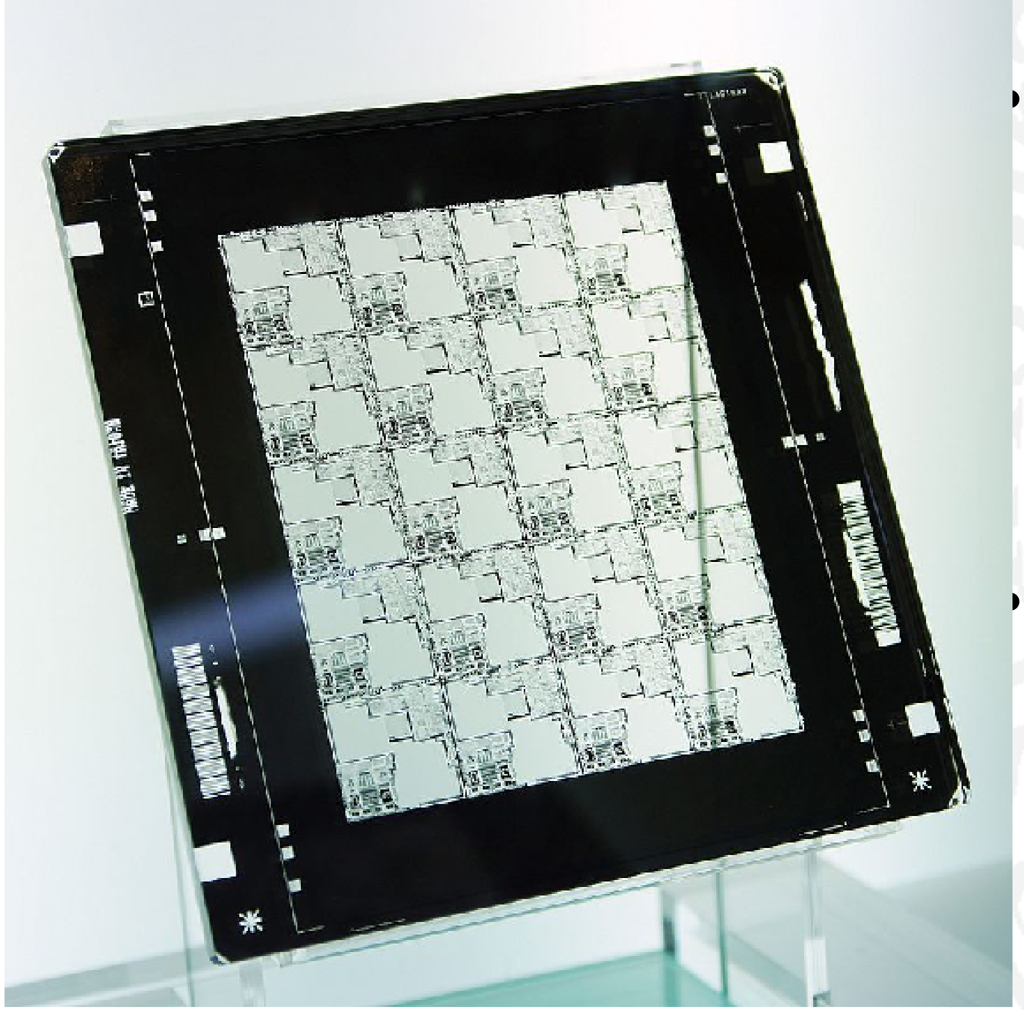
- A photoresist is a material that changes its chemo-physical properties if exposed/not exposed to a specific light excitation
- Photoresist can be:
  - **Positive**: it is cross-linked by heating treatments; chemical bonds can be destroyed by the excitation, thus making the parts of the photoresist exposed to it soluble in a specific solution (developer)
  - **Negative**: excitation determines the cross-linking of the photoresist, so the exposed parts becomes not soluble in the developer

Photolithography: Sources

Source	λ (nm)	Max. Output (mJ/pulse)	Frequency (pulses/s)	Common Nomenclature
Hg lamp	436			G line
Hg lamp	405			H line
Hg lamp	365			I line
KrF (laser)	248	10	2000	DUV
ArF (laser)	193	10	2000	193 DUV
F_2 (laser)	157	40	500	

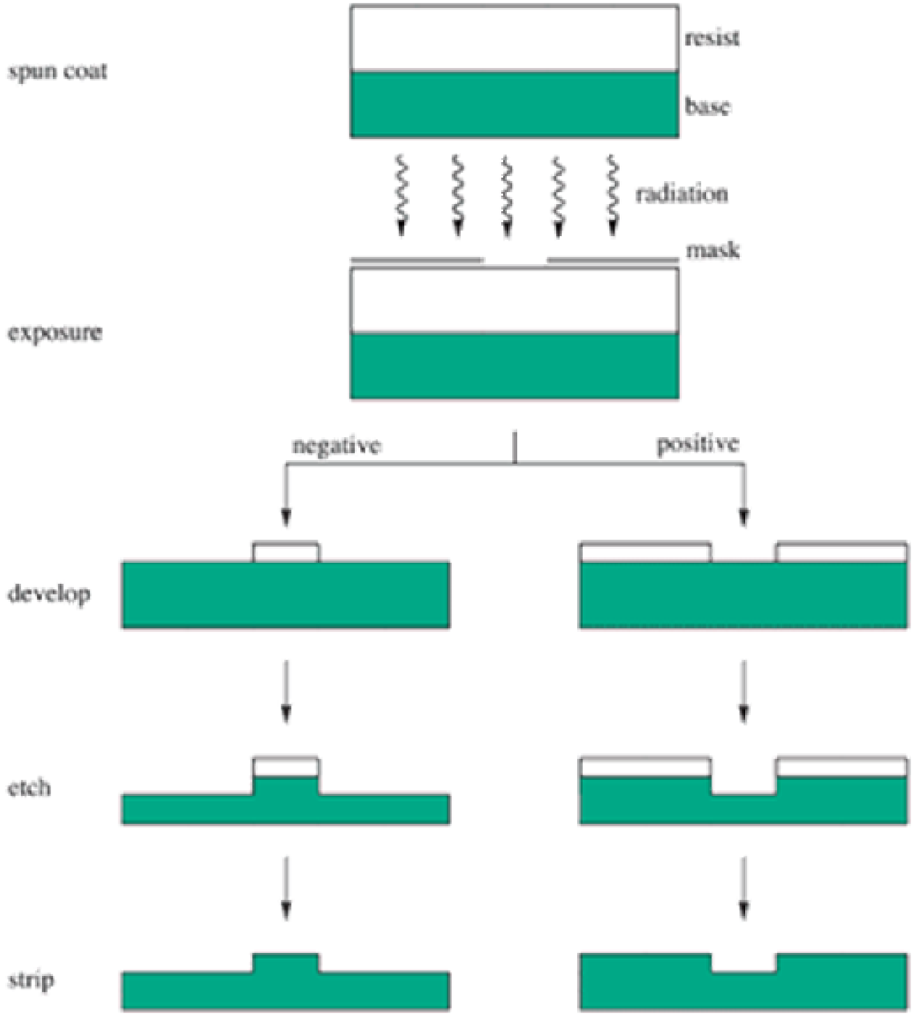
- Light sources are employed for the photoresist exposure;
- The source is chosen according to the required resolution.

Photolithography: Photomaks



- A **photomask** is an opaque plate with holes or transparencies that allow light to shine through in a defined pattern.
- They can be fabricated on different substrates (quartz, plastic, glass)

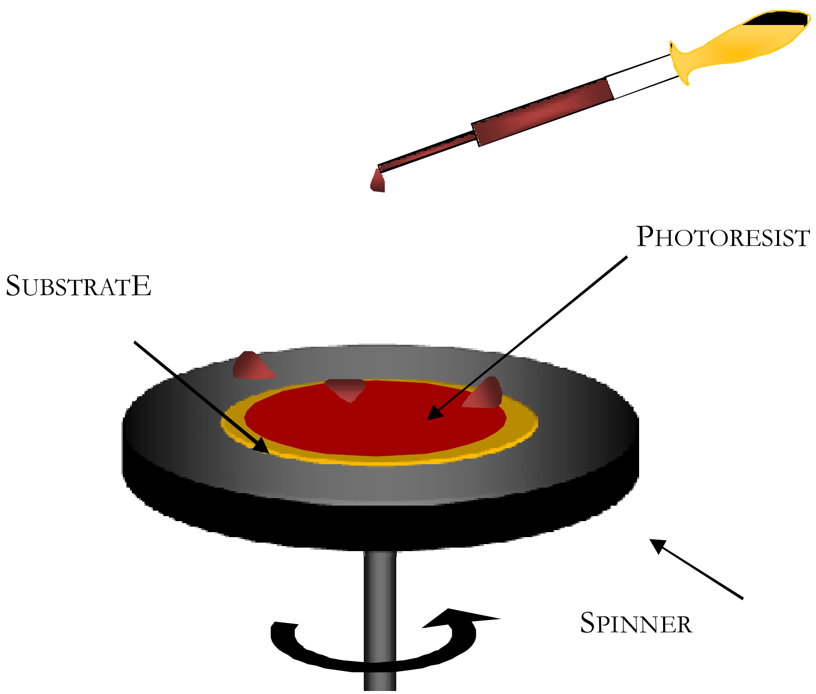
Photolithography: basics steps



A photolithographic process consists on 5 steps:

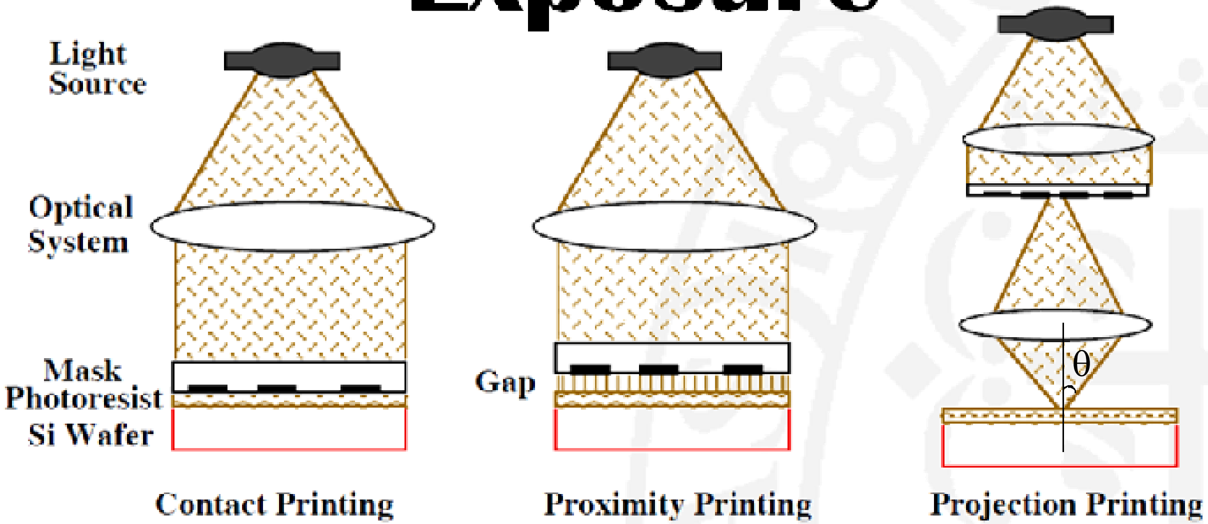
- Deposition of the photoresist
- Exposure of the sample to excitation source;
- Development
- Etching
- Stripping.

Photoresist deposition



- Photoresist is generally deposited by means of spin coating, or, in some cases, by spray coating;
- After the deposition, the photoresist is cured at low temperature to obtain cross-linking (positive) or solvent evaporation (negative).

Exposure

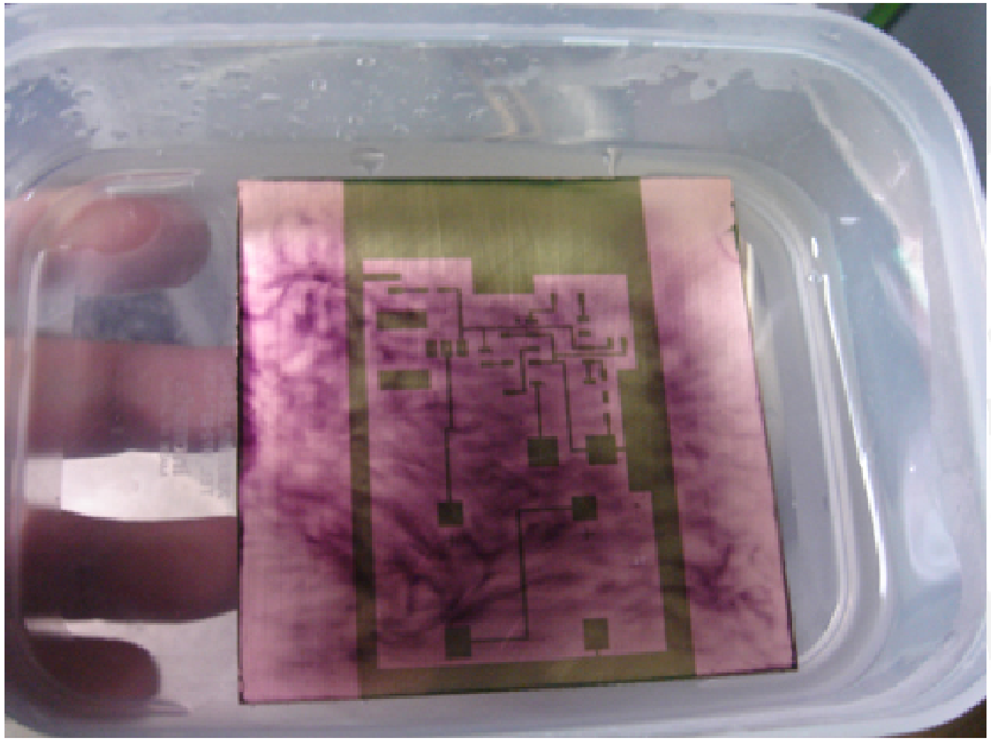


Exposure can be perfomed in different ways:

- **Contact**, if the mask is in contact with the photoresist;
  - 1:1 with the mask → resolution is those of the mask → high resolution masks are costly!
  - Contamination/scratiching of the sample
- **Proximity**, if the mask is near to the surface
  - 1:1 with the mask → resolution $\sqrt{\ }$, where g is the distance between the mask and the substrate
  - Prevent contamination
- **Projection**, if lens are used to project the pattern from the mask to the photoresist obtaining a relative increase of resolution.
  - A resolution higher than the one of the mask can be obtained (4x-5x); resolution is limited by λ according to the relationship

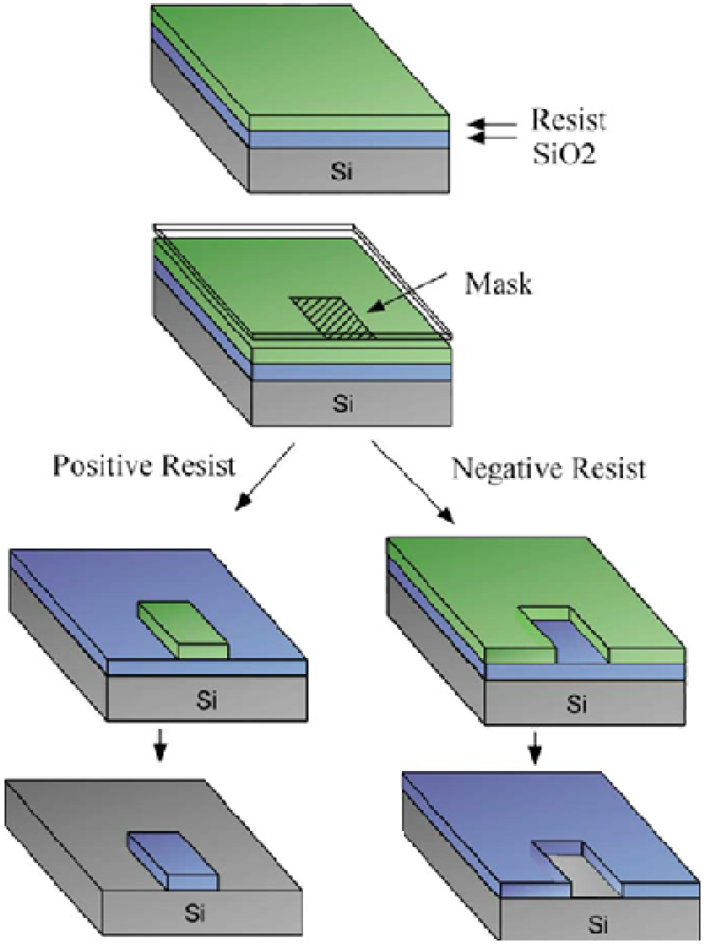
$$r \propto \frac{\lambda}{n \sin \theta}$$

Development



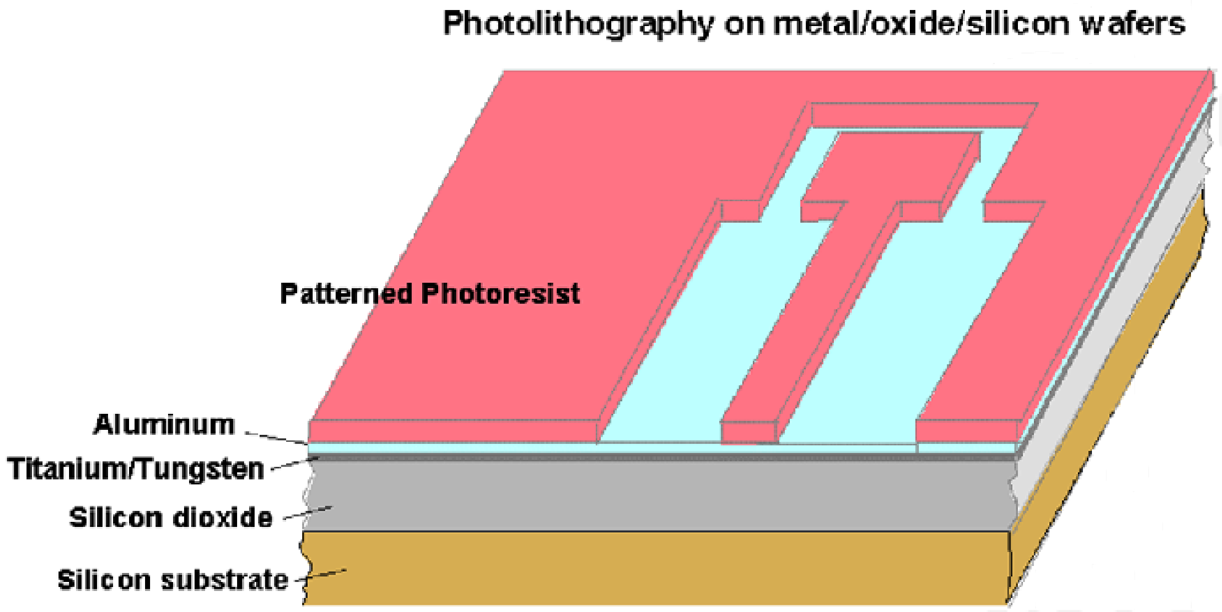
- Development is performed by immersing the substrate into a developer;
- Commercial photoresist have they own developer
- Typically, a low concentrated NaOH solution is employed

Exposure+Development: positive vs. negative photoresists



- A positive photoresist is used when the same shape of the mask would be transferred onto the substrate, as the cross-linked part is the one shadowed by the mask and it is not removed by developer;
- A negative photoresist is used when the shape complementary to the one in the mask would be transferred to the substrate, as the cross-linked part is the one not covered by the mask.

Chemical Etching and Stripping

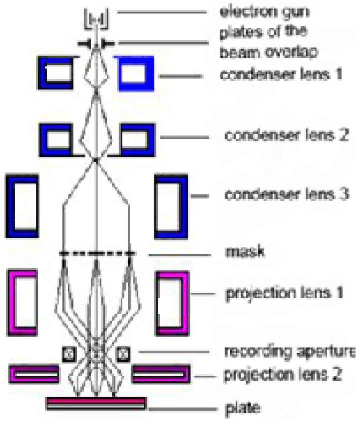


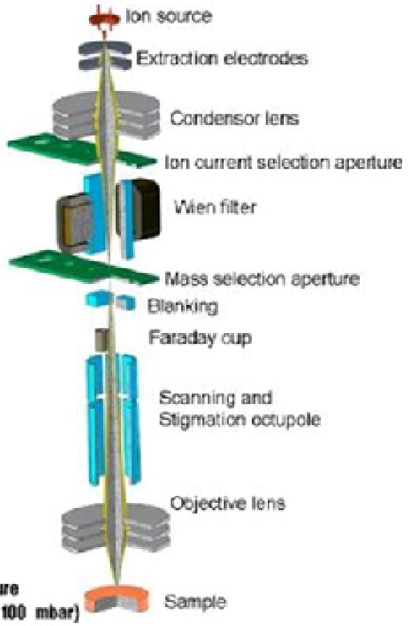
- After development, the cross-linked photoresist protect the underlying substrate;
- Some parts are exposed, and can be chemically removed using an etching solution;
- Each material has its own etcher!
- After chemical etching, the residual photoresist is removed with a solvent (generally acetone).

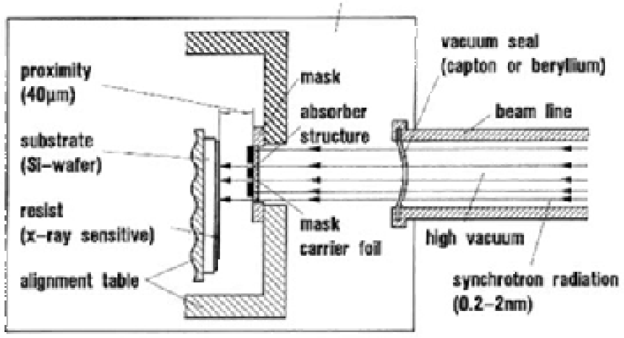
Kind of photolithographic processes

- Independently from the employed source, the resolution of a photolithographic process is limited by the wavelength λ
- To enhance resolution, it is necessary to decrease λ (the smaller is λ, the smaller is the minimum element resolved)
  - – UV radiation → λ~100nm
  - – High power laser → λ~10nm

Kind of photolithographic processes

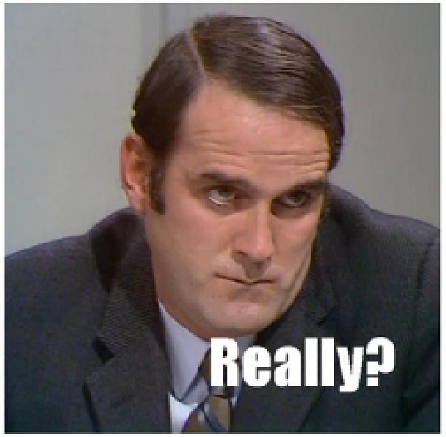


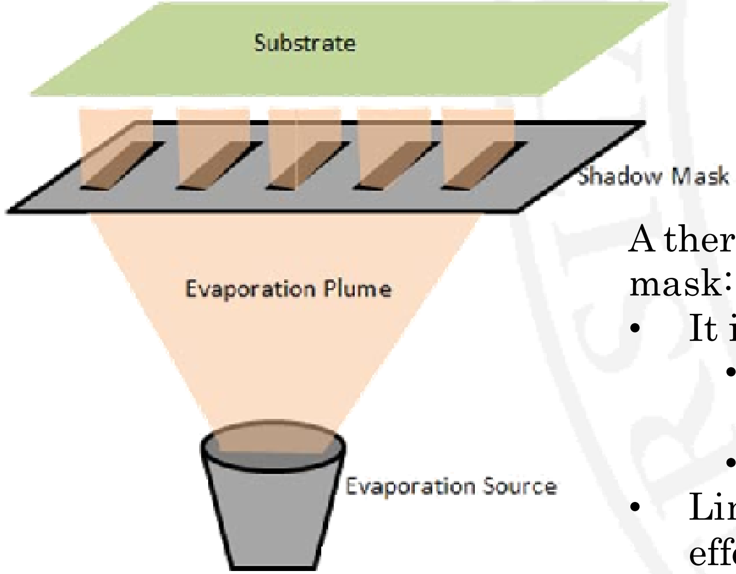




- To skip the limits of light radiation, electrons and ions are used:
- E-beam lithography:
  - $\lambda \sim 10^{-13}$ m→ resolution is not limited by wavelength, but by the photoresist (~20nm);
  - Can be maskless (numerical control of the beam)
- Ion-beam lithography:
  - Ions are heavier than electrons, so backscattering and diffraction are limited;
  - Possibly maskless (computer-controlled beam)
- X-Rays lithography:
  - Synchrotron radiation →λ~0.2-2nm
  - Very high resolution (15nm)
  - No lenses needed

Deposition+Patterning





A thermal evaporation through a shadow mask:

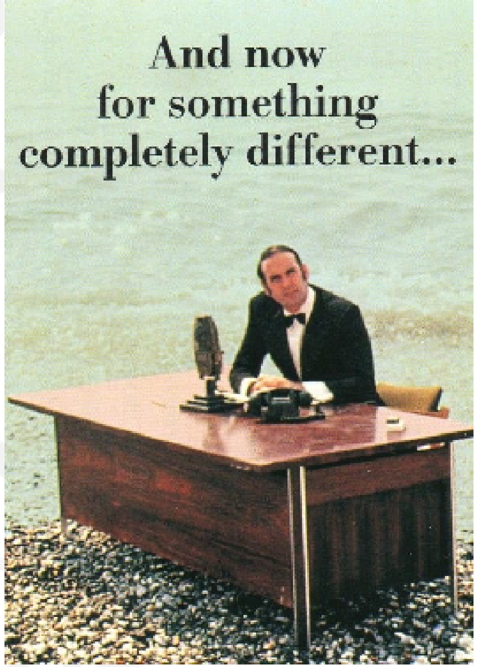
- It is used much more than you think!
  - Low resultion patterns (instead of photolithography);
  - Metal contacts on top of OSC;
- Limitations: low resultions, shadowing effects

Deposition+Patterning


Substrate

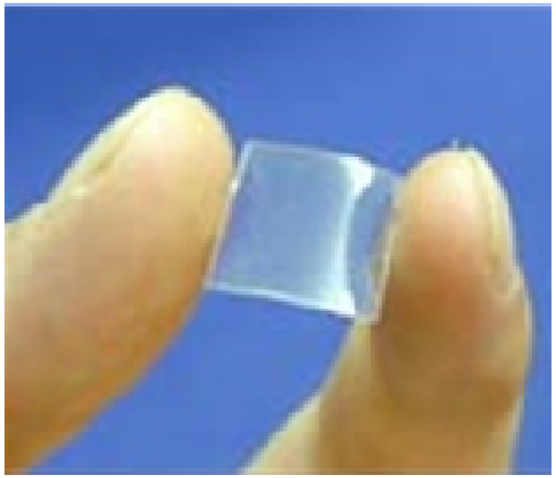
Deposition+Patterning?

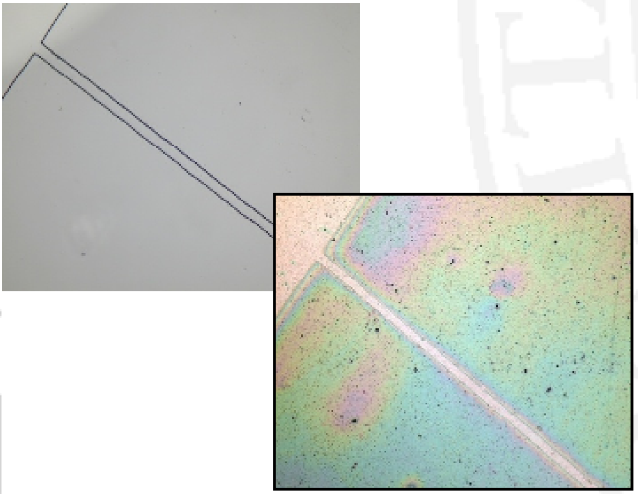
Patterned Substrate

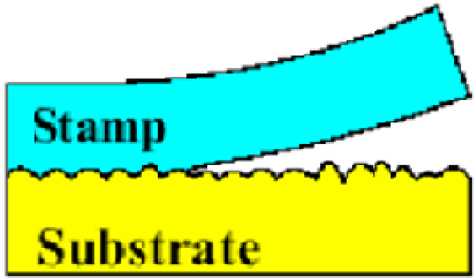


Can we make something more taking advantage of the intrinsic properties of organic materials?

Soft Lithography

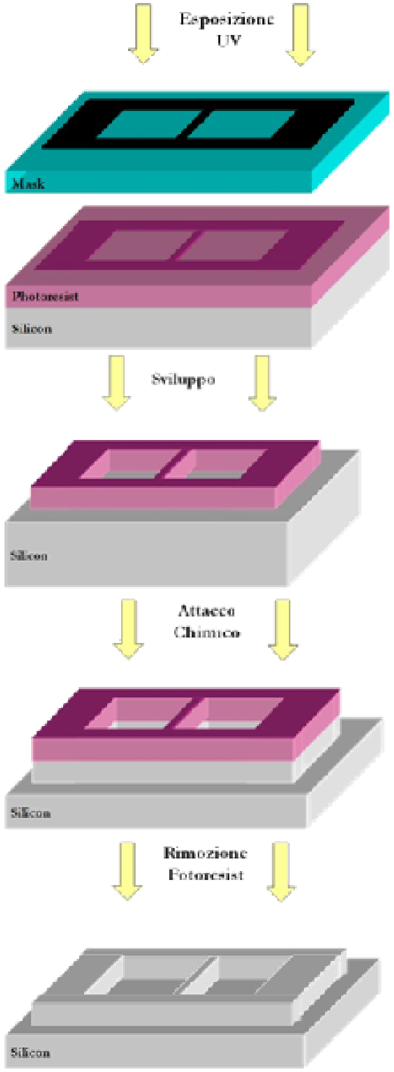


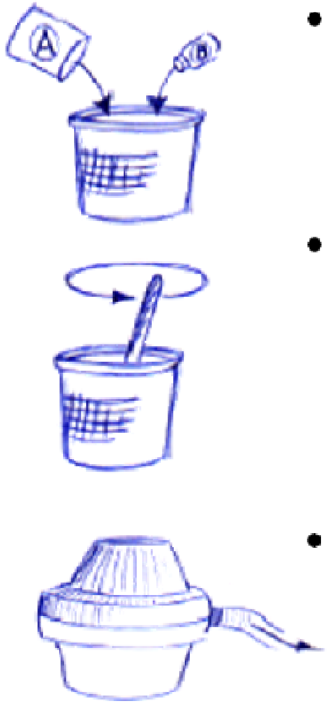




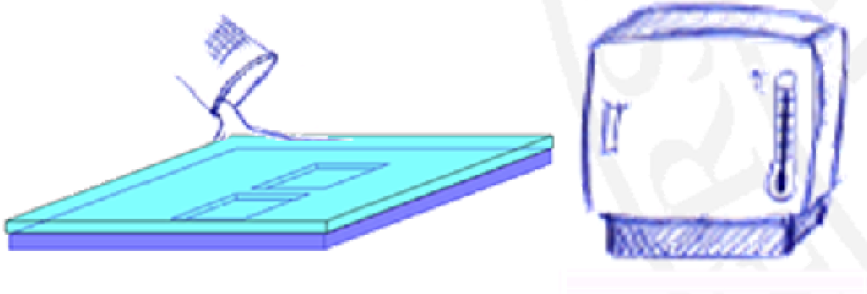
- A class of techniques that allow transferring materials using stamps.
- Stamps are generally made by elastomers, so make a conformal contact with the surface
- Stamps report the pattern to be transferred

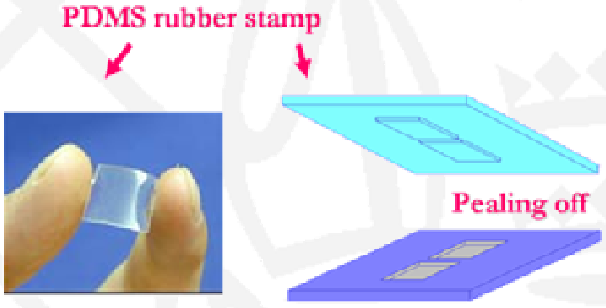
Soft Lithography: Stamp fabrication



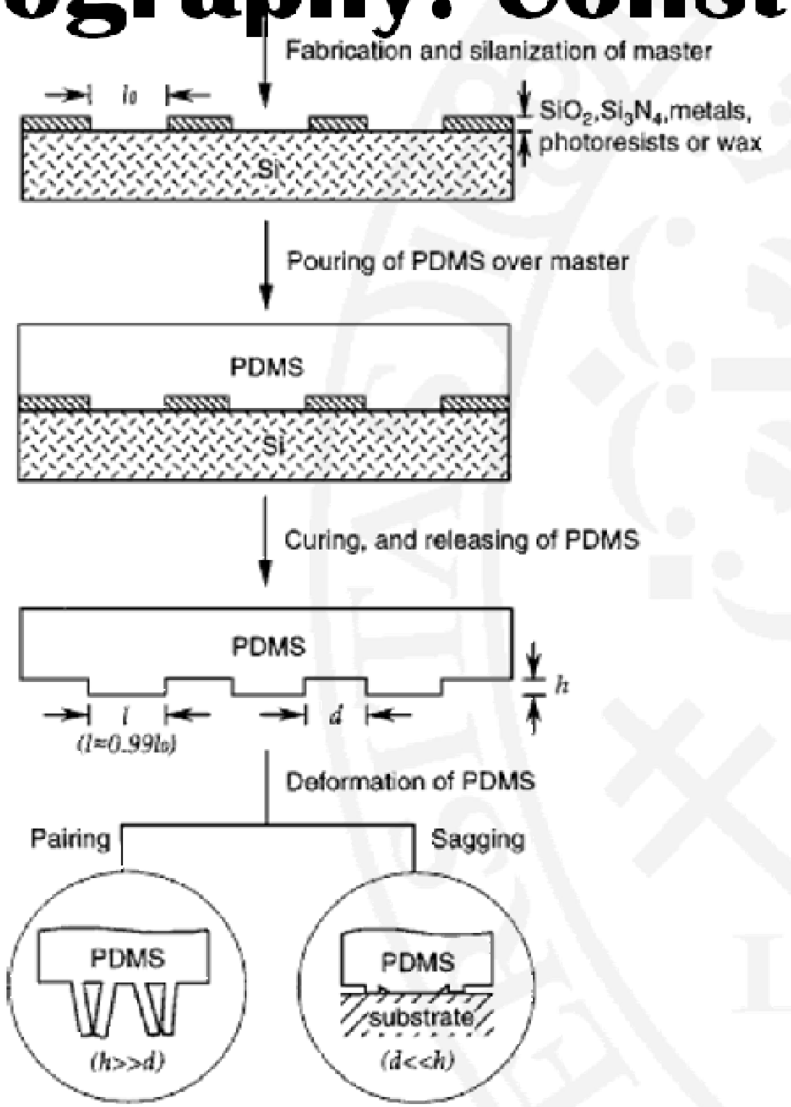


- The master is generally fabricated on silicon using a standard photolithographic process;
- The stamp is made by an elastomer (e.g., PDMS), which is prepared and transferred on the master, cured in over and then peeled off the master.
- One master can be used more than 100 times, each stamp more than 1000!





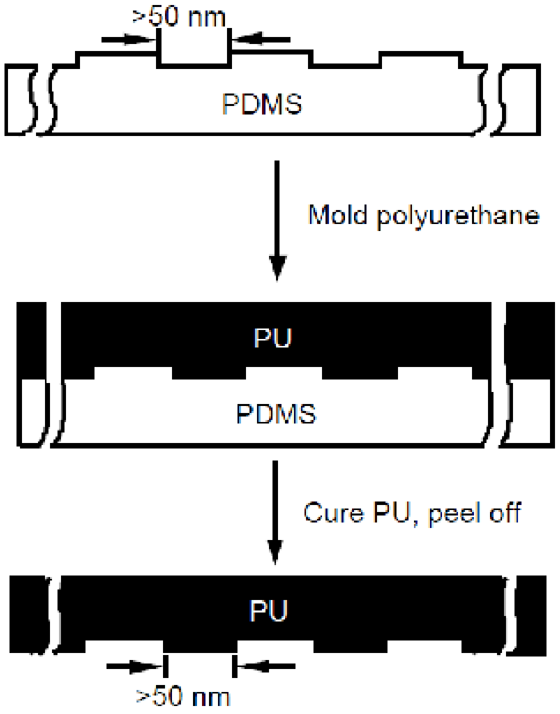
Soft Lithography: Constraints

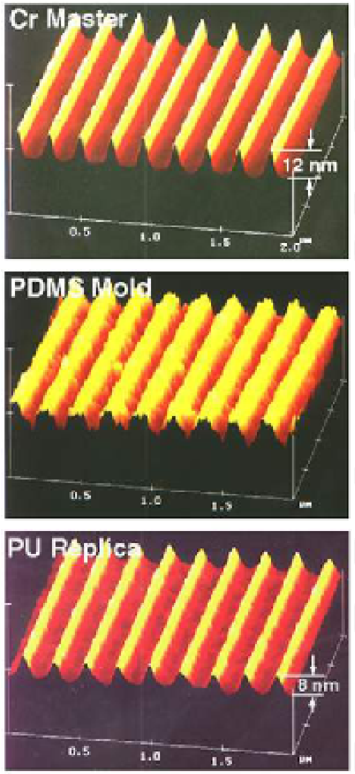


Soft Lithography: Techniques

- Replica Molding (REM)
- Microtransfer Molding (μTM)
- MicroMolding in Capillaries (MIMIC)
- Nano Imprint Lithography (NIL)
- MicroContact Prining (μCP)

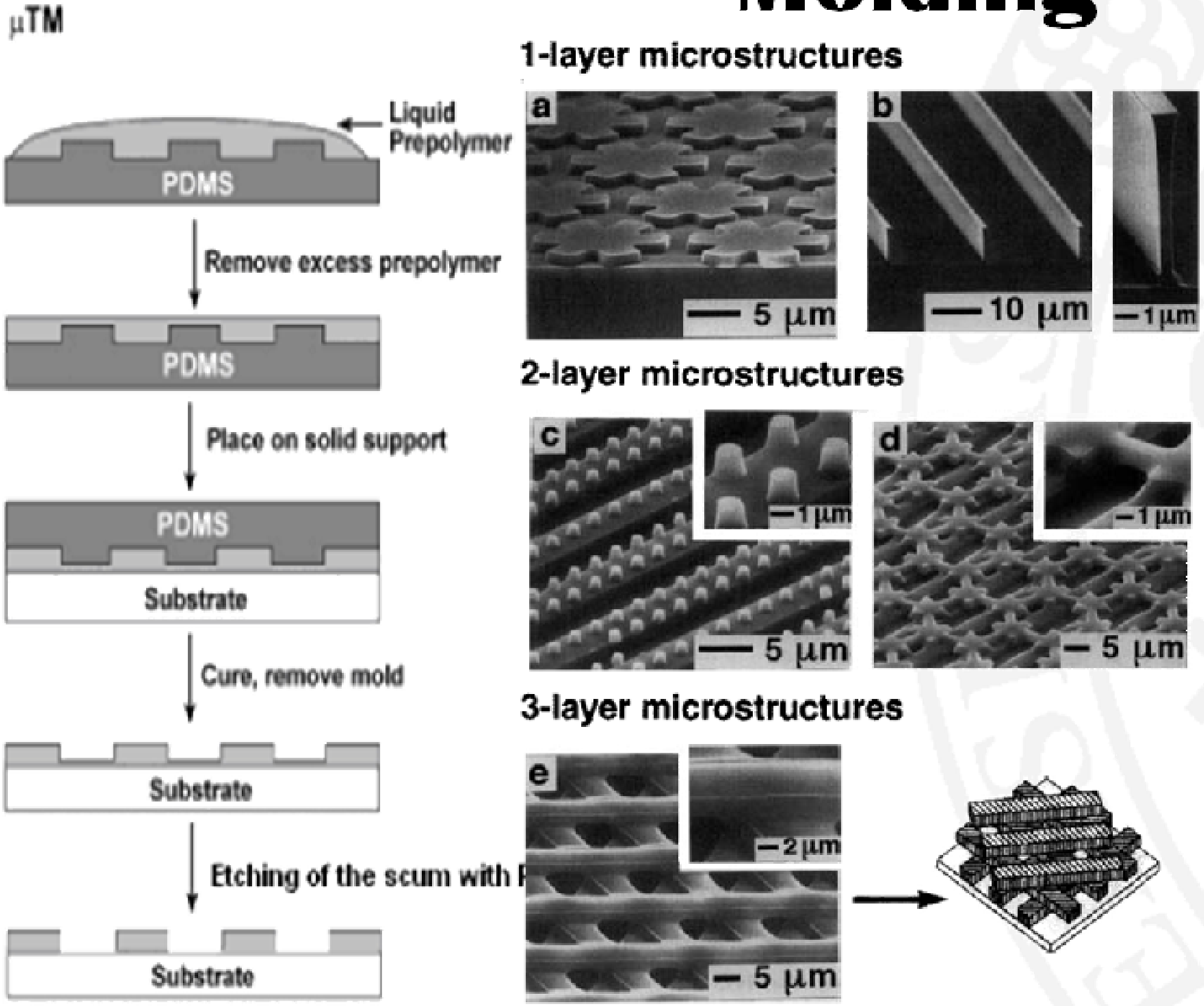
Soft Lithography: Replica Molding





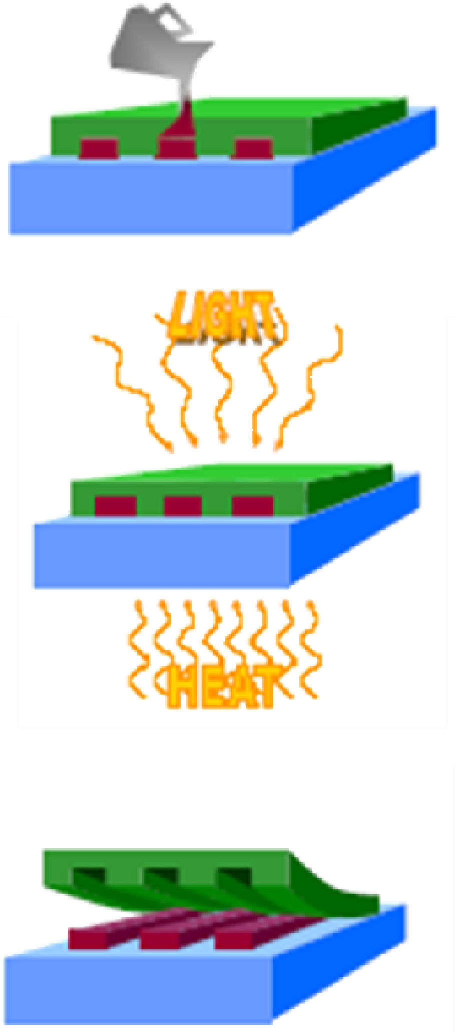
- Used for obtaining a 3D structure which is the negative of the stamp.
- Therefore, they are a rubber version of the master!

Soft Lithography: Micro Transfer Molding



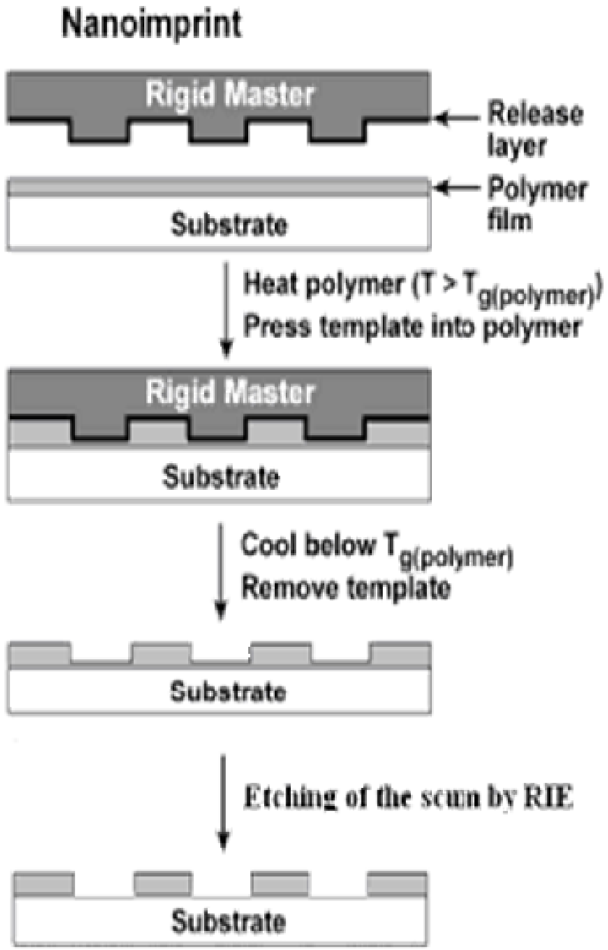
- Used for transfer a 3D structure on a substrate;
- A prepolymer is deposited onto the stamp;
- The stamp is placed on the substrate;
- After curing, the stamp can be removed while the polymer remain on the substrate;
- The transferred structure is the negative of the stamp.

Soft Lithography: Micro Molding in Capillaries



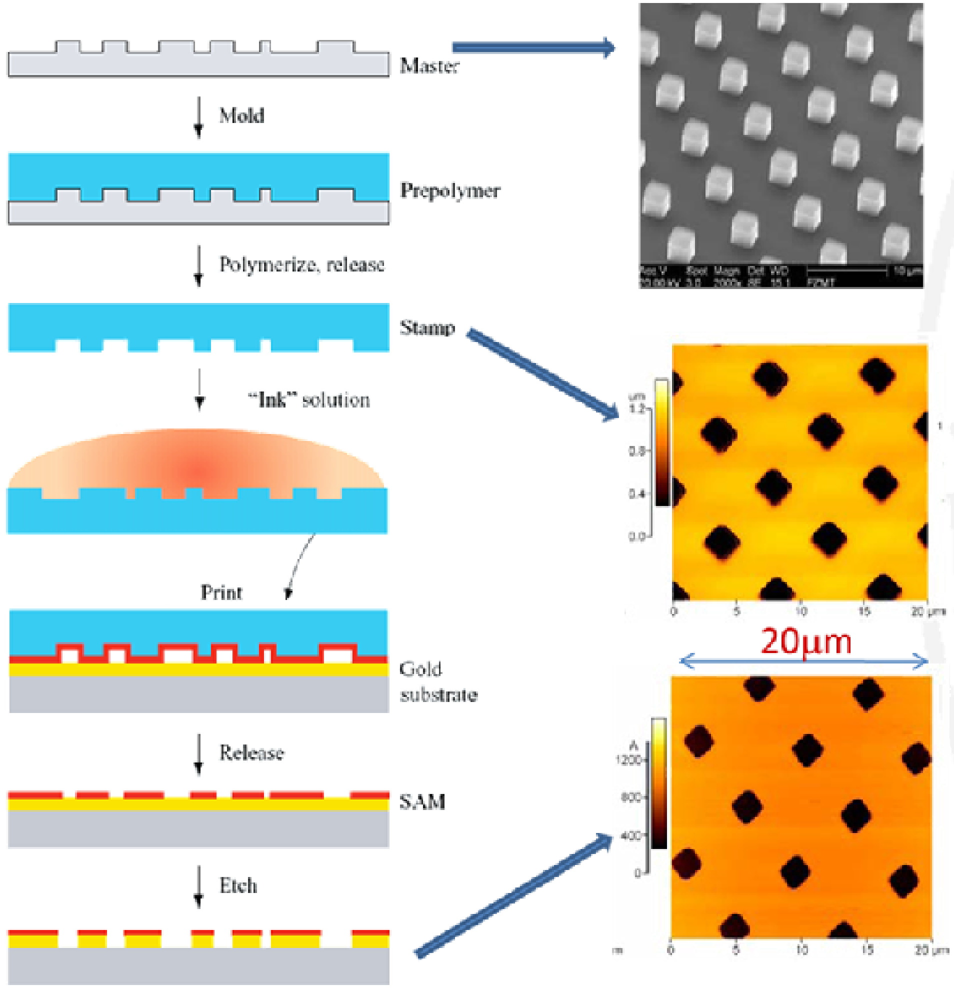
- The stamp is placed on the substrate;
- A liquid prepolymer (with low viscosity) is deposited, and fills holes by capillary effect;
- After thermal/light curing, the stamp can be removed and the polymer remains on the substrate
- Similar to µTM, the negative of the stamp is obtained.

Soft Lithography: Nano Imprint Lithography



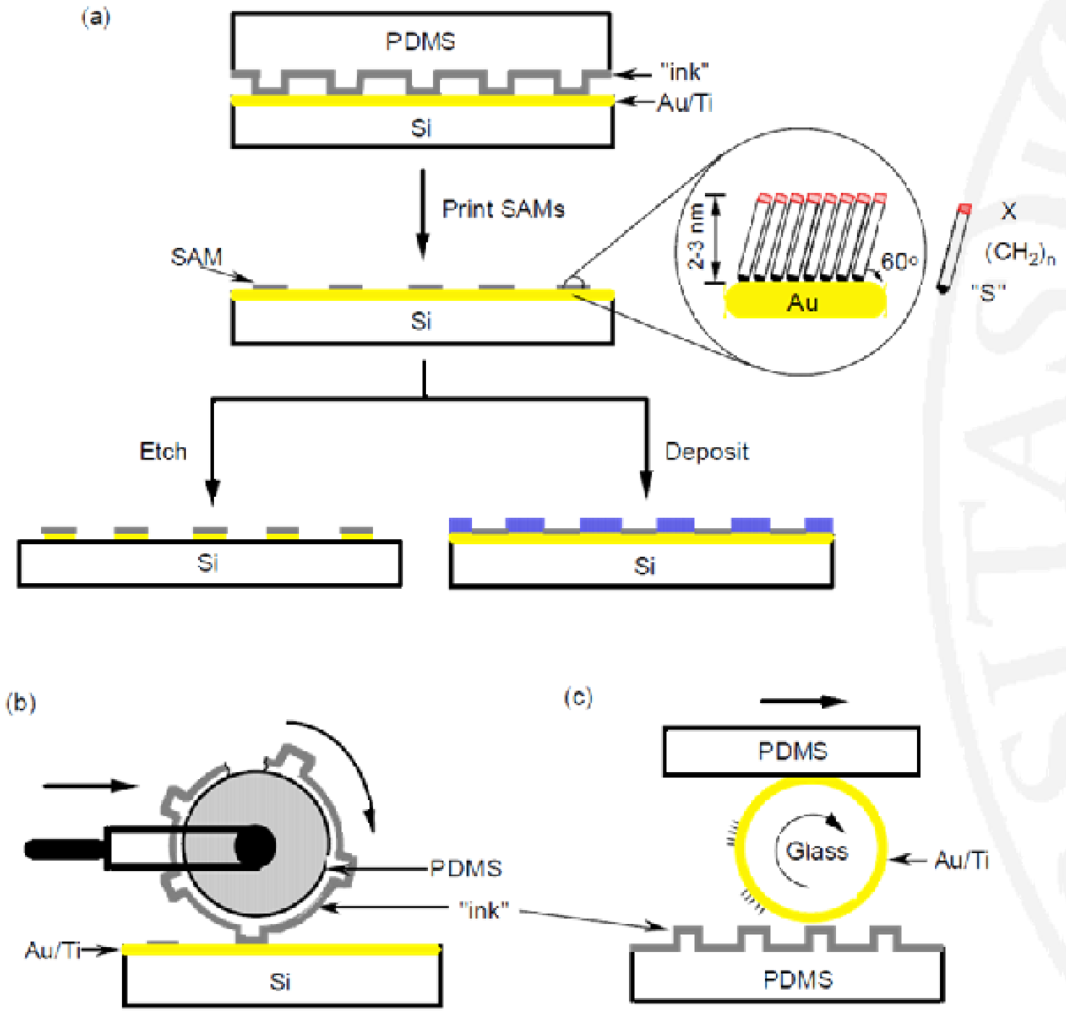
- The stamp make a mechanical pressure on a liquid polymer film;
- After thermal/UV curing, the stamp can be removed and the negative of the stamp remains on the substrate.

Soft Lithography: Micro Contact Printing



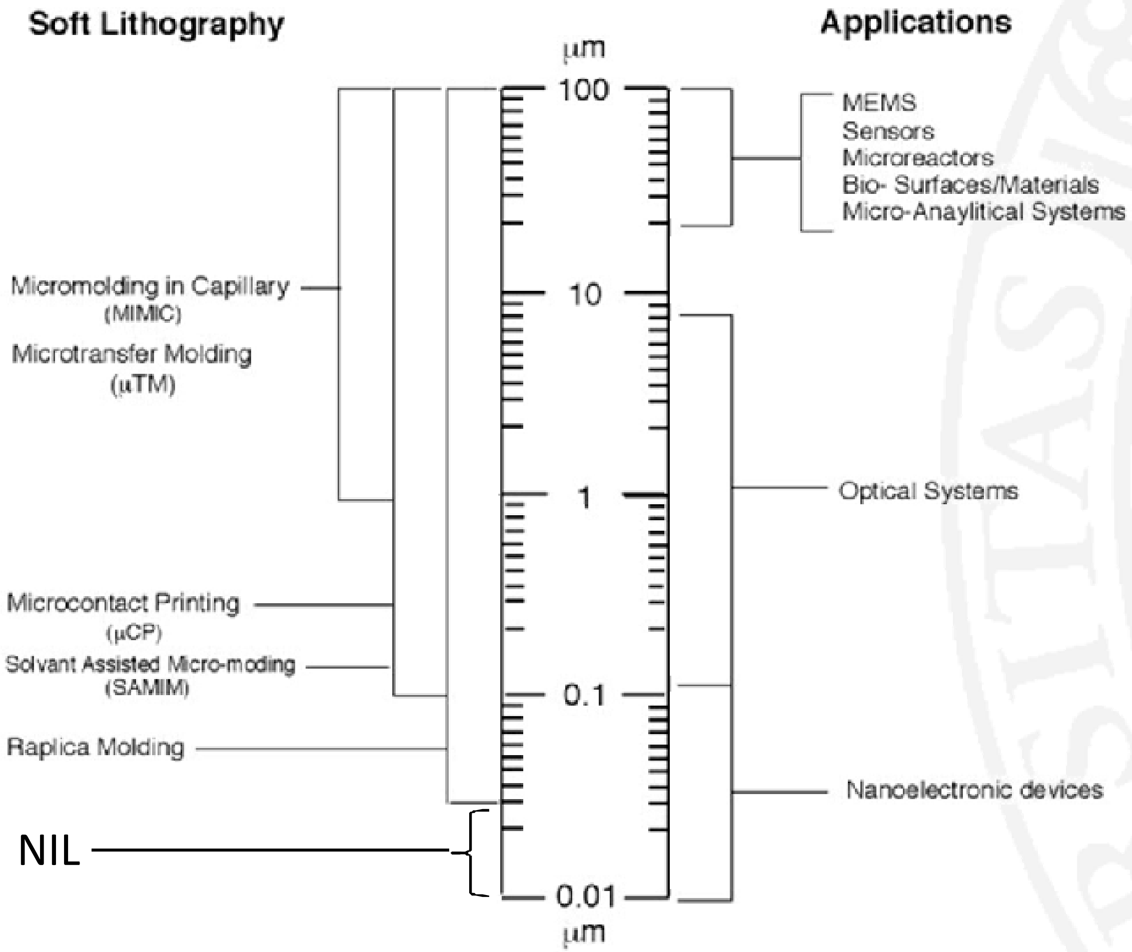
- The most diffused soft lithography technique;
- The ink is transferred onto the substrate playing on the different sticky coefficient between stamp and substrate
- Used to transfer several kinds of different materials (inorganic, organic single crystals, SAMs, proteins, DNA, …)

Soft Lithography: Micro Contact Printing



- The most diffused soft lithography technique;
- The ink is transferred onto the substrate playing on the different sticky coefficient between stamp and substrate
- Used to transfer several kinds of different materials (inorganic, organic single crystals, SAMs, proteins, DNA, …)
- It can be performed in several ways

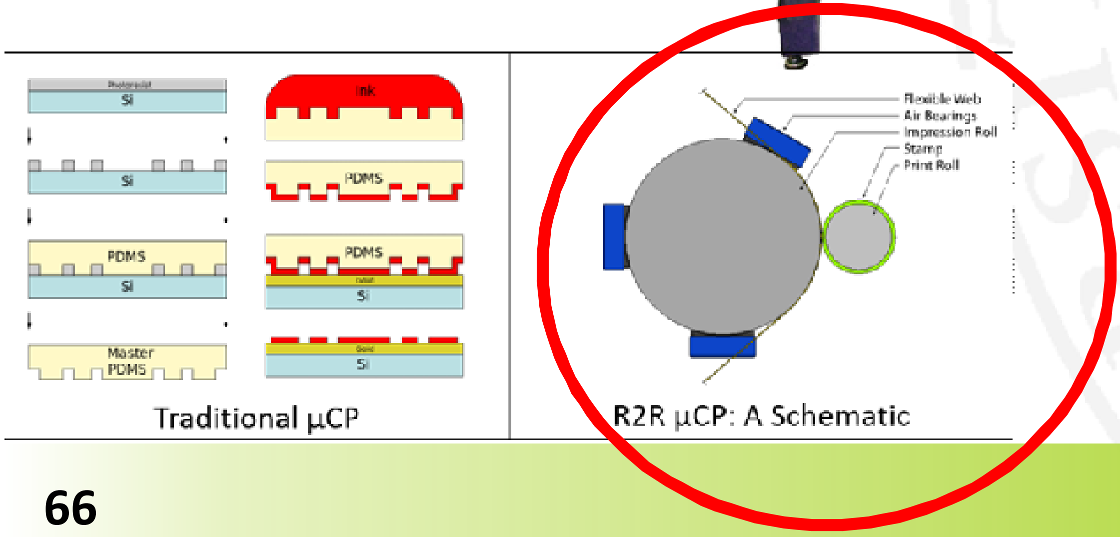
Soft Lithography: Pros and Cons



- **Advantages:**
  - Convenient and low cost
  - Rapid prototyping
  - Deformation of PDMS provides route to complex patterns
  - No optical diffraction limit
  - Non-planar or curved surfaces
  - Generation of 3D μ-structures
  - Control over surface chemistry
  - A broad range of materials
  - Applicable to manufacturing
  - Patterning over large areas
- **Disadvantages:**
  - Distortion of patterns
  - Poor registration/alignment
  - Compatibility with IC processes
  - Defects and their densities
  - MIMIC is a relatively slow process

From Soft Lithography to Roll-to-Roll

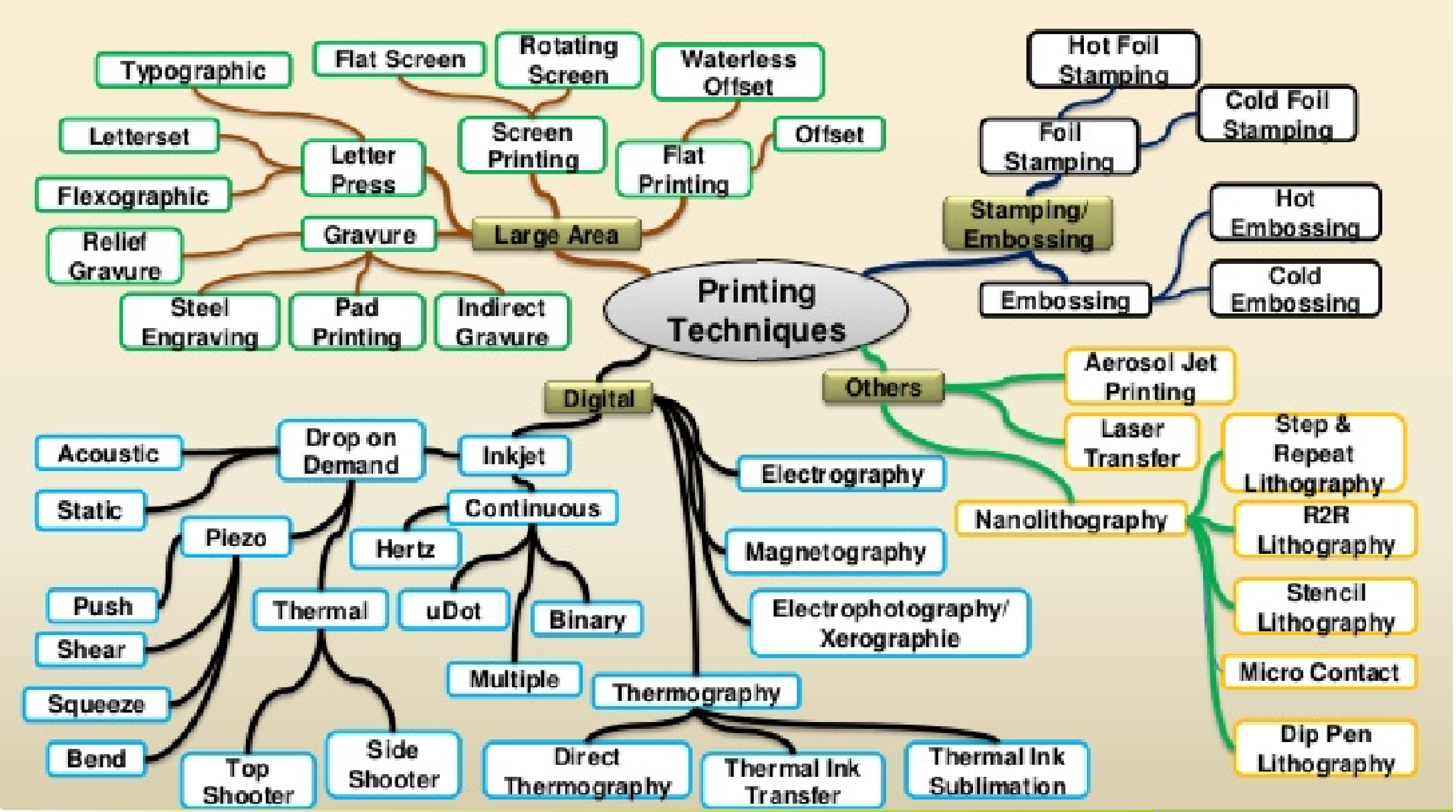
High speed,
High throughput
Low costs!



Traditional µCP

R2R µCP: A Schematic

Whats More?


Printing Techniques
Large Area
Letter Press
Typographic
Letterset
Flexographic
Gravure
Relief Gravure
Steel Engraving
Pad Printing
Indirect Gravure
Screen Printing
Flat Screen
Rotating Screen
Flat Printing
Waterless Offset
Offset
Stamping/ Embossing
Foil Stamping
Hot Foil Stamping
Cold Foil Stamping
Embossing
Hot Embossing
Cold Embossing
Others
Aerosol Jet Printing
Laser Transfer
Nanolithography
Step & Repeat Lithography
R2R Lithography
Stencil Lithography
Micro Contact
Dip Pen Lithography
Digital
Inkjet
Drop on Demand
Acoustic
Static
Piezo
Push
Shear
Squeeze
Bend
Thermal
Top Shooter
Side Shooter
Continuous
Hertz
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Binary
Multiple
Electrography
Magnetography
Electrophotography/ Xerographie
Thermography
Direct Thermography
Thermal Ink Transfer
Thermal Ink Sublimation