Lecture 10

Surface Modification techniques

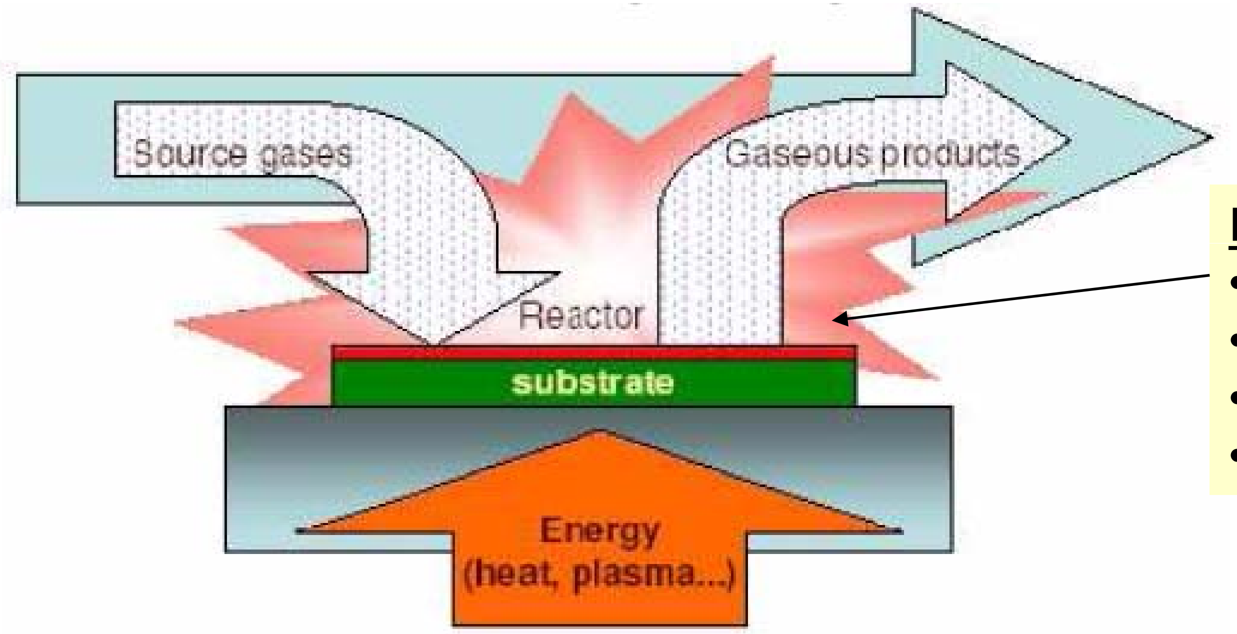
Surface modification techniques

- Chemical Vapor Deposition (CVD)
- Spin and dip coating
- Evaporation
- Sputtering
- Molecular Beam Epitaxy (MBE)
- Self-Assembled Monolayers
- Physisorbed Polymeric layers
- Polymerization on the surface. Plasma polymerisation

Ion plating, e.g. TiN

Chemical vapor deposition

- Deposition of homogeneous layers via gas reaction on a heated surfaces
- Commonly used for deposition of poly-Si, SiO_2, SiNx, diamond etc.



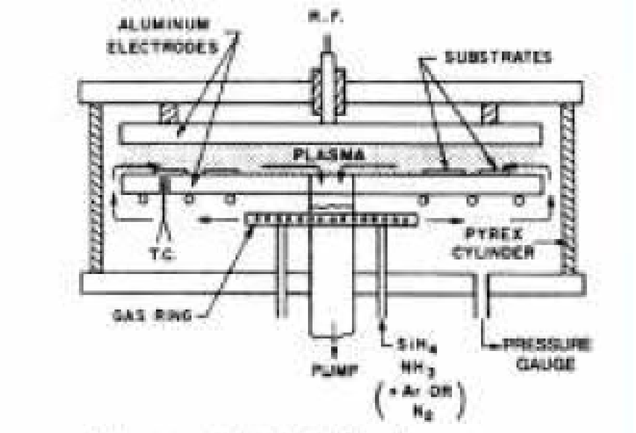
<u>Processes involved:</u>

- Adsorption on the surface
- Desorption from the surface
- Diffusion on the surface
- Bond formation

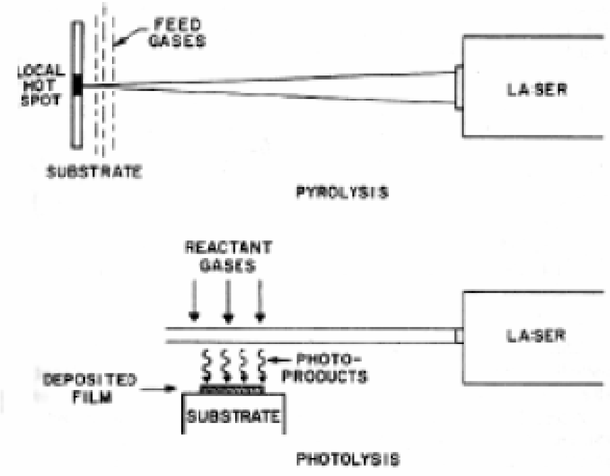
Chemical vapor deposition

- CVD reactor types:
  - Atmospheric-pressure CVD (APCVD), used mainly for thick oxides
    - fast deposition, simple, high throughput
    - mass-transport limited
    - poor uniformity, step coverage. Low purity.
  - Low-pressure CVD (LPCVD), P=1-10 mTorr, used for polysilicon, dielectric layers,
    - excellent purity, uniformity and step coverage
    - low deposition rates
    - surface reaction rate limited
  - Metal Organic CVD (MOCVD), used for optical technology and some metal deposition (W, Cu)
    - Advantages.: Highly flexible—> can deposit semiconductors, metals, dielectrics
    - Disadvantages: HIGHLY TOXIC!, Very expensive source material. Environmental disposal costs are high.
  - Plasma assisted deposition (plasma can lower required temperatures)
    - Advantages.: Uses low temperatures necessary for rear end processing.
    - Disadvantages: Plasma damage typically results.
  - Laser/Ion beam assisted deposition

PECVD



LECVD



Reactions types in CVD

- Pyrolysis
- Reduction
- Oxidation
- Compound formation
- Disproportionation
- Reversible transfer

Reactions types in CVD

- Pyrolysis – chemical decomposition or change induced by heat

Silane amorphous

$$SiH_{4(g)} \rightarrow Si_{(s)} + 2H_{2(g)} \qquad (650^\circ C)$$

$$Ni(CO)_{4(g)} \rightarrow Ni_{(s)} + 4CO_{(g)} \qquad (180^\circ C)$$

Ni carbonyl

- Reduction – any process in which electrons are added to an atom or ion (as by removing oxygen or adding hydrogen); always occurs accompanied by oxidation of the reducing agent

epitaxial

$$SiCl_{4(g)} + 2H_{2(g)} \rightarrow Si_{(s)} + 4HCl_{(g)} \qquad (1200^\circ C)$$

$$WF_{6(g)} + 3H_{2(g)} \rightarrow W_{(s)} + 6HF_{(g)} \qquad (300^\circ C)$$

$$MoF_{6(g)} + 3H_{2(g)} \rightarrow Mo_{(s)} + 6HF_{(g)} \qquad (300^\circ C)$$

Reactions types in CVD

- Oxydation

Silane

$$SiH_{4(g)} + O_{2(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)} \qquad (450^\circ C)$$

$$SiH_{4(g)} + 2H_{2(g)} + O_{2(g)} \rightarrow$$

$$\rightarrow SiO_{2(s)} + 4HCl_{(g)} \qquad (1500^\circ C)$$

soot

$$2AlCl_{3(g)} + 3H_{2(g)} + 3CO_{2(g)} \rightarrow$$

$$\rightarrow Al_2O_{3(s)} + 3CO_{(g)} + 6HCl_{(g)} \qquad (1000^\circ C)$$

Reactions types in CVD

- Compound formation

hard surface coatings

$$SiCl_{4(g)} + CH_{4(g)} \rightarrow SiC_{(s)} + 4HCl_{(g)} \qquad (1400^{\circ}C)$$

$$TiCl_{4(g)} + CH_{4(g)} \rightarrow TiC_{(s)} + 4HCl_{(g)} \qquad (1000^{\circ}C)$$

$$BF_{3(g)} + NH_{3(g)} \rightarrow BN_{(s)} + 3HF_{(g)} \qquad (1100^{\circ}C)$$

MOCVD:

$$(CH_3)_3Ga_{(g)} + AsH_{3(g)} \rightarrow GaAs_{(s)} + 3CH_{4(g)} \qquad (650 - 750^{\circ}C)$$

Reactions types in CVD

- Disproportionation – a chemical reaction in which a single substance acts as both oxidizing and reducing agent, resulting in the production of dissimilar substances

$$2GeI_{2(g)} \underset{\leftarrow 600\text{ C}}{\overset{300\text{ C}\rightarrow}{\leftrightarrow}} Ge_{(s)} + GeI_{4(g)}$$

lower-valent state is more stable at high T

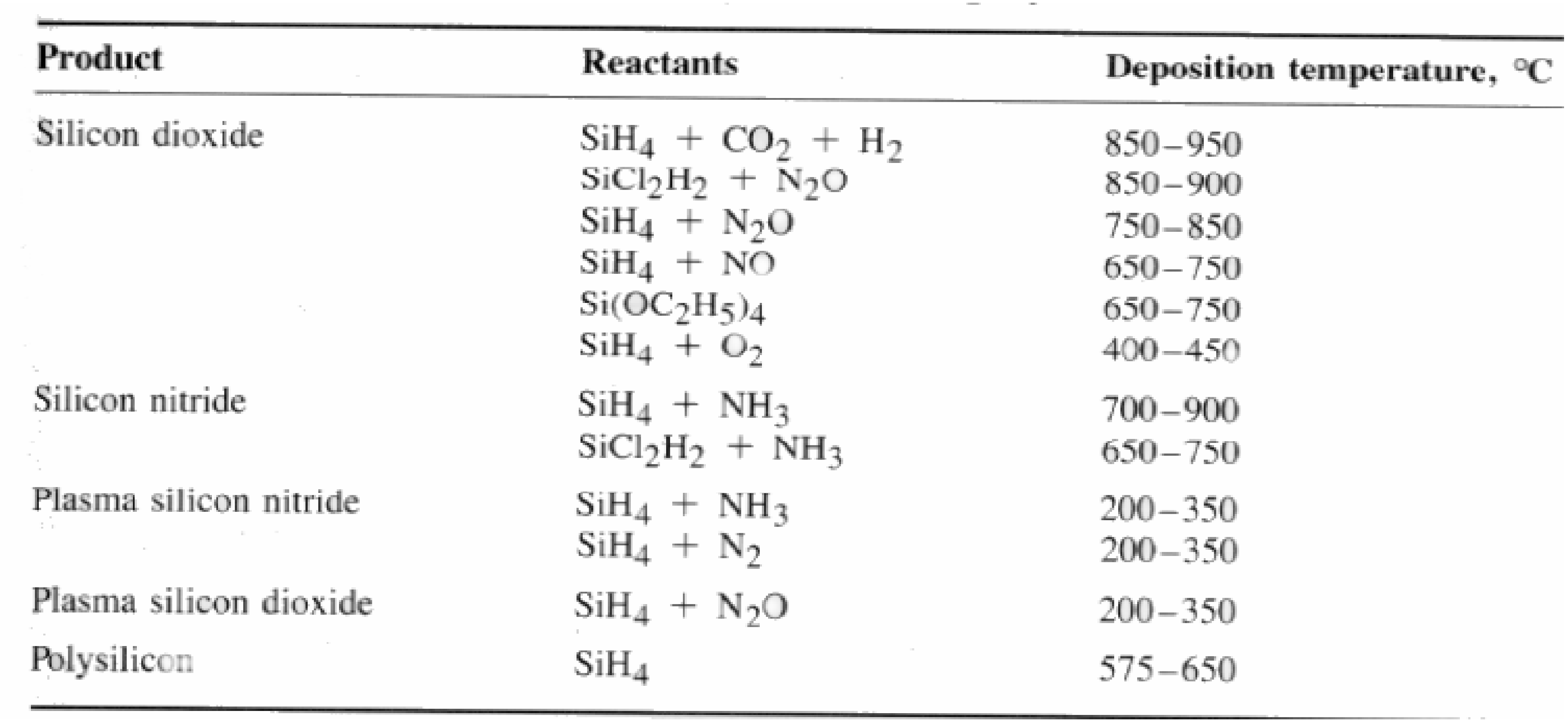
Al, B, Ga, In, Si, Ti, Zr, Be, Cr can be deposited this way

- Reversible transfer

$$As_{4(g)} + As_{2(g)} + 6GaCl_{(g)} + 3H_{2(g)} \underset{\leftarrow 850\text{ C}}{\overset{750\text{ C}\rightarrow}{\leftrightarrow}} 6GaAs_{(s)} + 6HCl_{(g)}$$

Chemical vapor deposition

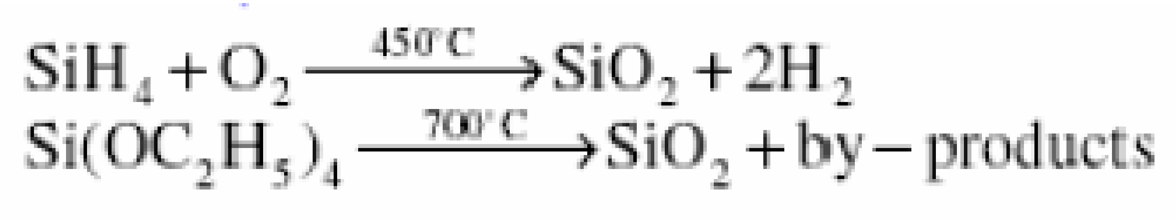
- Typical reaction for CVD



Product	Reactants	Deposition temperature, °C
Silicon dioxide	$SiH_4 + CO_2 + H_2$	850–950
	$SiCl_2H_2 + N_2O$	850–900
	$SiH_4 + N_2O$	750–850
	$SiH_4 + NO$	650–750
	$Si(OC_2H_5)_4$	650–750
	$SiH_4 + O_2$	400–450
Silicon nitride	$SiH_4 + NH_3$	700–900
	$SiCl_2H_2 + NH_3$	650–750
Plasma silicon nitride	$SiH_4 + NH_3$	200–350
	$SiH_4 + N_2$	200–350
Plasma silicon dioxide	$SiH_4 + N_2O$	200–350
Polysilicon	SiH_4	575–650

Chemical vapor deposition

- Example: SiO_2 deposition



$$SiH_4 + O_2 \xrightarrow{450^\circ C} SiO_2 + 2H_2$$

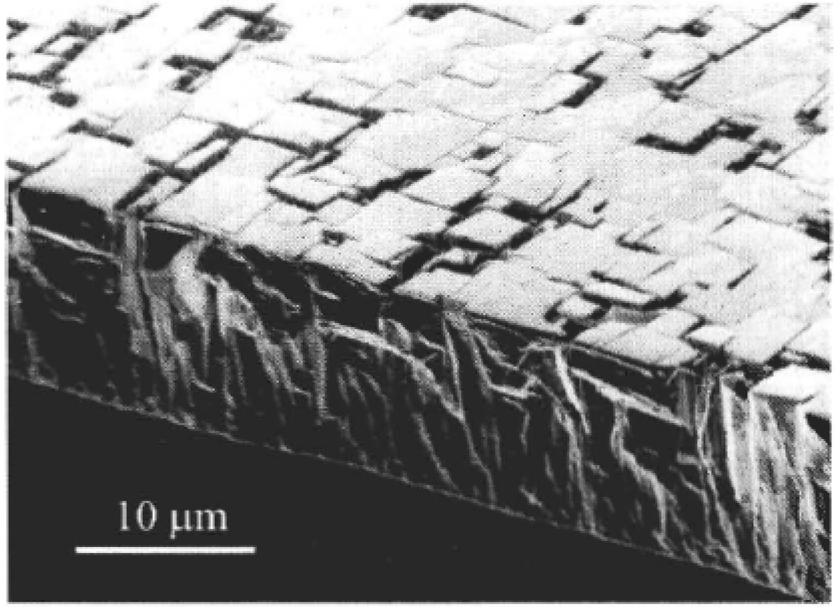
$$Si(OC_2H_5)_4 \xrightarrow{700^\circ C} SiO_2 + by - products$$

  - TEOS gas (Tetraethylorthosilane)
  - process condition: T=700ºC, P=30 Pa (mean free path ~100µm)
  - sometimes O_3 is added to reduce the reaction temperature (formation of reactive radicals at ~200ºC)

Chemical vapor deposition

- Example: CVD diamond film deposition

- CVD diamond films:
  - hard coating
  - low friction coefficient
  - chemicall inert
  - optically transparent
  - can be doped to become conductive



- Chemistry: at 800ºC

$$H_2 \longrightarrow 2H^*$$

$$CH_4 + H^* \longrightarrow CH_3^* + H_2$$

on the surface

$$\left\{ \begin{aligned} &\sim CH + H^* \longrightarrow \sim C^* + H_2 \\ &\sim C^* + CH_3^* \longrightarrow \sim CCH_3 \end{aligned} \right.$$

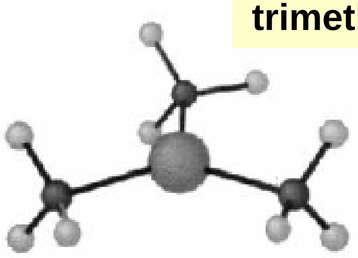
carbon seed layer on the surface required (e.g. evaporated)

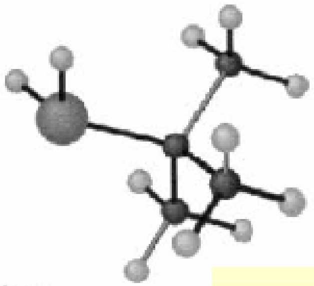
Chemical vapor deposition

- Metal Organic Chemical Vapor Deposition (MOCVD)

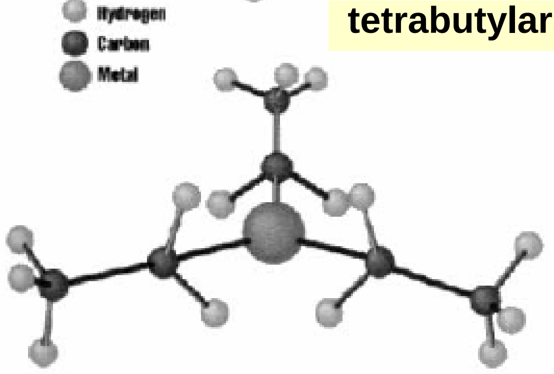
- The idea
  - Many materials that we wish to deposit have very low vapor pressures and thus are difficult to transport via gases.
  - One solution is to chemically attach the metal (Ga, Al, Cu, etc…) to an organic compound that has a very high vapor pressure.
  - The organic-metal bond is very weak and can be broken via thermal means on wafer, depositing the metal with the high vapor pressure organic being pumped away.
- Disadvantages
  - Care must be taken to insure little of the organic byproducts are incorporated. Carbon contamination and unintentional hydrogen incorporation are sometimes a problem.

trimethylgallium





tetrabutylarsine



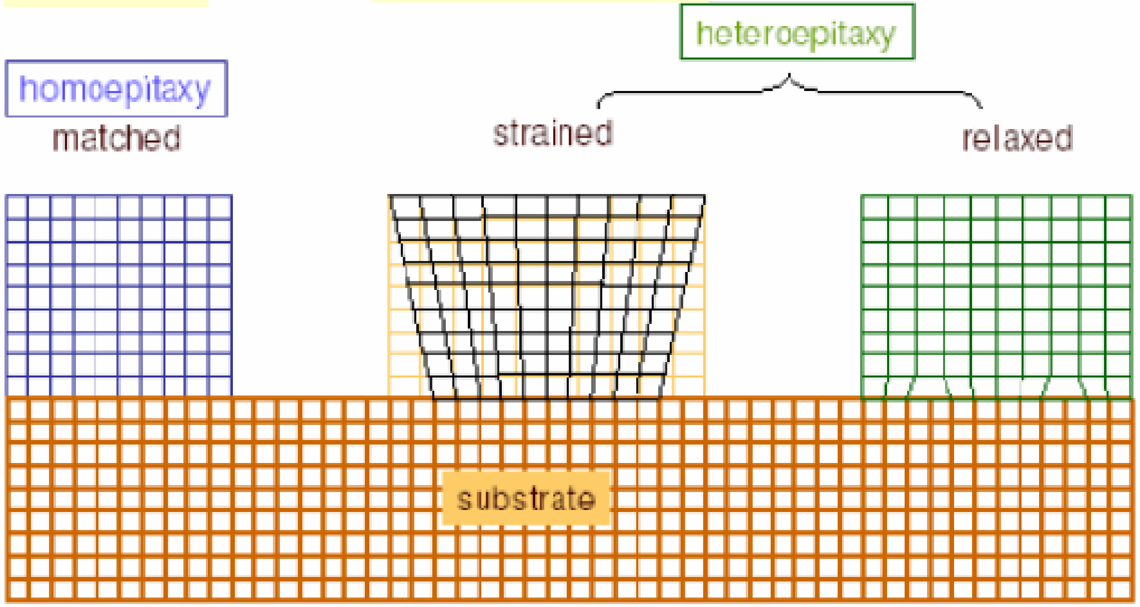
triethylgallium

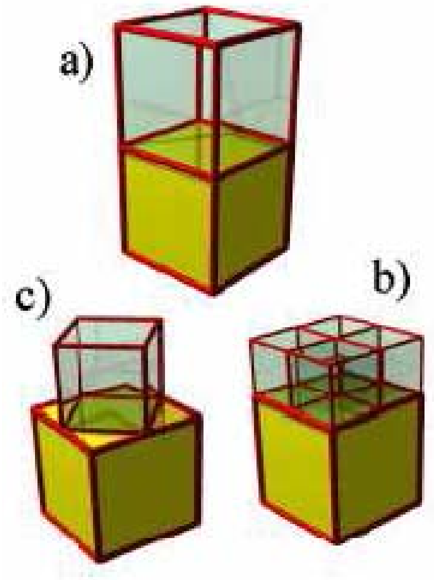
Epitaxy

- Epitaxy – formation of a single crystalline film on top of another crystalline material

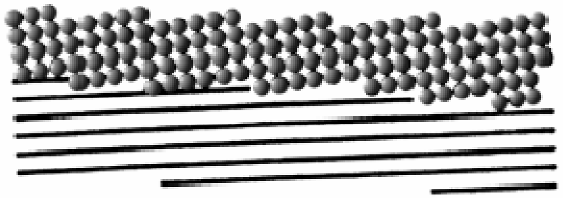
Si on Si

AlAs on GaAs



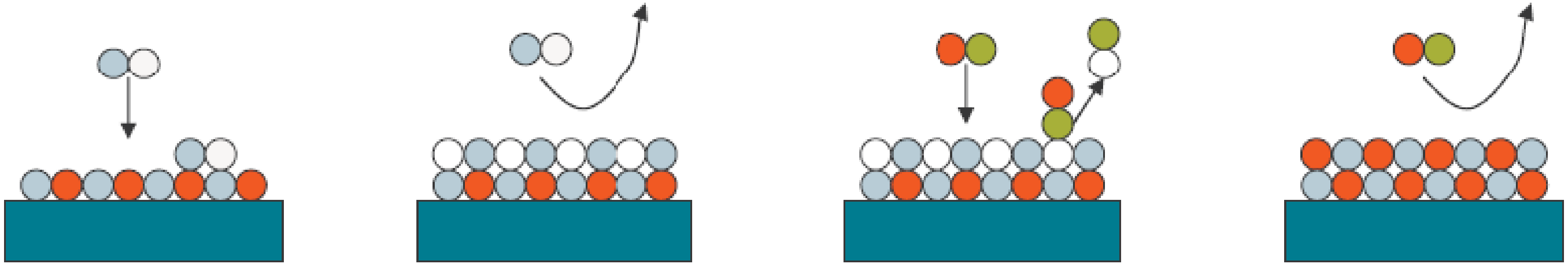


Tilted-layer epitaxy

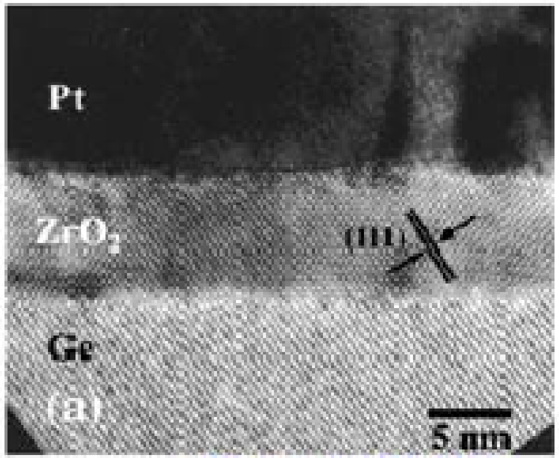


Atomic layer epitaxy

- Self-limiting growth, one layer at a time:



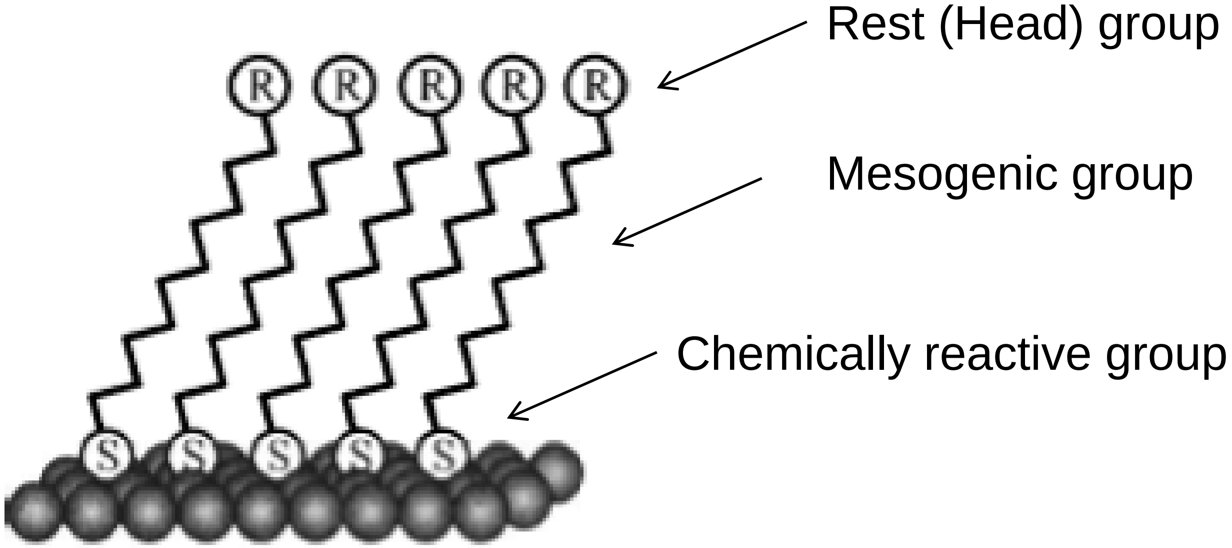
- Popular for II-IV oxides
- Electrochemical ALE possible



Kim et al, APL 2003

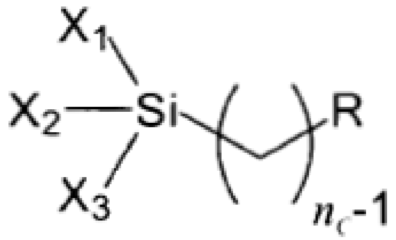
Self-Assembled monolayers (SAMs)

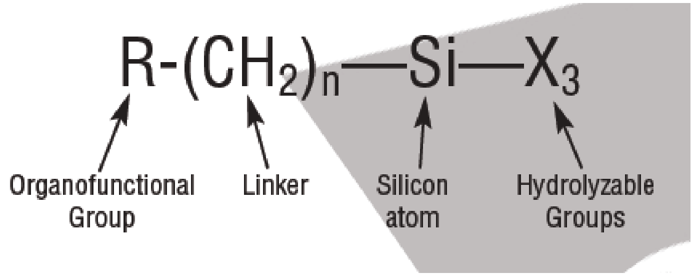
- Several type of monolecules (thiols, silanes, isocianides, amines, organic acids etc.) are capable of forming SAMs on specific surfaces
- The process is governed by
  - chemical bond formation between the head group and the surface
  - vdWaals interaction between the mesogenic groups
  - interaction between the tail groups



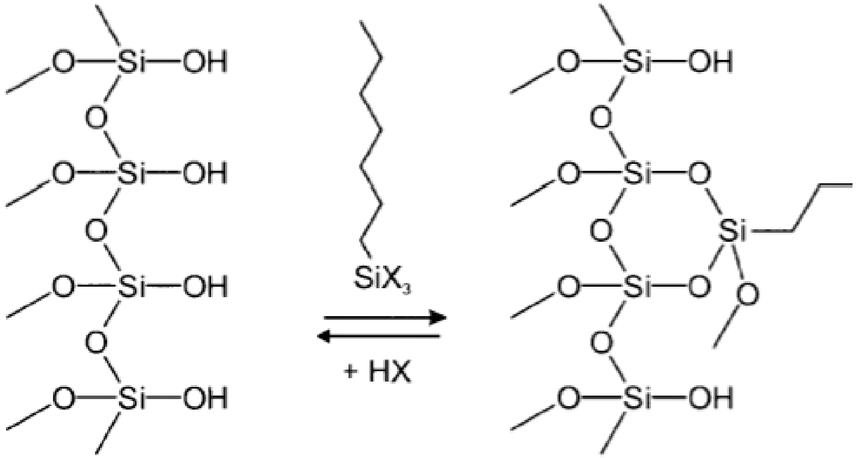
Self-Assembled monolayers (SAMs)

- Silanes

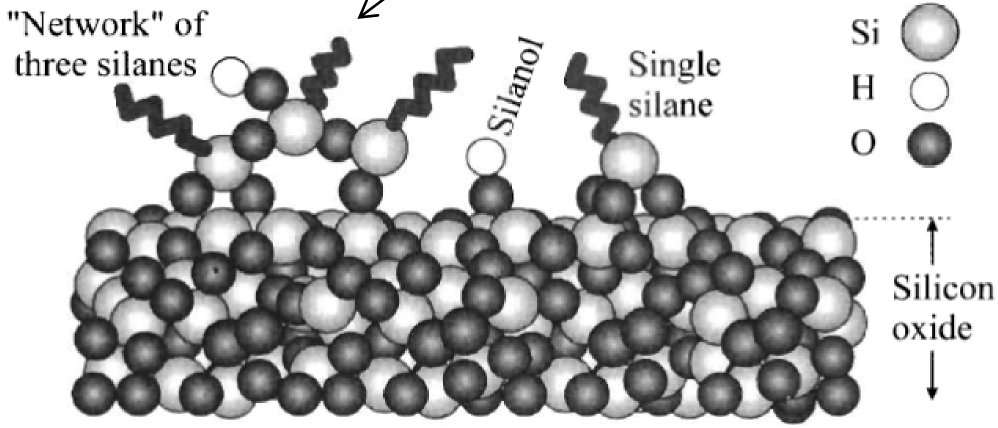




- Silanes react with silanol (~SiOH) groups on the surface
- Silanization reaction scheme



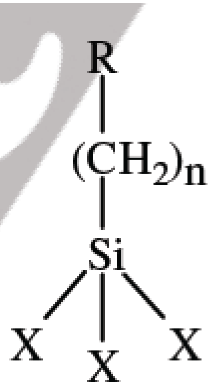
higher roughness



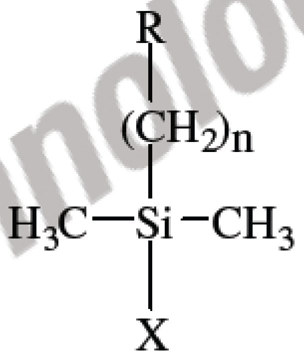
- Water competes with the ~OH groups on the surface causing silanes polymerization to polysiloxane network and should be excluded from the reaction.

Self-Assembled monolayers (SAMs)

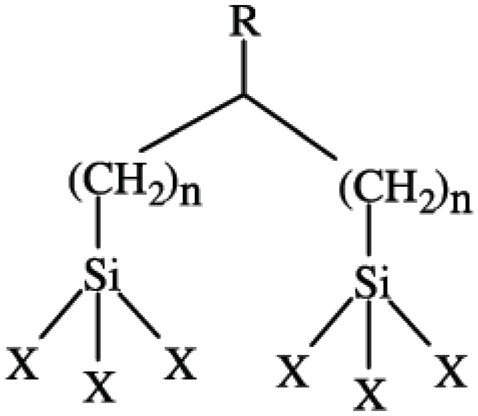
- Silanes tips and tricks (from Gelest, Inc)



Trialkoxysilane



Monoalkoxysilane



Dipodal Silane

mainstream approach

better film uniformity

better adhesion and hydrolytic stability

Self-Assembled monolayers (SAMs)

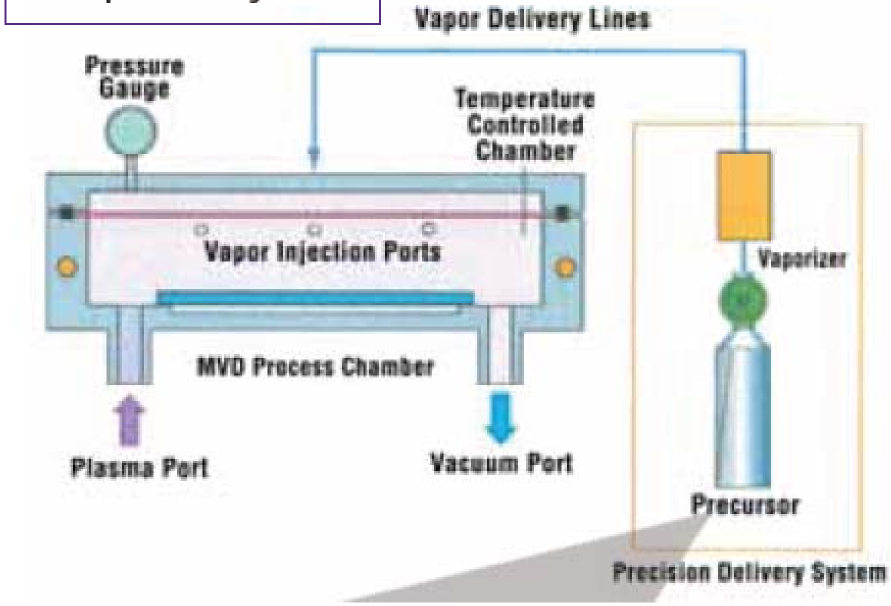
Silanes deposition (from Gelest, Inc)

- Deposition from solution
  - Dipping;
  - Spin coating:
  - Spray coating

Common lab process: Deposition from anhydrous solutions typ. 2-5% of chlorosilanes, methoxysilanes, ethoxysilanes in abs. ethanol, toluene etc. Pre-drying of substrates is required. Post cure at 110C is desirable.

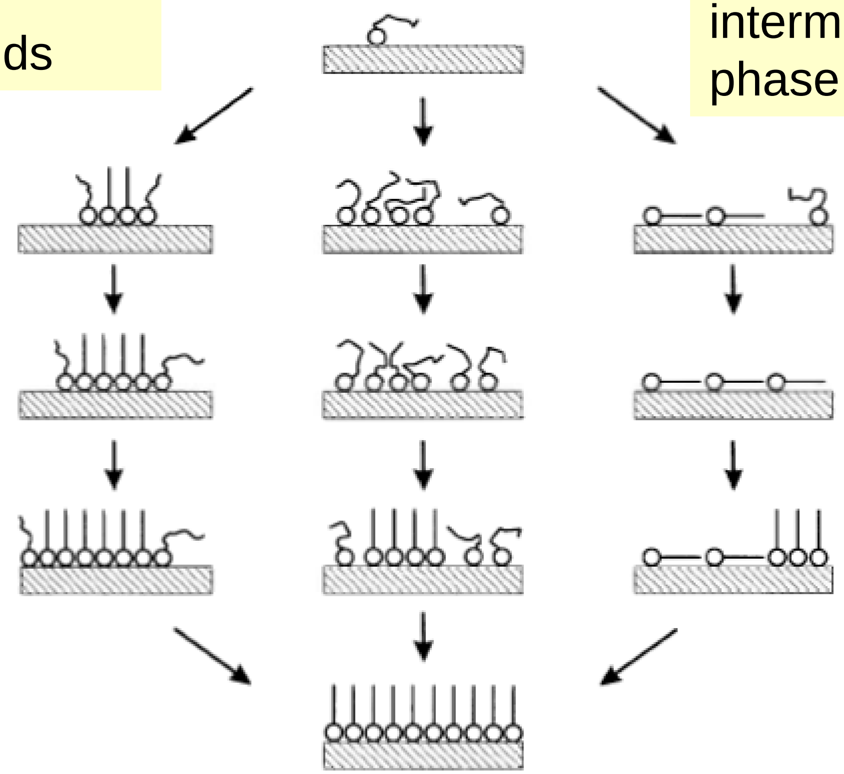
- Vapour phase deposition

Apparatus for vapor phase silylation.



Self-Assembled monolayers (SAMs)

- SAM growth models:



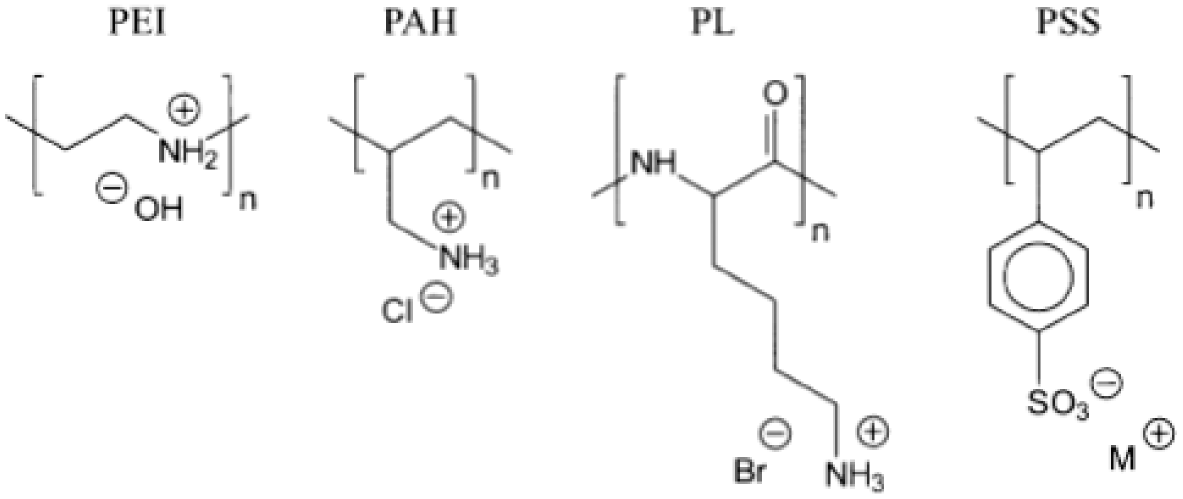
growth of two-dimensional crystalline islands

via formation of intermediate disordered phase

via formation of intermediate ordered phase

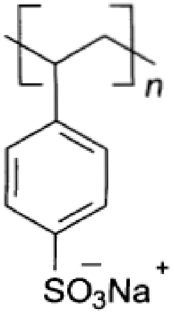
Physisorption of polymers

- Macromolecules tend to adsorb irreversibly to the surfaces due to large amount of “bonds” formed (even if the single “bond” energy is <kT)
- Polyelectrolytes: charged polymers, e.g. DNA, polyethylenamine, polysulfonate etc.)

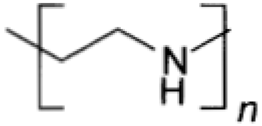


Electrostatic Layer-by-Layer Deposition

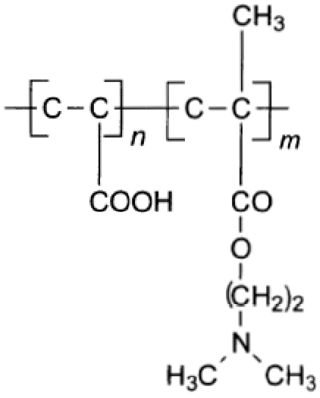
- polyelectrolytes
  - **strong** – fully dissociated, constant charge in the solution in the full range of pH
  - **weak** – dissociated within the limited range of pH
  - **polyampholytes** – sign of electrostatic charge can be reversed by varying pH (e.g. proteins)



Poly(styrene sulfonate) (PSS)



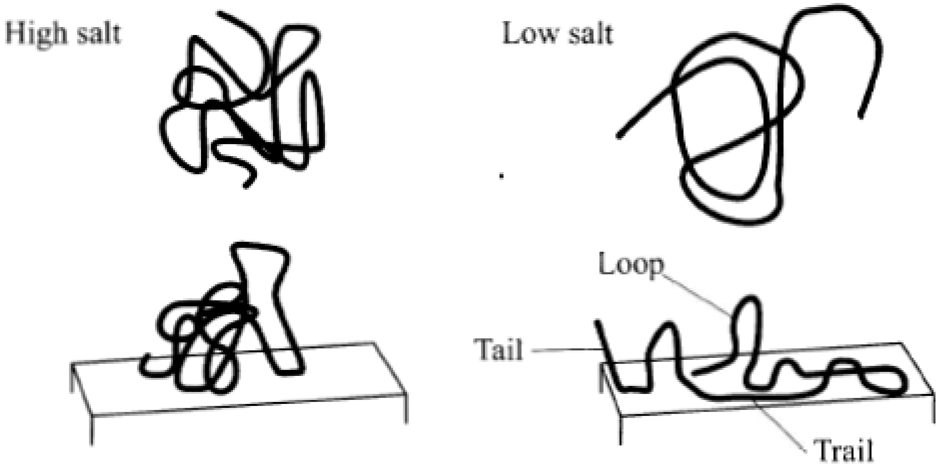
Polyethilenimine (PEI)



Copolymer of acrylic acid and dymethilaminoethyl methacrylate

Physisorption of polymers

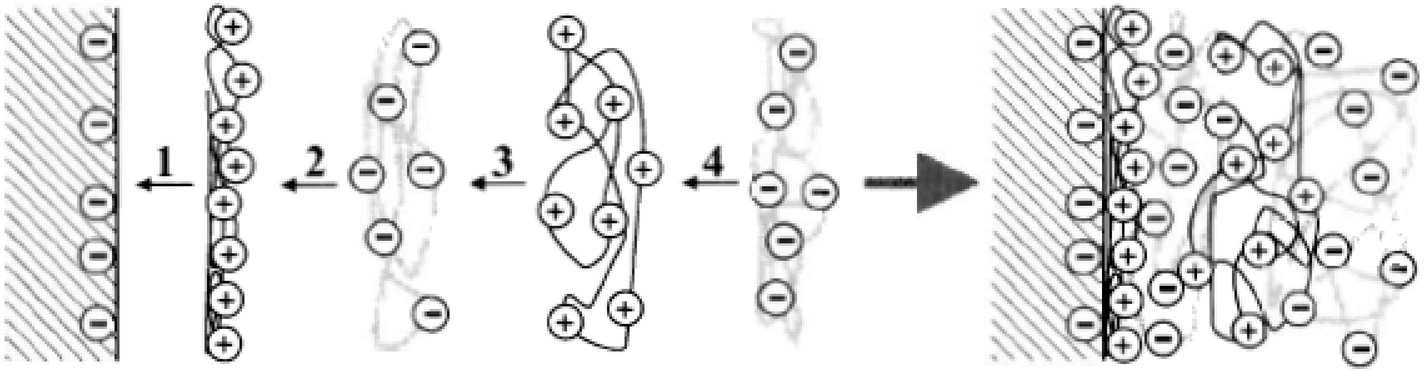
- Adsorption of polyelectrolyte depends on pH and ionic strength



- Example: deposition of DNA on mica

Physisorption of polymers

- Layer-by-Layer assembly of polyelectrolytes



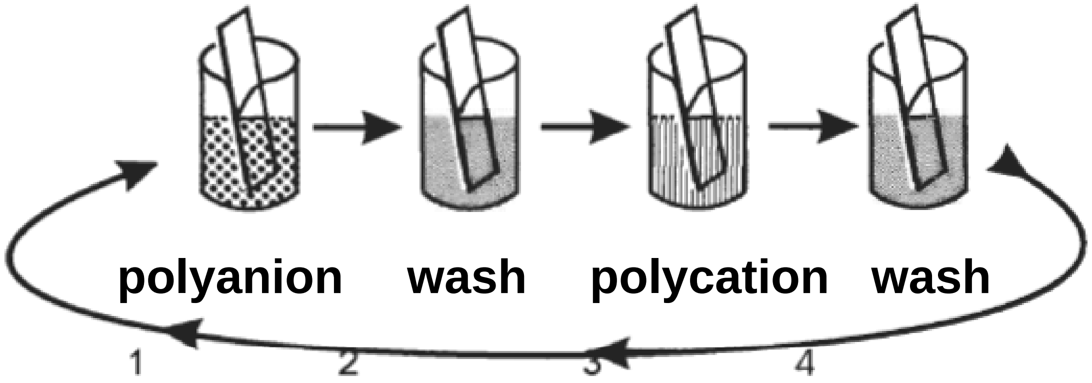
negatively charged
electrolyte
adsorbed, e.g. PEI

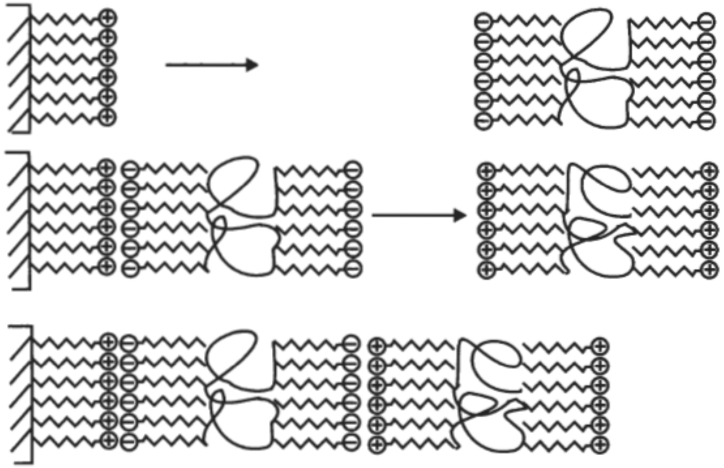
typical surface
potential of
silicon wafer -
10mV

positively charged
electrolyte
adsorbed, e.g. PEI

Electrostatic Layer-by-Layer Deposition

- LbL process works through sequential immersion in polyanion and polycation solutions





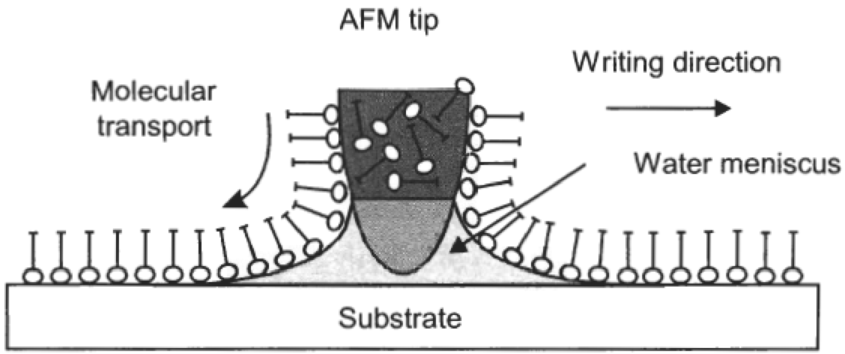
- any substrate with surface charge is suitable! (e.g. mica, silicon, glass, colloids etc.)

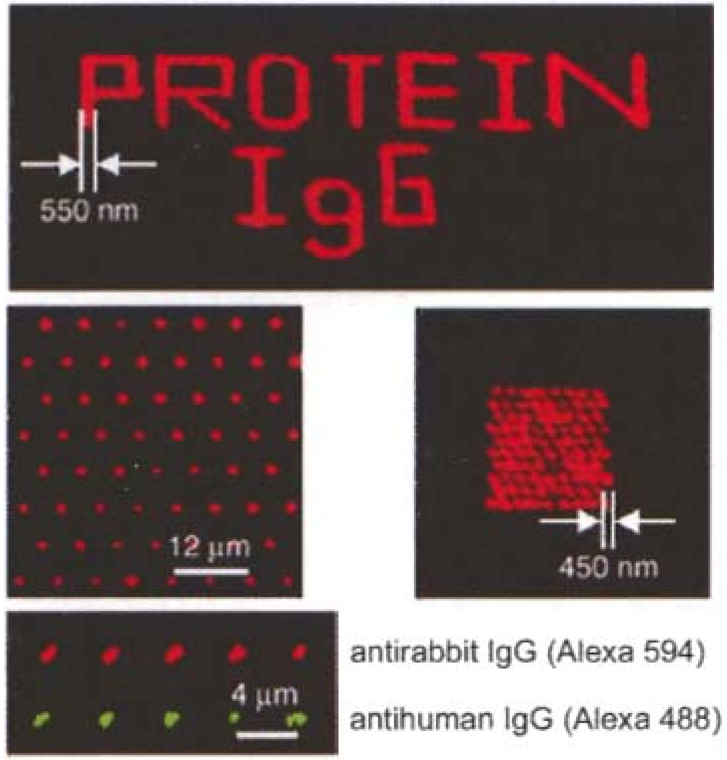
Electrostatic Layer-by-Layer Deposition

- Morphology :
  - non-linear growth, usually starts with islands on charged surface defects
  - depends on the conformation of the polymeric chain (e.g. coil – flatter monolayers vs globule – roughter monolayers)

Dip-Pen Nanolithography

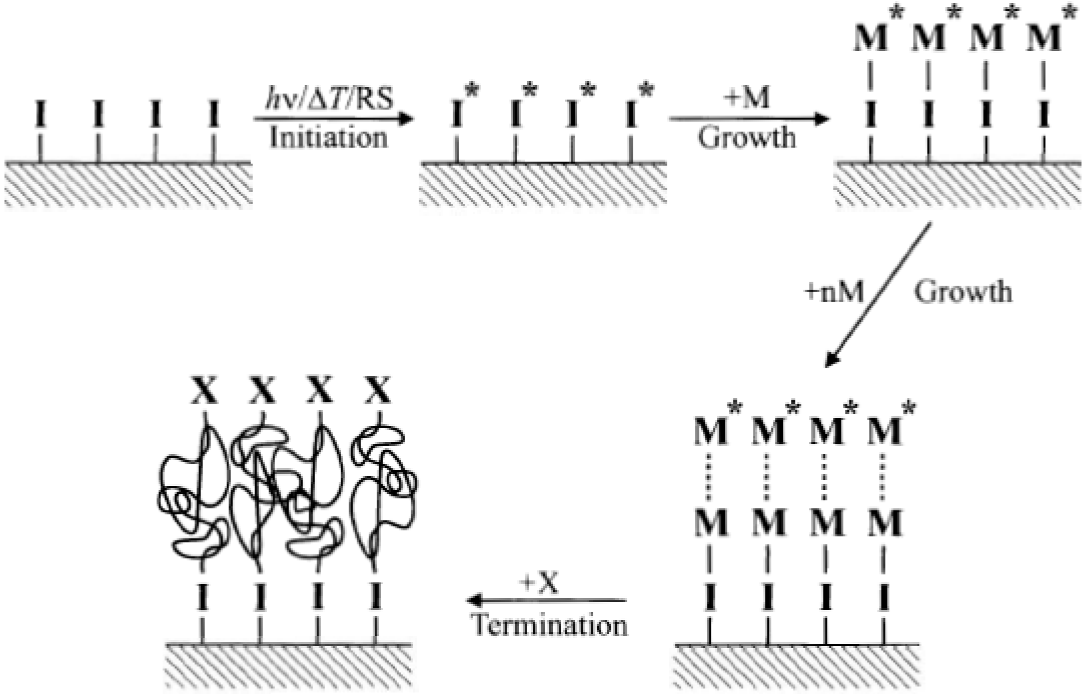
- Molecules are first adsorbed on an AFM tip and than transferred to the substrate (“inversed LB”)





Polymerization on the surfaces

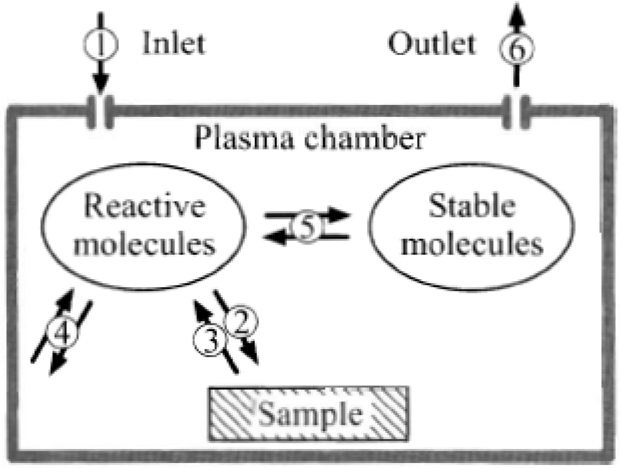
- Polymerization approaches:
  - “Grafting-to”: adsorption or chemical coupling of a polymerized chain to the surface. Disadvantage: density is limited by the size of polymer coil;
  - “Grafting-from” or surface-initiated polymerization



- Activation types: radical and living ionic (anionic or cationic).
  Living ionic gives better monodispercity, but sensitive to contamination

Plasma Polymerization

- substrate is placed in the chamber containing vapor of an organic monomer and a buffer gas
- in plasma, the monomer forms radicals that initiate polymerization
- polymeric layer on the surface usually has higher branching and cross/linking degree than a conventional polymer



Problems

End of chapter problems:

- 10.1
- 10.2
- 10.5