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Other deposition methods

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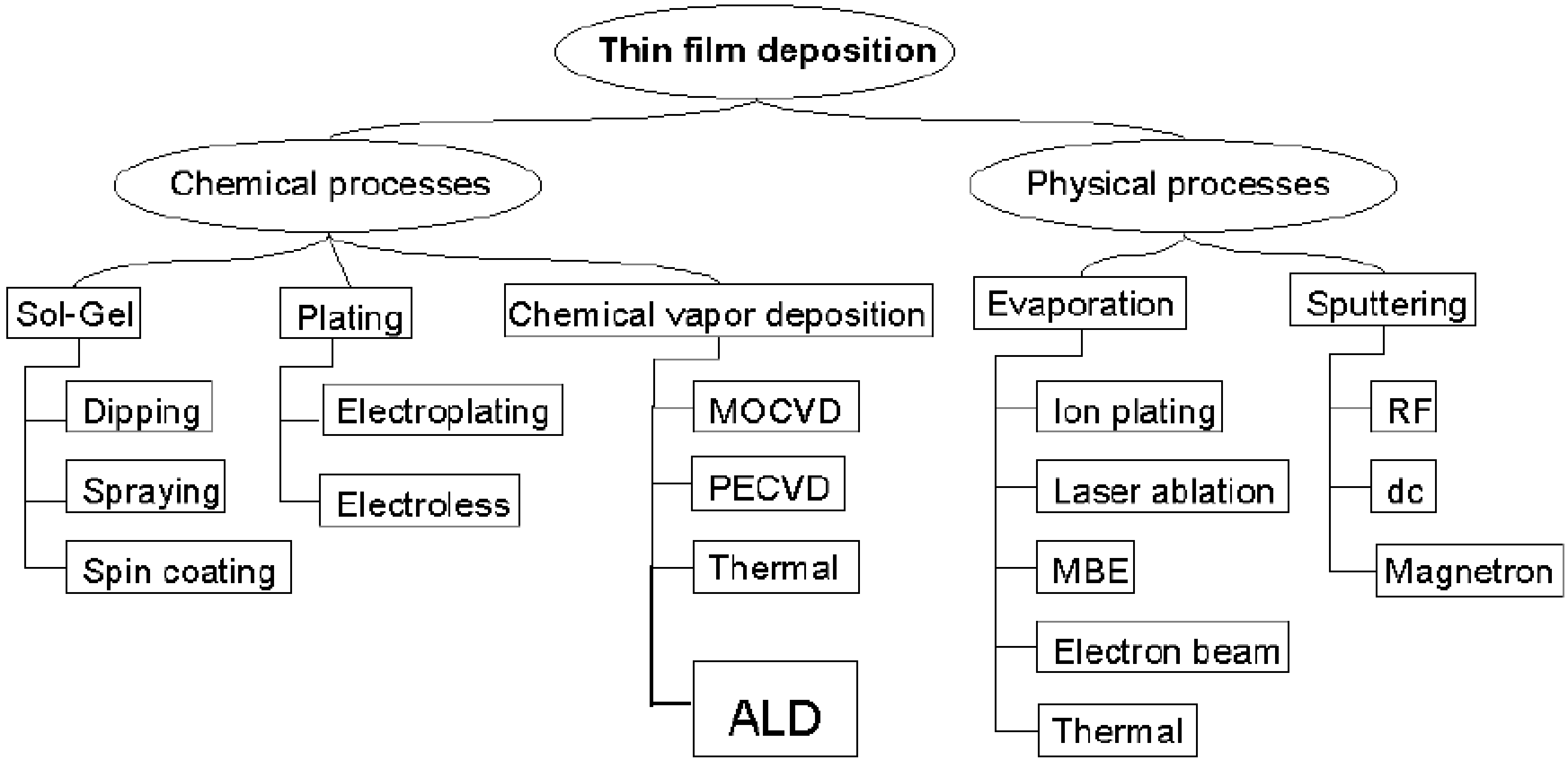

Thin film deposition
Chemical processes
Physical processes
Sol-Gel
Plating
Chemical vapor deposition
Evaporation
Sputtering
Dipping
Spraying
Spin coating
Electroplating
Electroless
MOCVD
PECVD
Thermal
ALD
Ion plating
Laser ablation
MBE
Electron beam
Thermal
RF
dc
Magnetron

Liquid phase deposition

- Electrochemical
- Electroless
- Spin coating
- Dip coating
- Self-assembled monolayers
- Sol-gel
- Liquid flame spray

Room temperature (mostly)

Electroplating

W Ruythooren *et al*

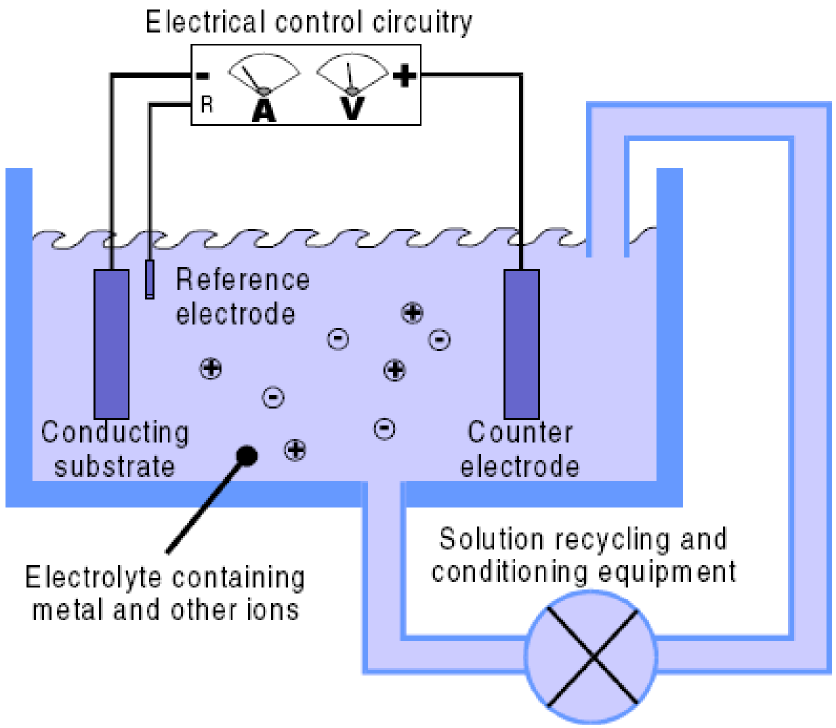


Figure 1. Schematic representation of a set-up for electrochemical deposition.

Typical plated metals:

-nickel (Ni), NiFe,

-CoP

-copper (Cu)

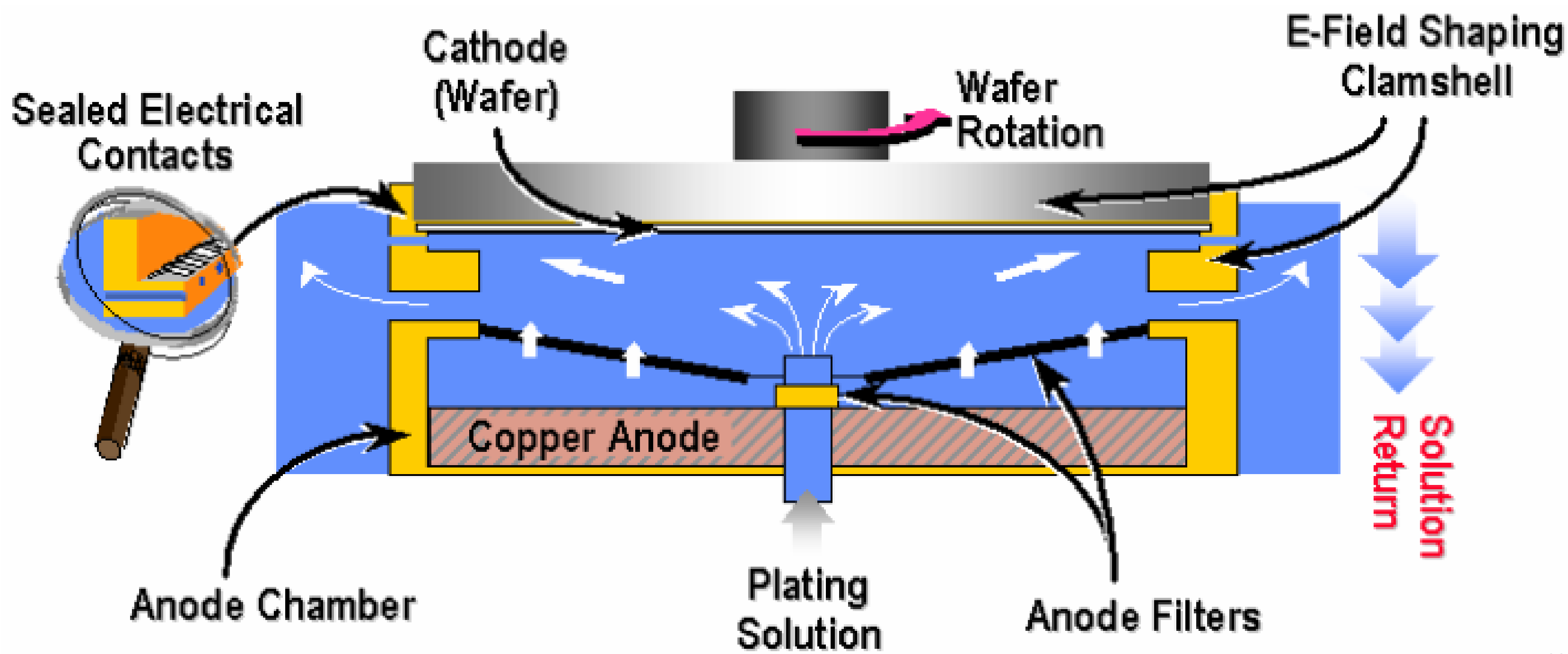
-gold (Au)

Not applicable to:

-aluminum (Al)

-most refractory metals (W, Ti, ...)

Commercial plating bath for IC metallization



Novellus

Plating bath efficiency in metal usage is 10-90%
➔ plating costs vary a lot

Scales in electroplating

1. Bath scale:
circulation of the liquid

2. Microscale:
local pattern density

3. Feature scale:
inside microstructures

W Ruythooren *et al*

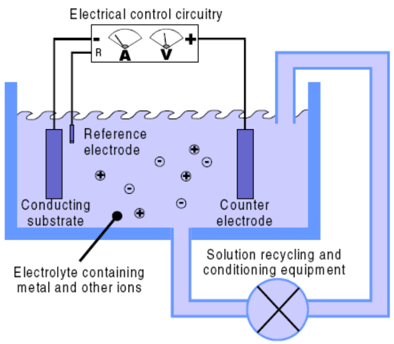
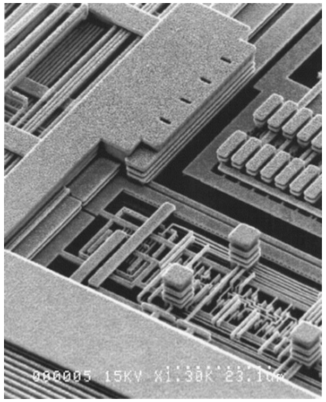
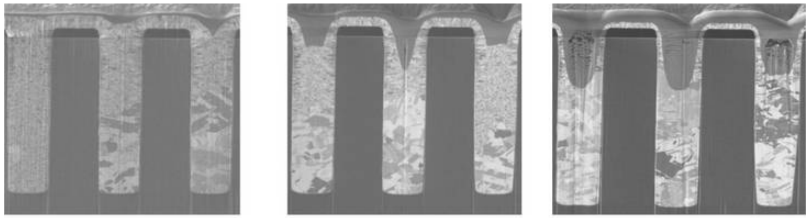


Figure 1. Schematic representation of a set-up for electrochemical deposition.

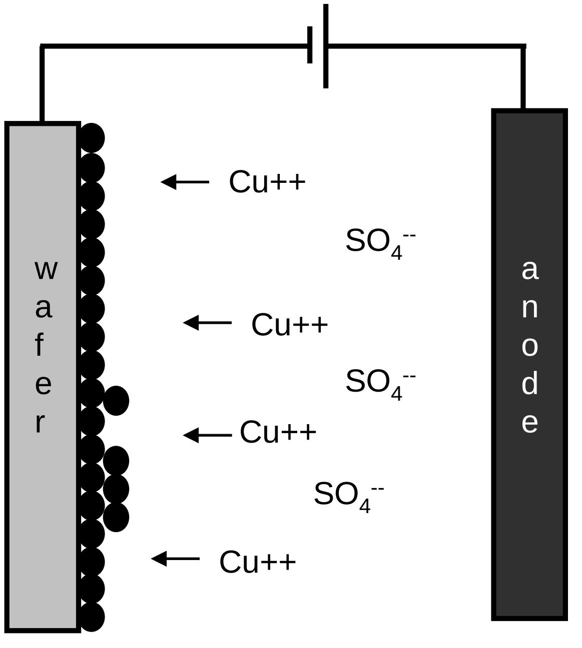




(a) (b) (c)

Copper plating

At cathode
$Cu^{2+} + 2\ e^{-} \rightarrow Cu(s)$



At anode
$Cu \rightarrow Cu^{2+} + 2\ e^{-}$

electrolyte: $CuSO_4$

Plating bath composition

- compounds supplying metal ions

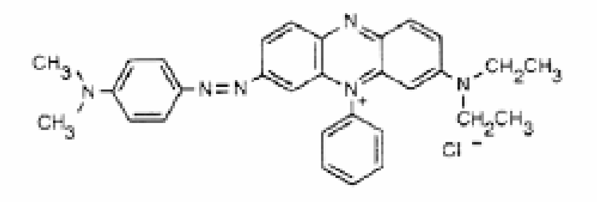
- supporting ions for
  - improving conductivity
  - stabilizing the solution
  - preventing excessive anode passivation

- pH adjusting compounds
  - acids, bases, buffers

Copper: a commercial solution

$CuSO_4 \cdot 5H_2O$	0.24 M
H_2SO_4	1.8 M
PEG, M = 3350 g/mol	300 mg/l
Cl^-	50 mg/l
SPS (bis(3-sulphopropyl)disulphide)	~ 1 mg/l
JGB (Janus Green B)	~ 1 mg/l

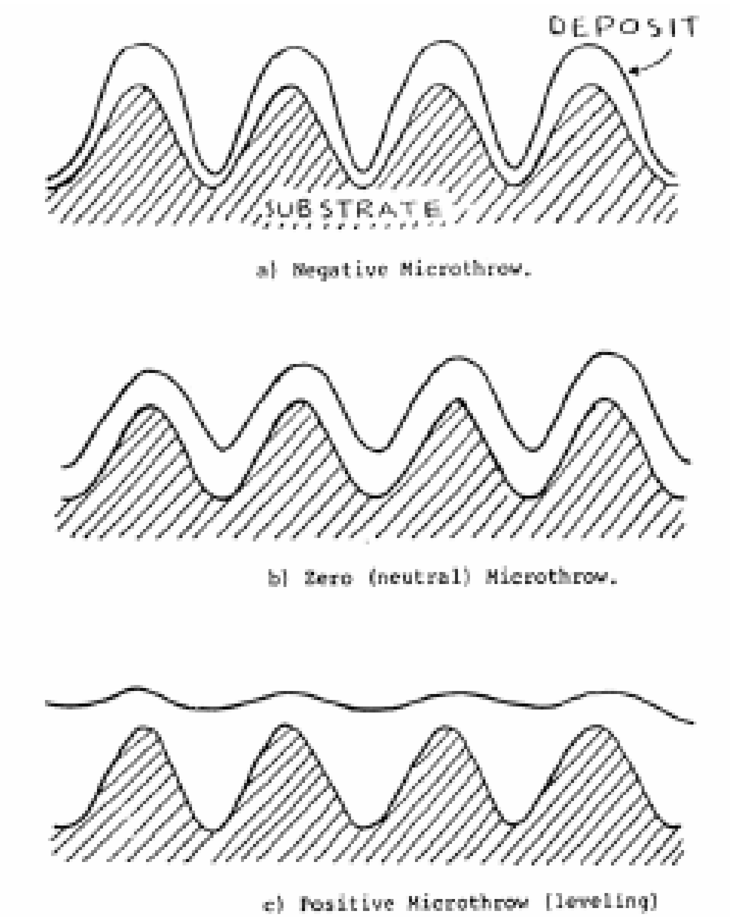
- PEG (polyethylene glycol): $H(OCH_2CH_2)_nOH$
- SPS: $HO_3S(CH_2)_3S\text{-}S(CH_2)_3SO_3H$
- JGB:

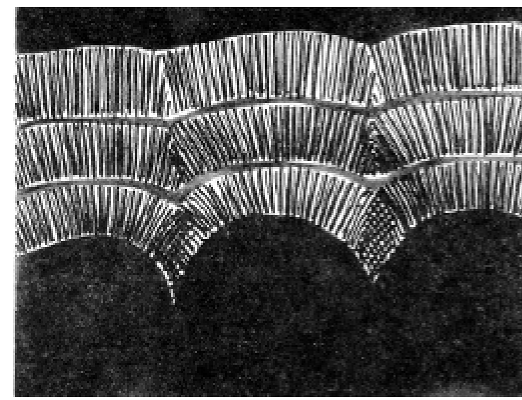


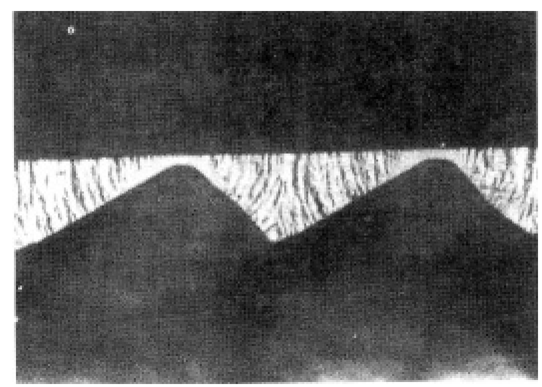
Additives

- mg/l - a few %, 10^{-4} - 10^{-2} mol/l
- brighteners, levelers, grain refiners, stress relievers
- inhibitors, accelerators
- surfactants (assist removal of hydrogen bubbles)
- adsorbed and/or included
- consumed or not in electrochemical reactions
- mechanistic understanding limited, largely proprietary and trial-and-error based

Leveling/throwing power

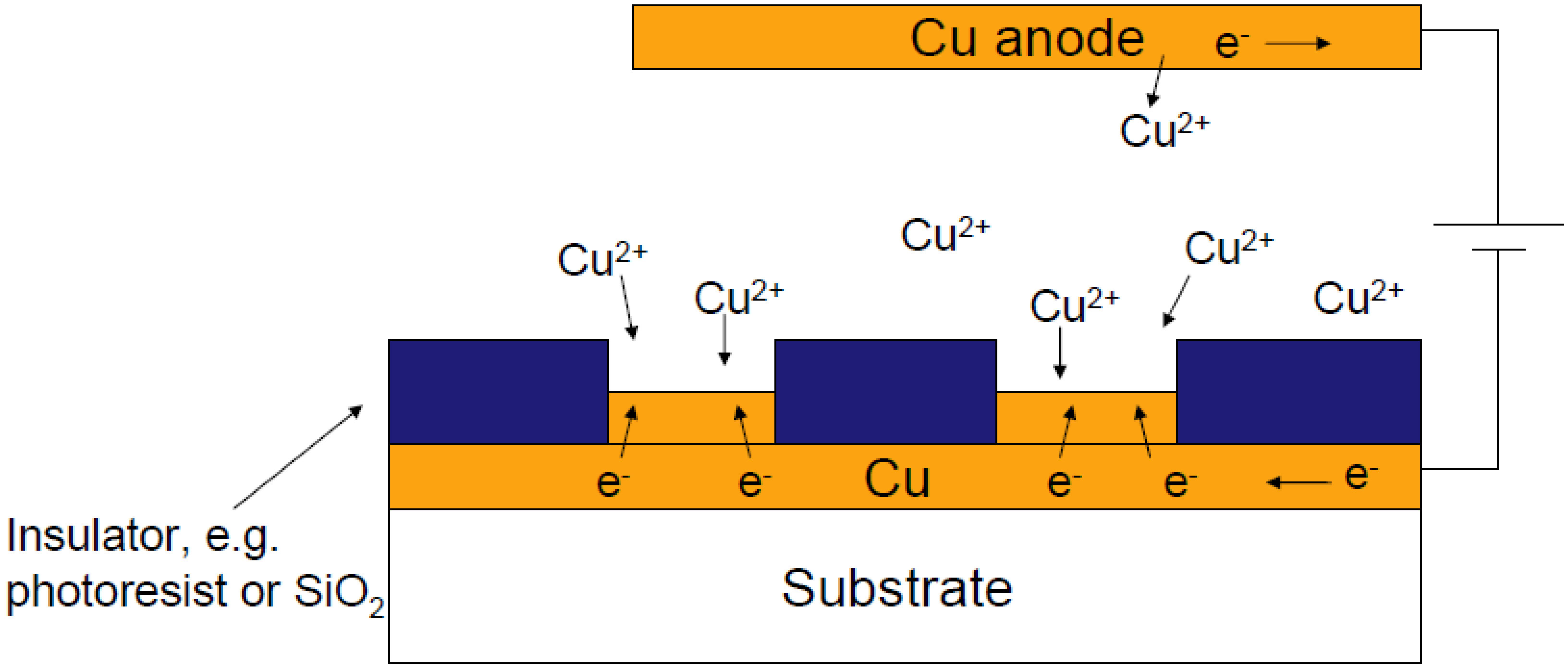




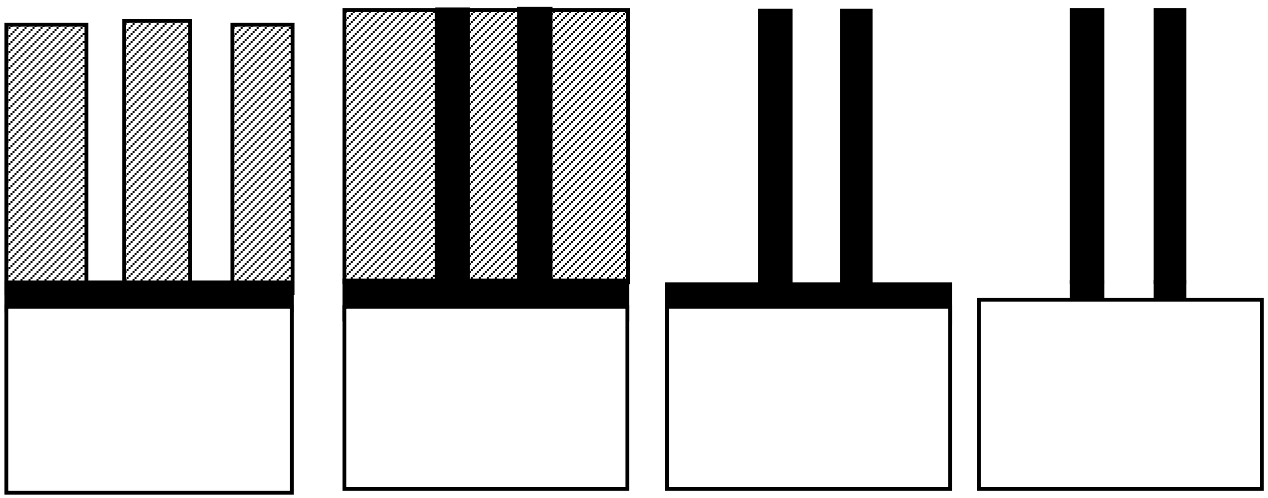


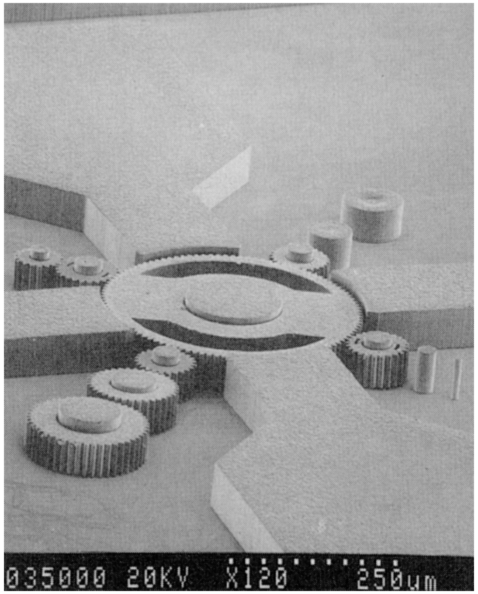
Selective area deposition

Electrodeposition occurs only in those areas where electrons are available
→ selective area deposition



Electroplated structures

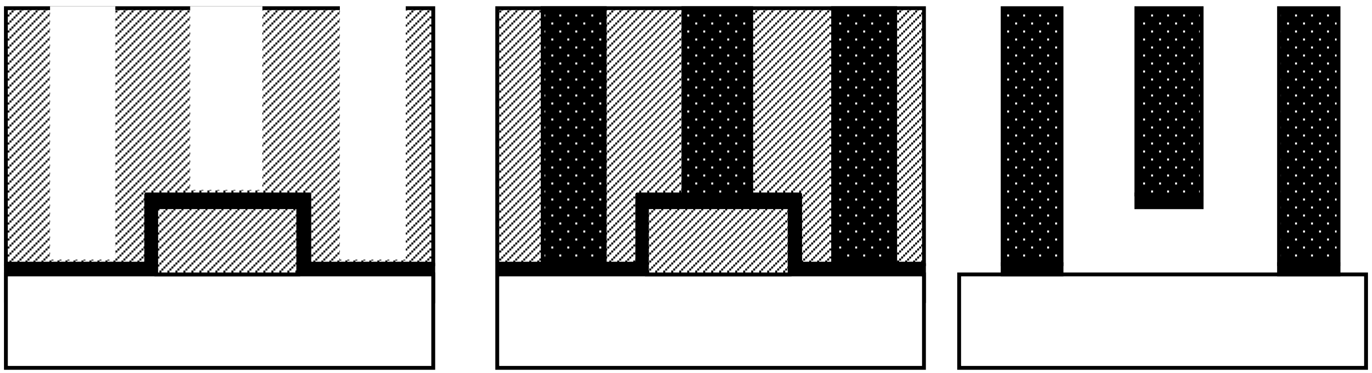


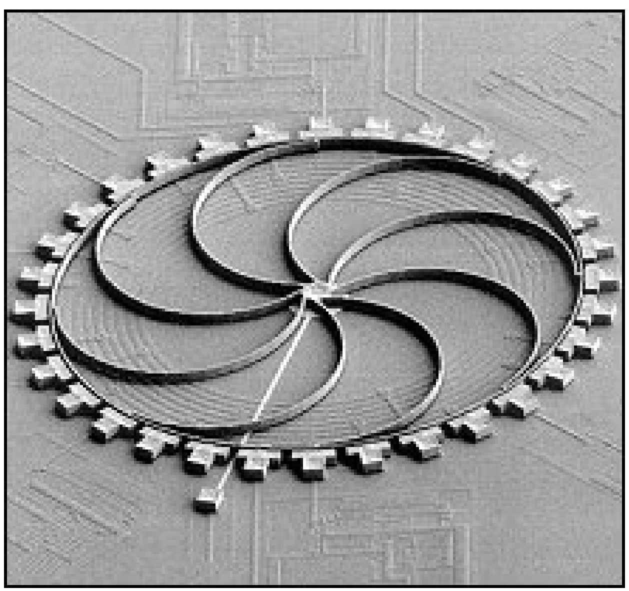


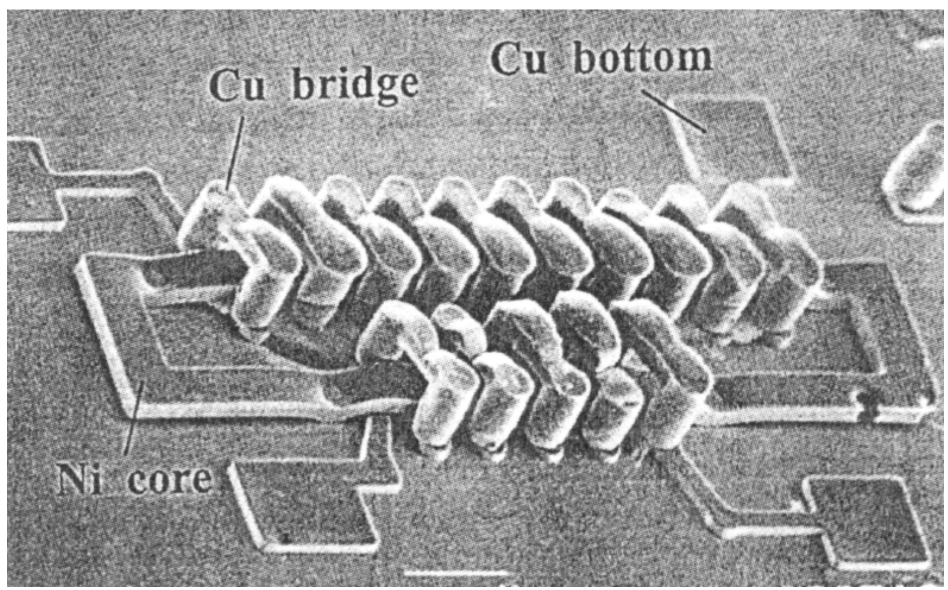
1. Seed layer sputtering
2. Lithography
3. Electroplating metal
4. Resist stripping
5. Seed layer removal

Nickel gear structures on silicon made by electroplating. Reproduced from Guckel, H. (1998),

Released plated metals







Electrodeposition processes controlled by:

- deposition potential
  - constant
  - time dependent (pulsed, cycled)
  - continuously adjusted to hold the current constant
- equilibrium potentials
- precursor concentrations
- pH
- ionic strength
- additives
- temperature
- stirring

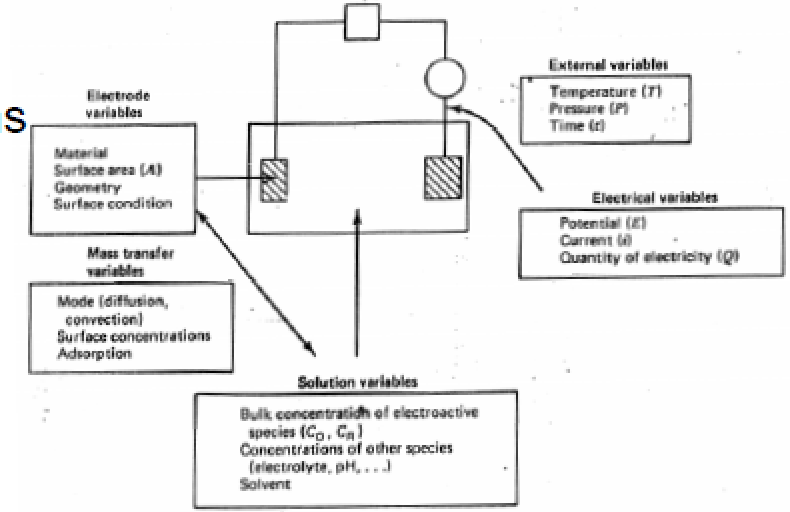


Figure 1.3.2
Variables affecting the rate of an electrode reaction.

Electroless deposition

Film deposition is based on a redox reaction which is accomplished without an external voltage source.

Typical metals: Ni, Co, Pd, Pt, Cu, Au, Ag and their alloys

- catalytic (an autocatalytic process)
- noble or rather noble (low oxygen affinity)

Applications:

- Cu metallization for microelectronics and printed circuit boards
- Ag mirrors
- protective coatings, e.g. Ni(NiP_x)

Electroless reactions

Electroless deposition of metals occurs via a reduction where electrons are provided by a reducing agent in the solution

$$ML_m^{n+}(aq) + ne^- \rightarrow M(s) + mL(aq)$$

$$Red(aq) \rightarrow Ox(aq) + ne^-$$

Typical reducing agents

- hypophosphite $H_2PO_2^-$
- formaldehyde HCHO
- borohydride BH_4^-
- dialkylamine borane R_2NHCBH_3
- hydrazine NH_2NH_2

The oxidation of the reductant is catalyzed by a metal surface (autocatalytic).

Activation/seed layer

When depositing on noncatalytic metals or insulating surfaces, the substrates are activated, e.g. by

- a thin sputtered metal film
- colloidal Pd
  made by subsequent dips in $SnCl_2$ and $PdCl_2$ solutions

The role of the catalytic surface:

- catalyze the oxidation of a reductant
  - dehydrogenation
  - hydrogen evolution
- serve as a medium for electron transport from local microanodes to local microcathodes

Copper electroless deposition

Two subreactions (reduction and oxidation):

- $(CuEDTA)^{2-} + 2\,e^- \rightarrow Cu + EDTA^{4-}$ $E^O = -\,0.216\ V$
- $2\,HCHO + 4\,OH^- \rightarrow H_2 + 2\,HCOO^- + 2\,H_2O + 2\,e^-$
  $E^O = -1.14\ V$

Overall reaction:

$(CuEDTA)^{2-} + 2\,HCHO + 4\,OH^- \rightarrow Cu + H_2 + 2\,HCOO^-$
$+ 2\,H_2O$

$E^O = E^O(\text{reduction}) - E^O(\text{oxidation}) =$
$-\,0.216\ V - -1.14\ V = 0.924\ V$

$\rightarrow \Delta G^0 = -zFE^0 < 0$

→ the process is spontaneous and the solution metastable

→ homogeneous precipitation is kinetically inhibited

→ the heterogeneous deposition reaction is catalyzed

Copper for IC metallization

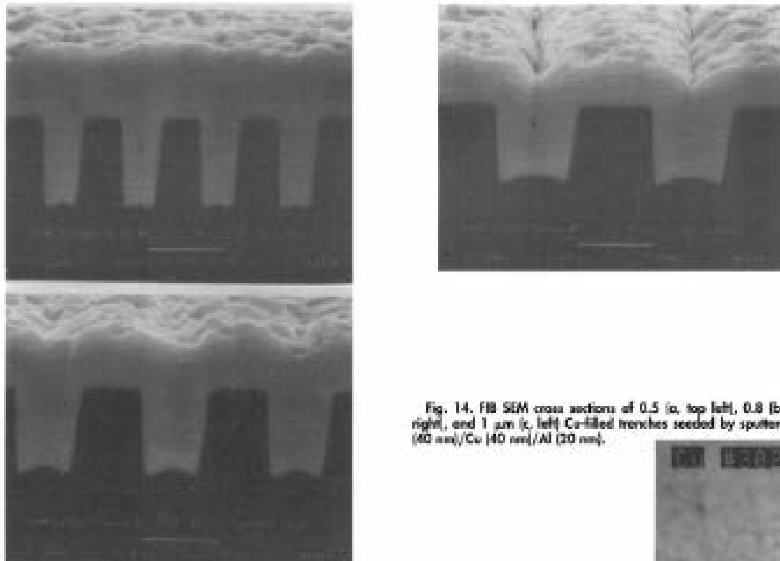
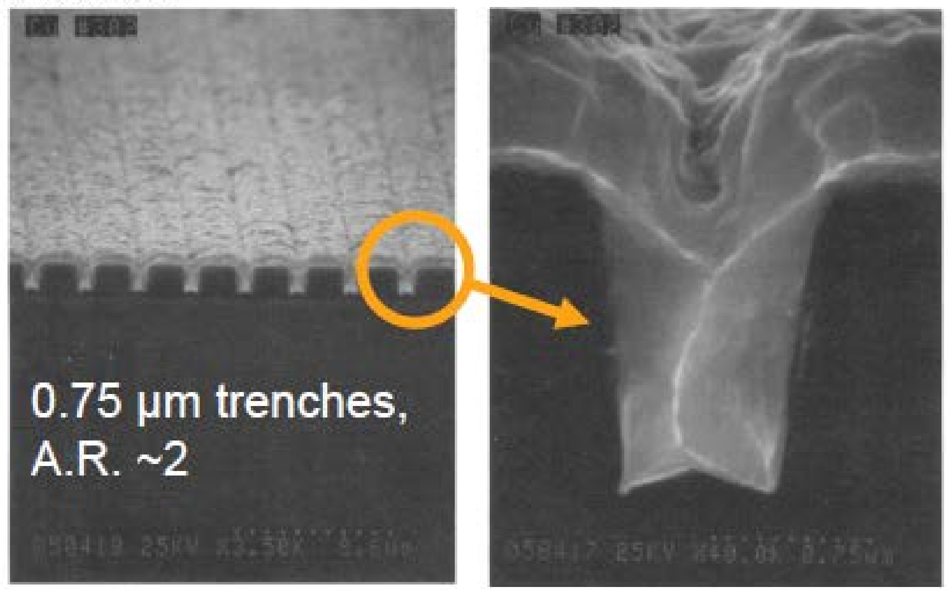
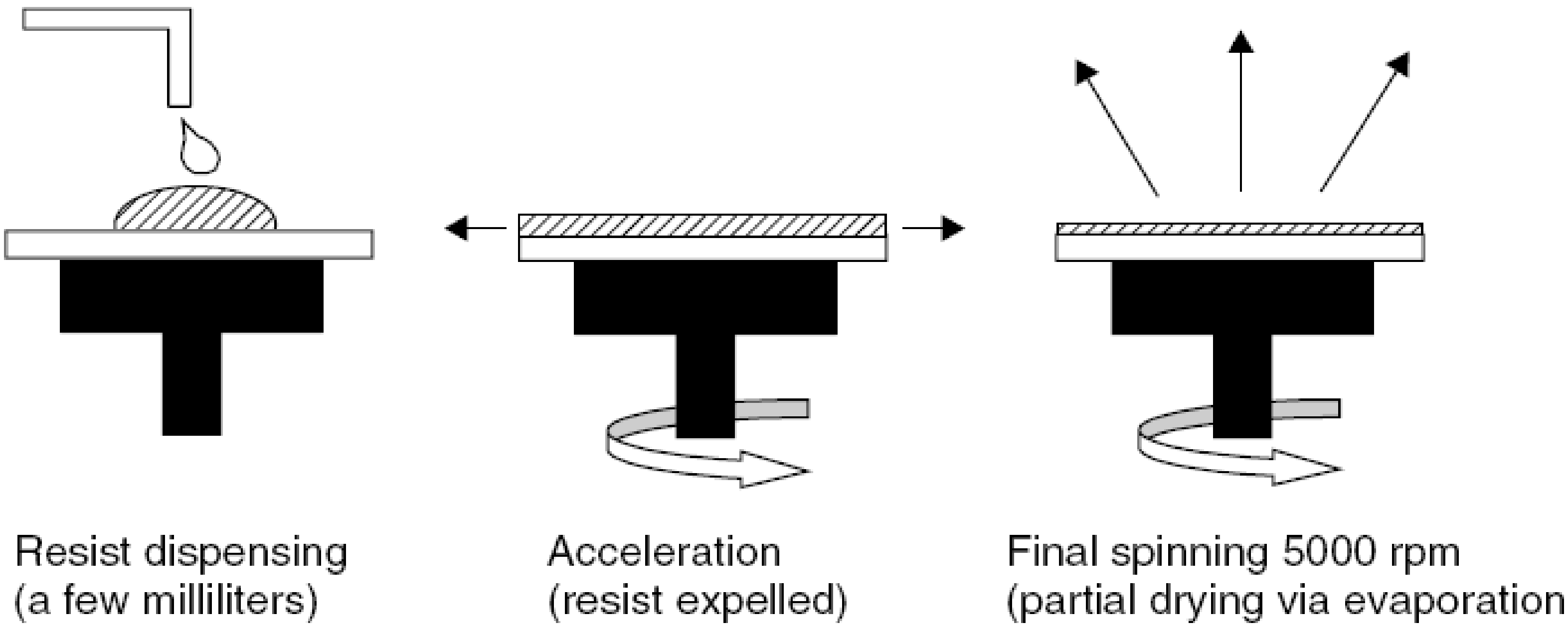


Fig. 14. FIB SEM cross sections of 0.5 (a, top left), 0.8 (b, top right), and 1 μm (c, left) Cu-filled trenches seeded by sputtered Ti (40 nm)/Cu (40 nm)/Al (20 nm).



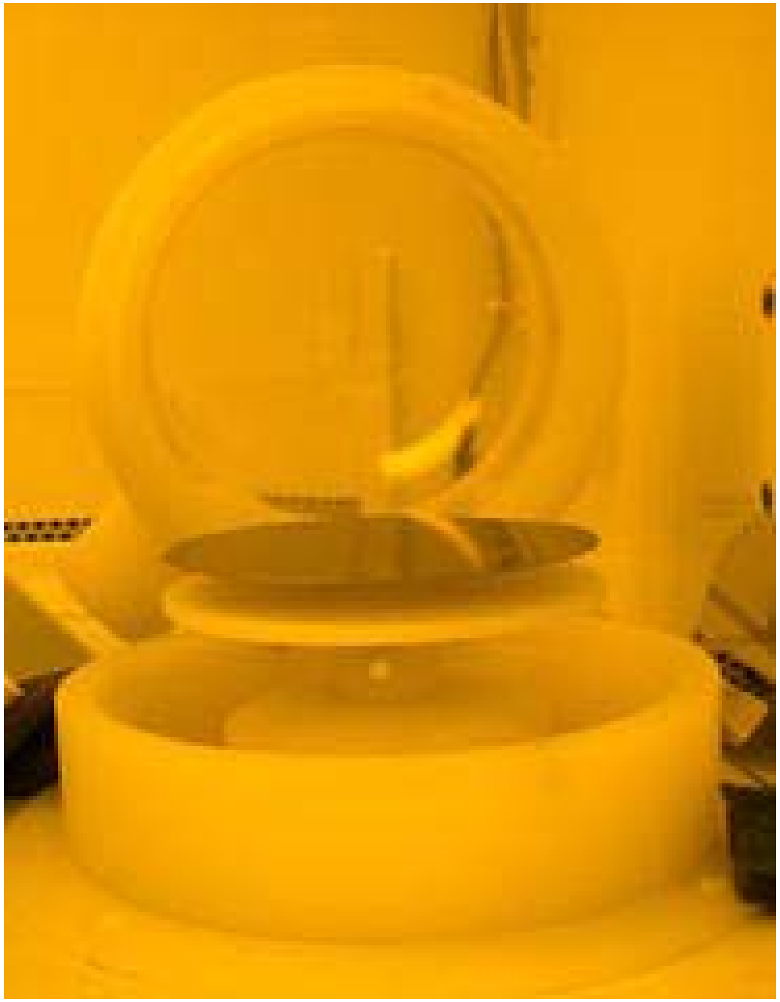
V. M. Dubin et al., J. Electrochem. Soc. 144 (1997) 898

Spin coating



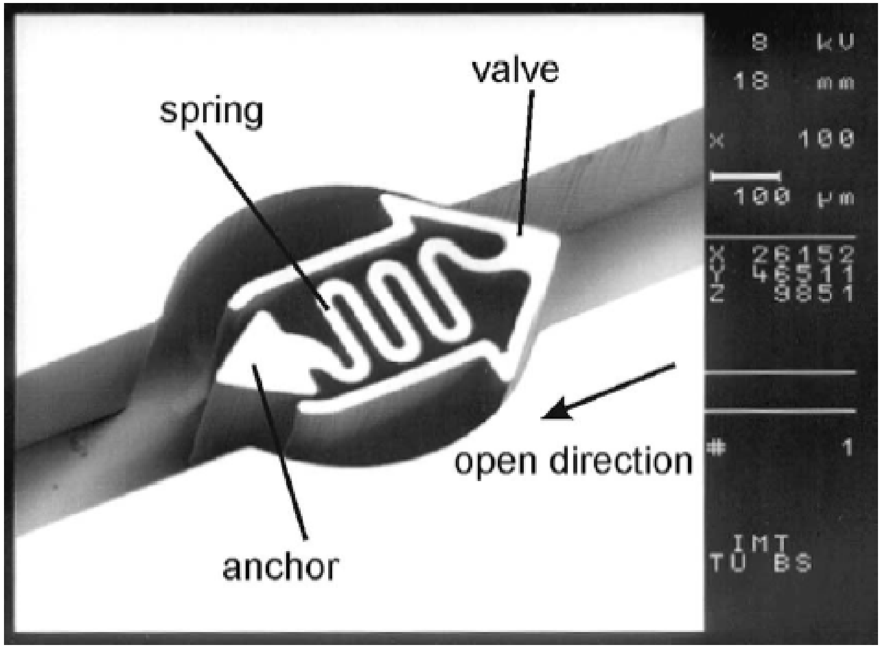
Film thicknesses from 100 nm to 1 mm

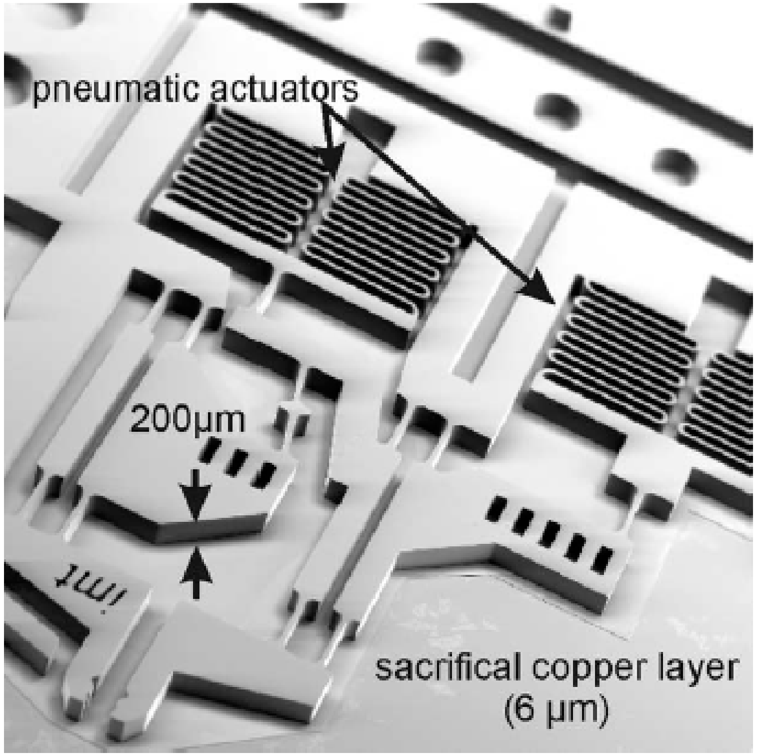
Spin coaters



Variables:
•Spin speed
•Acceleration
Polymer variables:
•Viscosity
•Evaporation rate

Spin-coated polymers

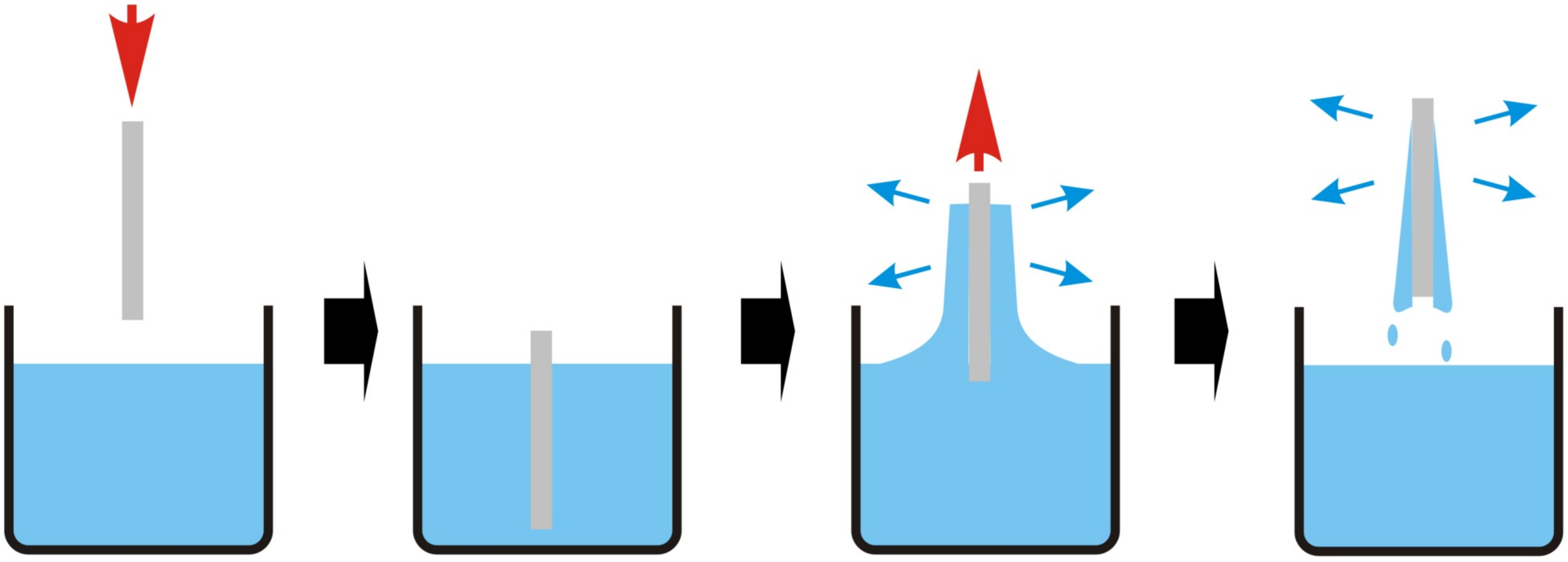




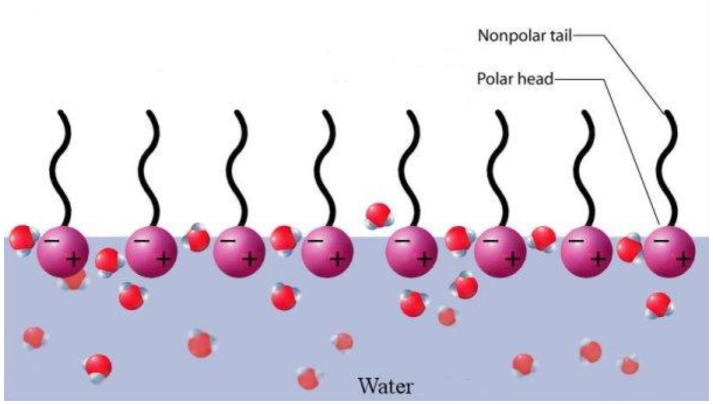
Seidemann, Volker; Butefisch, Sebastian; Buttgenbach, Stephanus. Sensors and Actuators, A (2002), A97-98 457-461.

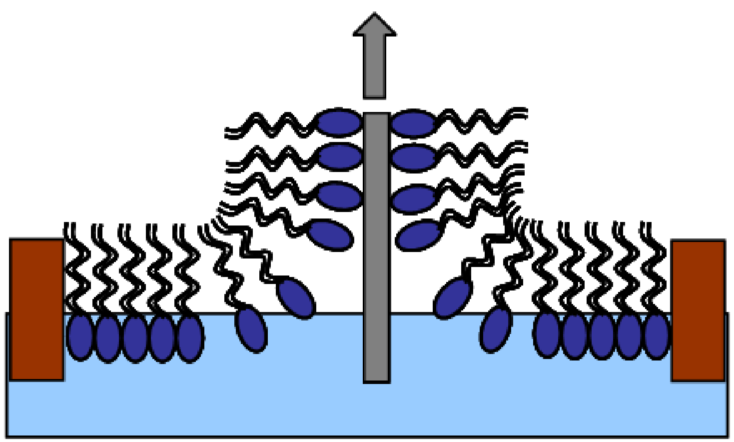
Dip coating

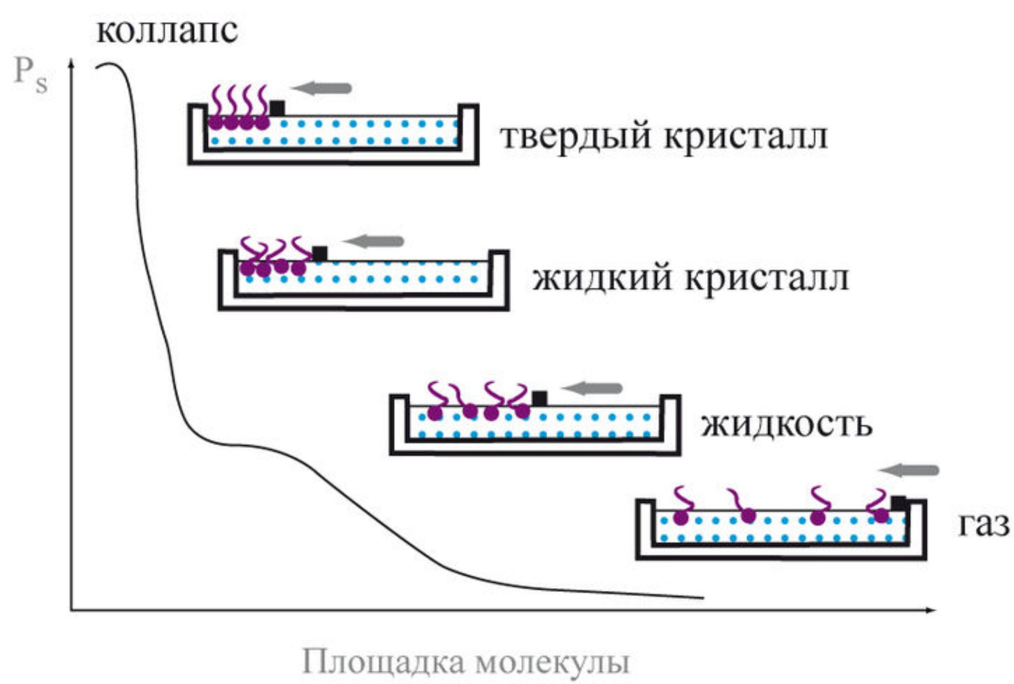
Immersion: at a constant speed
Dwell time: static
Withdrawal: again at a constant speed to avoid any judders. The faster the substrate is withdrawn from the tank the thicker the coating material that will be applied to the board.



Langmuir-Blodgett mechanism



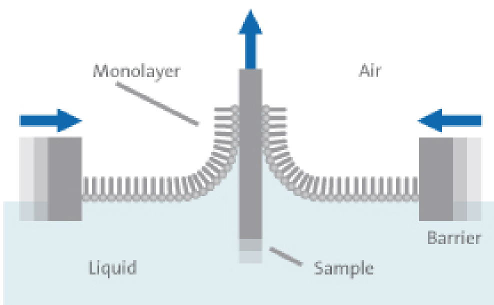




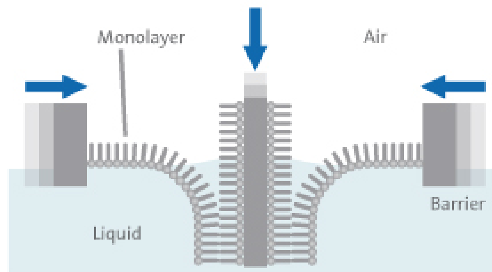
Surface pressure controls the distance between molecules ("gas", "liquid" and "solid" phases).

Langmuir-Blodgett film deposition

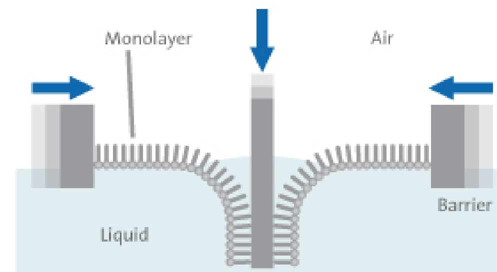
LB DEPOSITION ON A HYDROPHILIC SURFACE



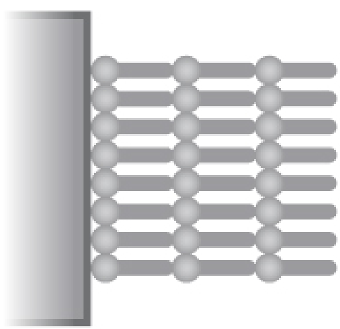
LB DEPOSITION ON A HYDROPHILIC SURFACE - 2ND LAYER



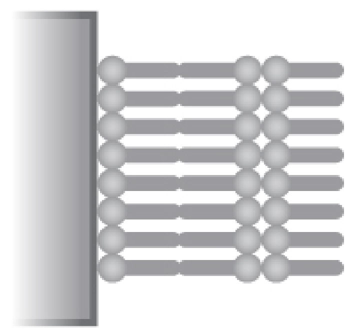
LB DEPOSITION ON A HYDROPHOBIC SURFACE



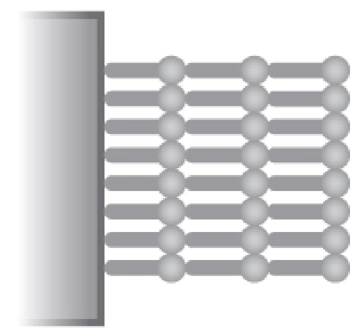
Z-TYPE ON A HYDROPHOBIC SURFACE



Y-TYPE ON A HYDROPHOBIC SURFACE

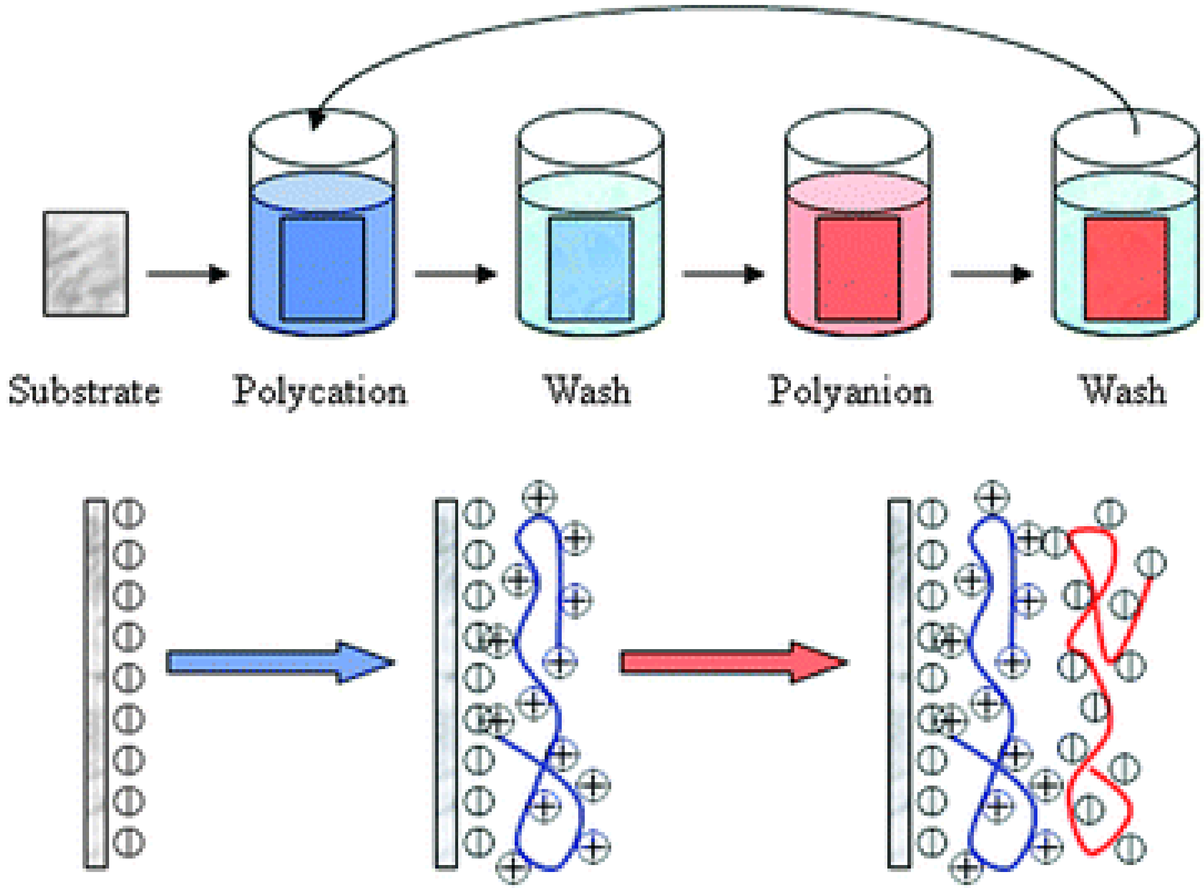


X-TYPE ON A HYDROPHOBIC SURFACE



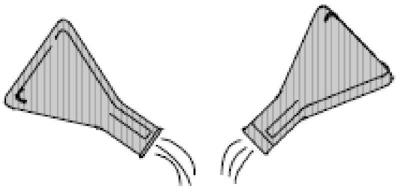
Layer-by-Layer assembly

Alternatively negatively and positively charged layers are deposited successively until the desired thickness is reached (compare: ALD).

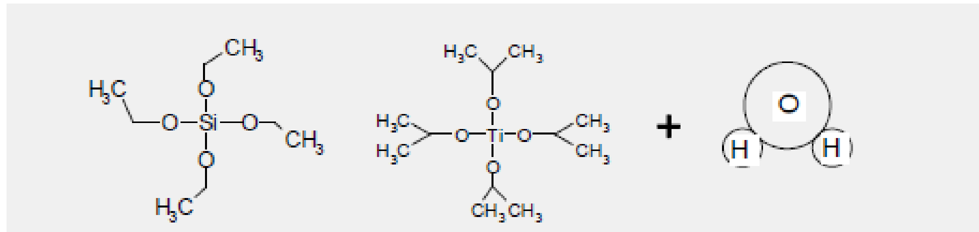


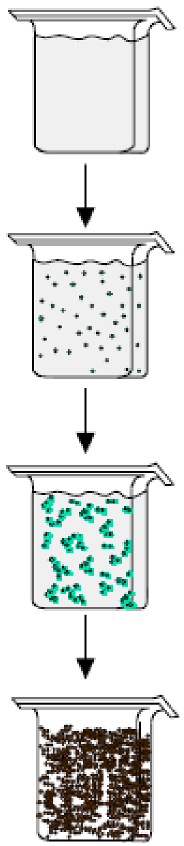
Sol-gel

SOL-GEL METHOD



1





1

2

3

4

2 **hydrolysis and condensation → small particles (D=1-100 nm) → a colloidal dispersion, a stable suspension, i.e., a SOL**

3 **growth and aggregation of particles**

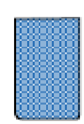
4 **particles and polymers collide and unite → another colloidal dispersion is formed, a GEL**

5 **aging at low temperature → evaporation**

6 **drying and heat-treatment to ceramic materials**

5 →

6 →



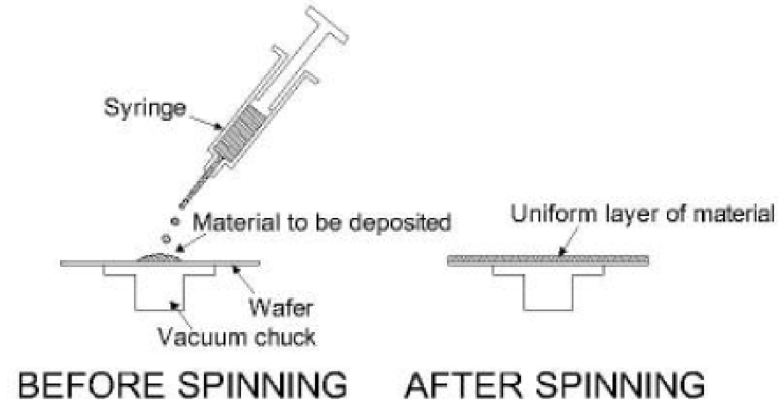
SiO_2 & TiO_2

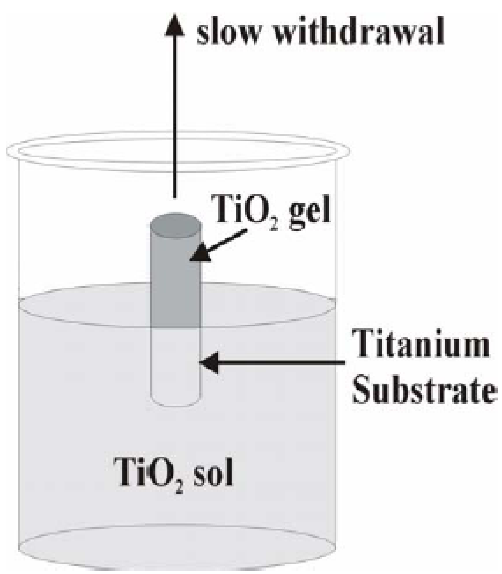
Sami Areva, Turku Biomaterials Centre

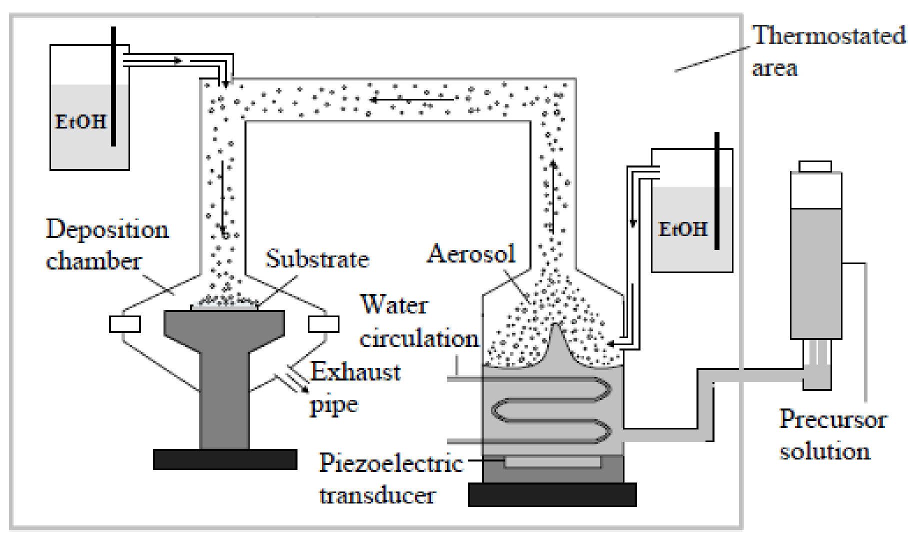
Sol-gel

Coating methods

- spin coating
- dip coating
- spraying/aerosol coating
- brushing



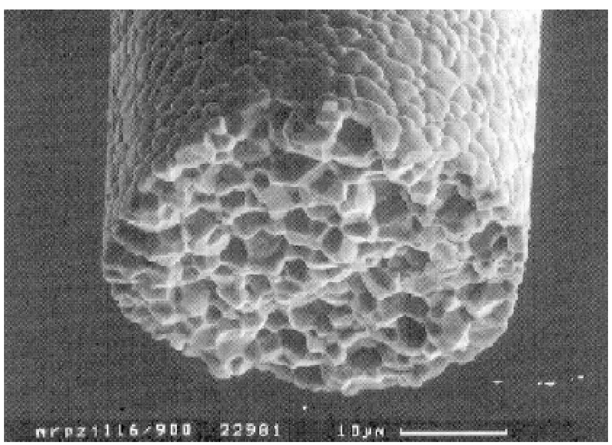




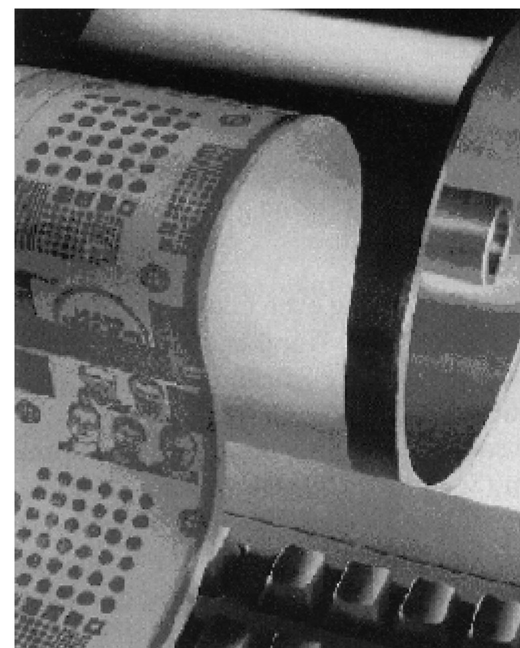
Versatile !

Low temperature allows coating on many substrates
Multicomponent films of uniform composition
Coating on various geometries

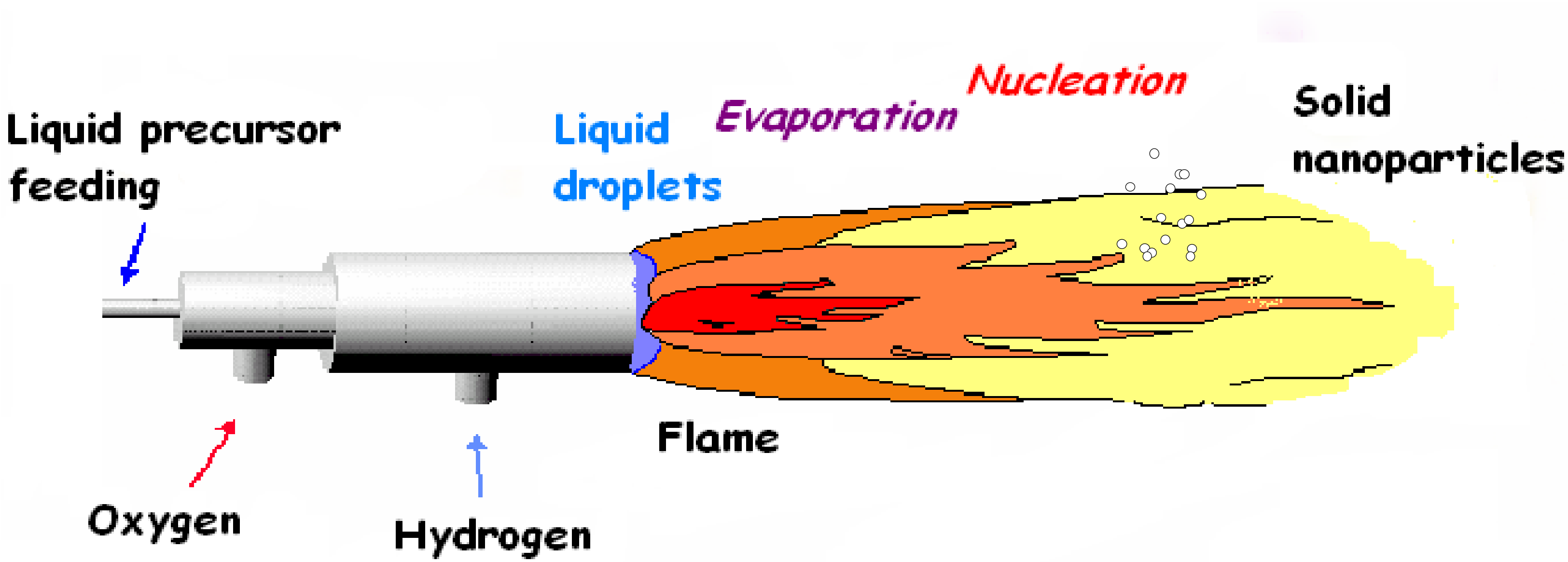
BUT: prone to cracking
residues of organics and water

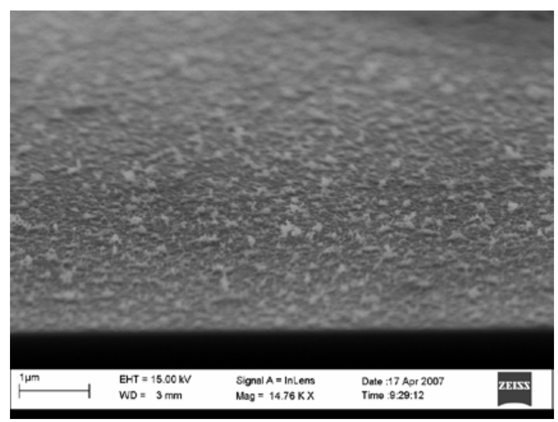


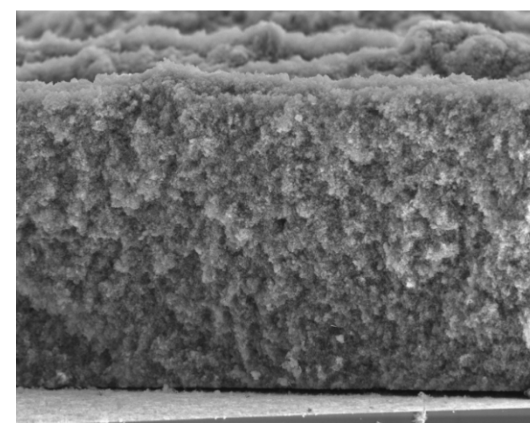
PZT fiber and PZT printing plate by sol-gel



Liquid Flame Spray







Aromaa et al. 2007, *Biomolecular Engineering*, 24,543
Keskinen et al. 2004, *JMater. Res.* 19,1544.
Mäkelä et al. 2004, *J Mater. Sci.* 39,2783.

Liquid Flame Spray

Nanoparticle production rate: 0.001-1.0 g/min

Nanoparticle (median) size: 2-200 nm

Particulate material:

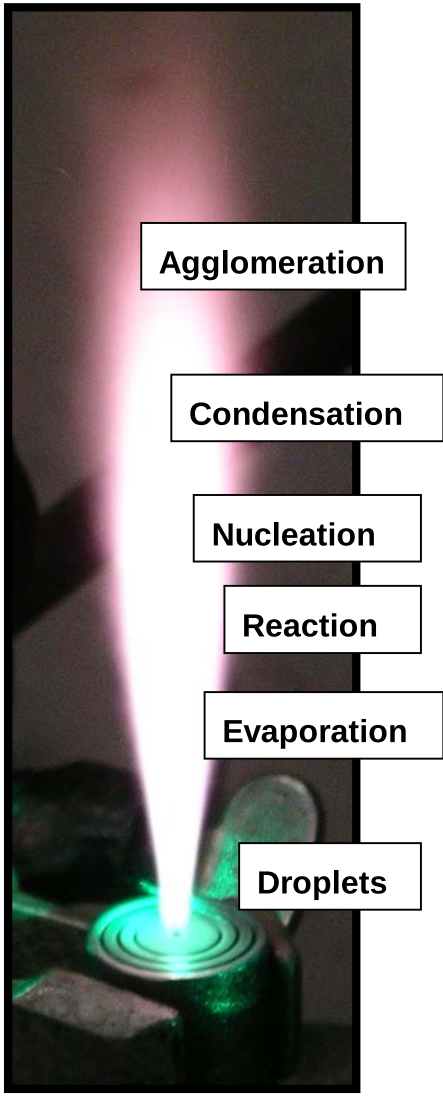
Noble metals: Ag, Pd, Pt, Au

Oxides & mixtures/composites: Na, Mg, Sr, Si, Ti, Al, V, Cr, Mn, Fe,

Co, Ni, Cu, Zn, Sn, Y, Zr, Mo, Ag, W, Pl, Er, Nd, Pr, Yb, Eu, Se, …

Most common materials produced (by TUT Aerosol Synthesis Group):

TiO_2, SiO_2, Ag, Fe_xO_y …



Aromaa et al. 2007, *Biomolecular Engineering*, 24,543
Keskinen et al. 2004, *JMater. Res.* 19,1544.
Mäkelä et al. 2004, *J Mater. Sci.* 39,2783.

Flame methods

Precursor may be liquid or gaseous

Diffusion flames

gases & reactants introduced from different ducts, to diffuse together later

Premixed flames

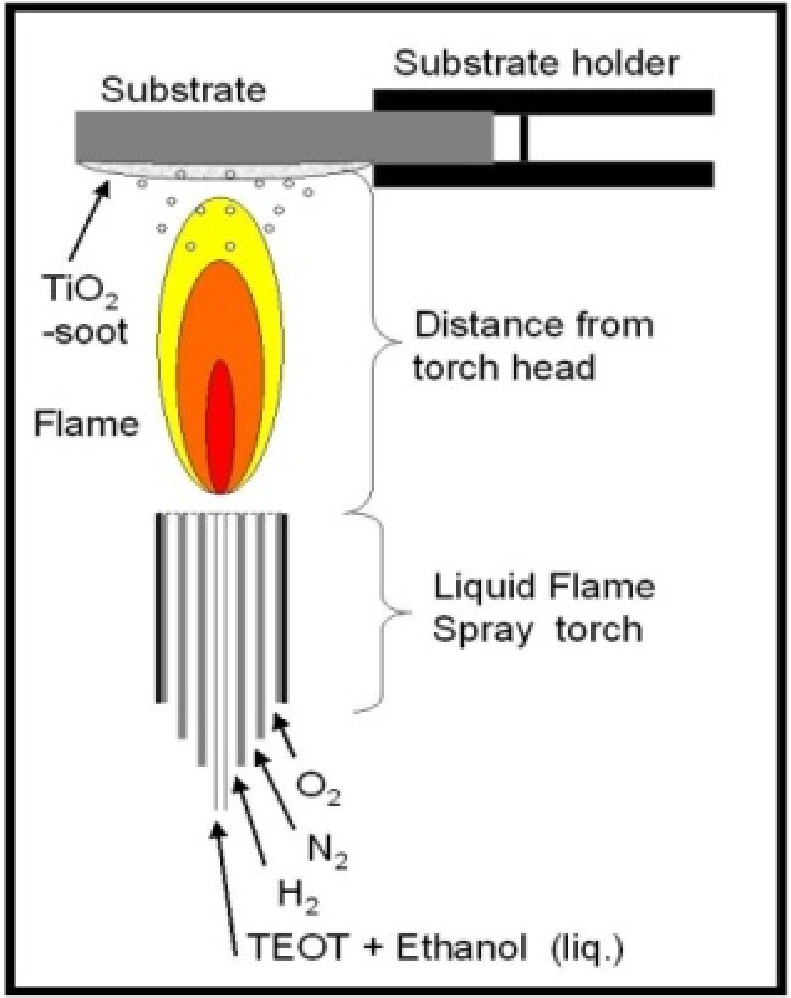
fuel & oxygen mixed beforehand

H_2 - O_2 -flame

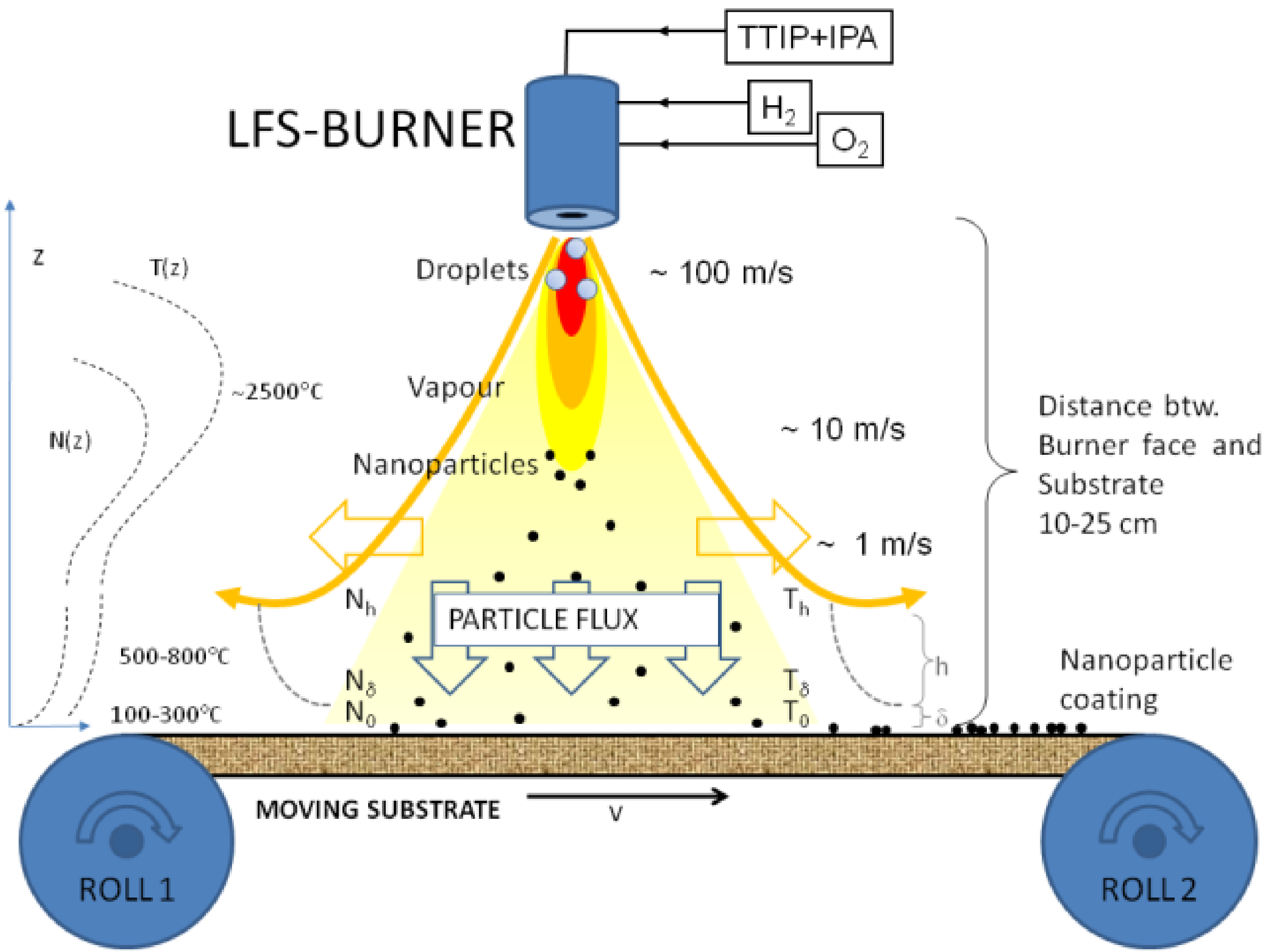
higher T due to H_2,
higher gas velocity for nebulizing liquid precursor

Reducing flame

deliberately controlled shortage of O_2,
along with inert gas shielding



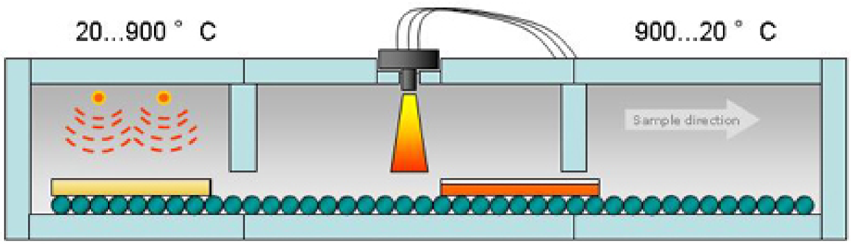
Roll-to-roll LFS



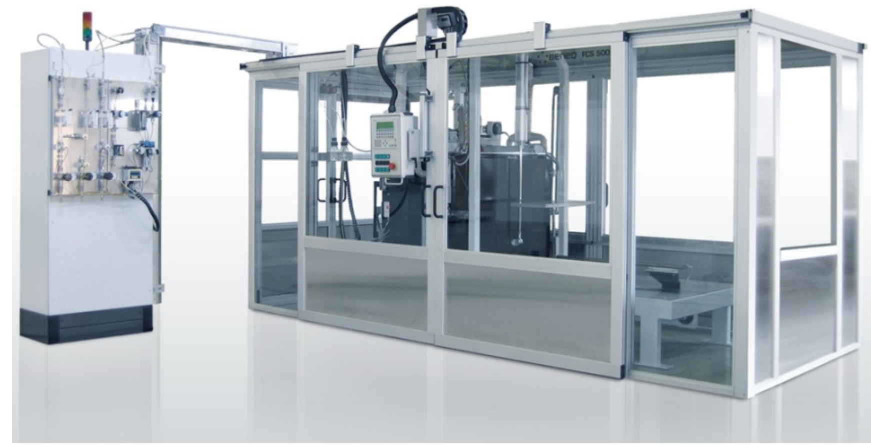
Up-scaling of flame methods

Beneq

nHALO in laboratory use



- nHALO technology is easily harnessed to enable laboratory-scale particle synthesis, surface modification and coating on various types of substrates.

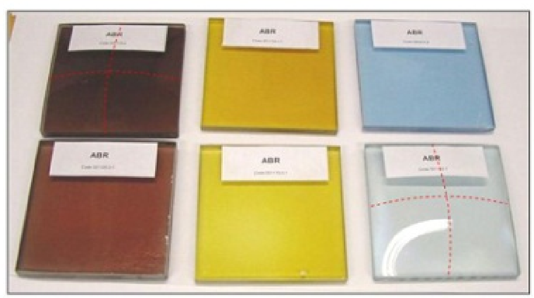


Example of shielding the nHALO -flame coating process at Beneq Ltd. (www.beneq.com)

Beneq © 20

Beneq

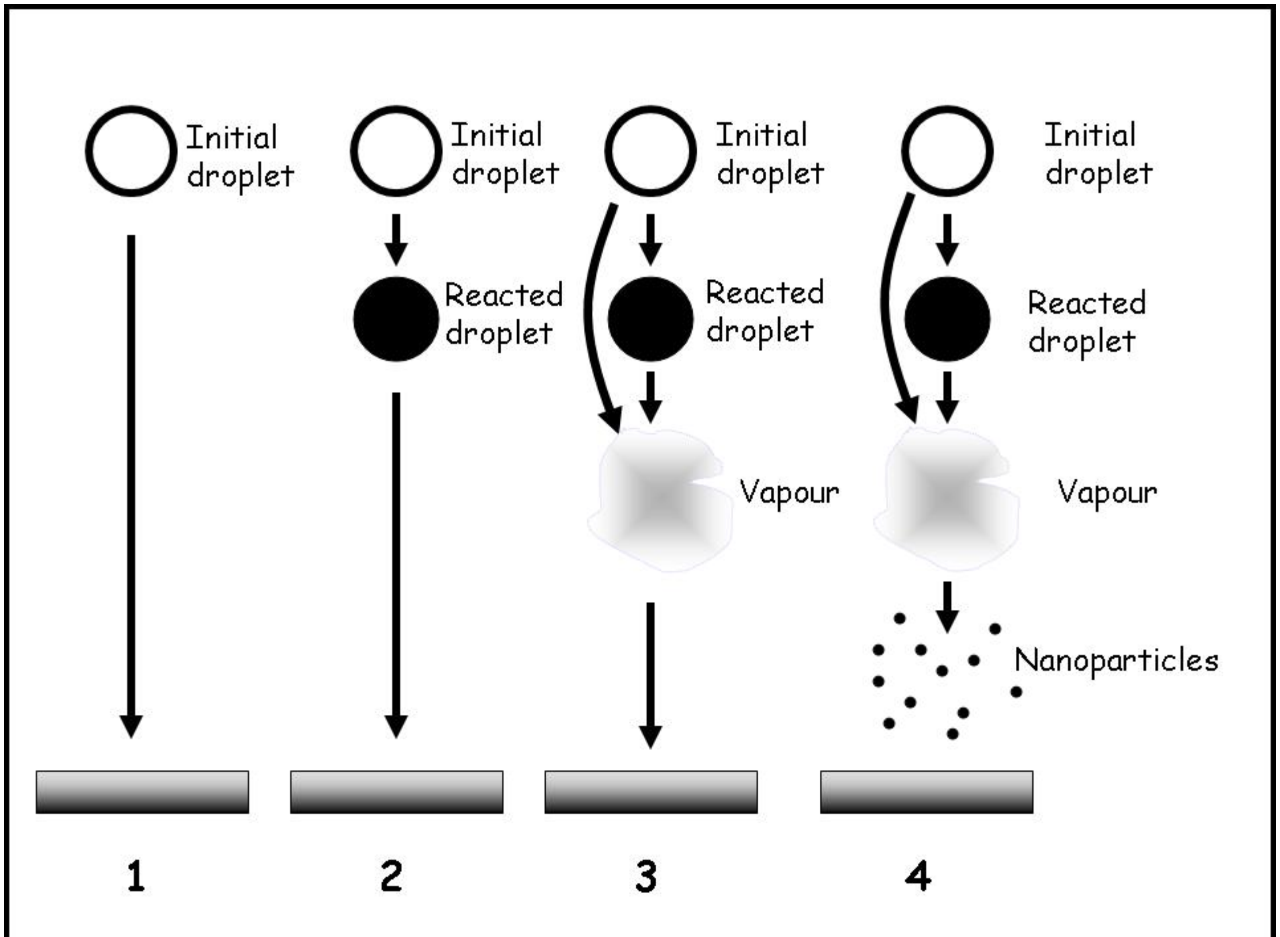
nHALO colour samples



The picture above depicts a current selection of colours available with nHALO glass surface modification. The surfaces of the panes are glossy. Two of the samples have been bent to demonstrate the stability of the colour (dashed red double curvature lines).

CVD from liquid precursor

When a liquid precursor is used in droplet form … and applied to a coating process



According to: Choy, 2003
Prog. Material Sci. **48**, 57.

Different terminologies used:

1
'Spray drying'
'Spray coating'
'Spray pyrolysis'
…

2
'Spray pyrolysis' & Deposition
…

3
'CVD'
'Aerosol Assisted CVD'
nAERO
…

4
'Liquid Flame Spray' (LFS)
'Direct Nanoparticle Deposition' (DND)
'Hot Aerosol Layering' (nHALO)
'Rapid Nanoparticle Deposition'
…

LFS vs. CVD

- In CVD the surface reaction is the desired one
- In LFS gas phase reaction is utilized

➔ substrate does not have to be at high temperature

Wet vs. vacuum methods

+ inexpensive set-ups
+ can be scaled to large areas
+ low temperature allows various substrate materials
+ very thick films often possible
+ no (toxic) gases needed

-film quality usually inferior to vacuum techniques
-often specific to certain materials, non-transferable
-large volumes of liquid