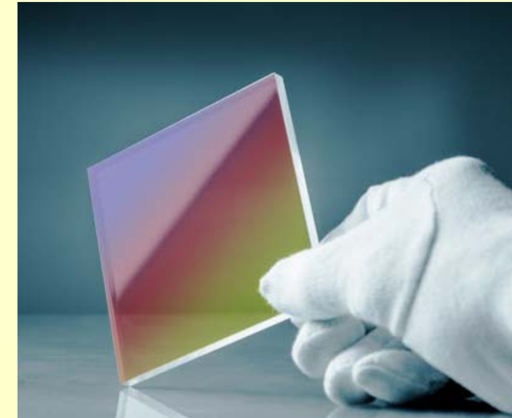
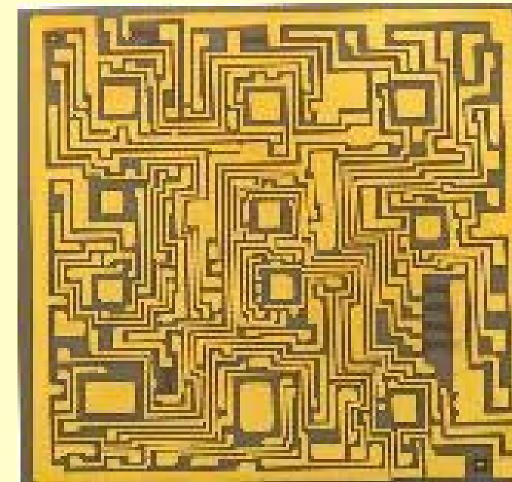
Applications of Thin Films



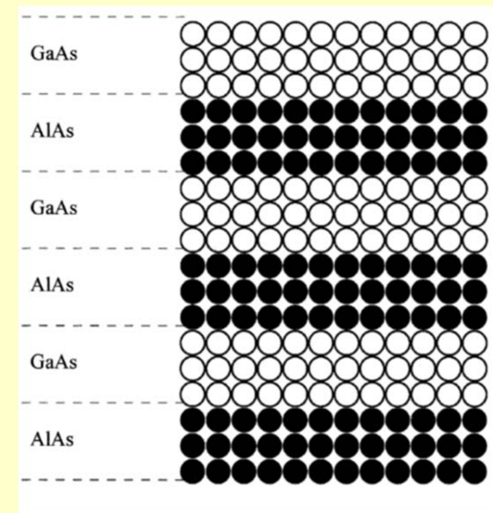


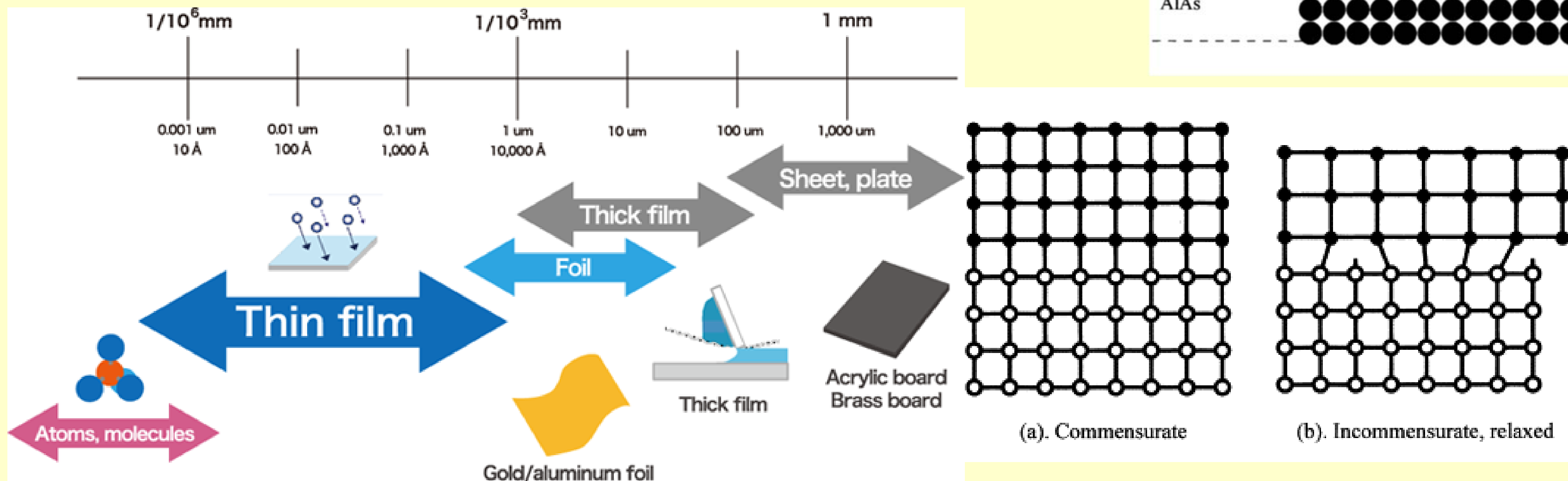
- **Protective coatings - Hard films**
- **Optical coatings - Filters, mirrors, lenses**
- **Microelectronic devices**
- **Optoelectronic devices, Photonic devices**
- **Electrode surfaces**
- **Photoelectric devices, photovoltaics, solar cells**
- **Xerography, Photography, Lithography**
- **Catalyst surfaces - Heterogeneous catalysis**
- **Information storage, magnetic, magneto-optical, optical memories**

Properties of Thin Films

- Crystalline, amorphous, microcrystalline
- Monolayer, multilayer, superlattice, junctions
- Free-standing, supported
- Epitaxial (commensurate), incommensurate

Superlattice





(a). Commensurate

(b). Incommensurate, relaxed

Properties of Thin Films

- **Thickness (1 Å – 1 μm)**
- **Surface-to-volume ratio**
- **Structure - surface versus bulk, surface reconstruction**
- **Surface morphology, roughness**
- **Chemical composition (oxides, metals, nitrides, carbides,…)**
- **Hydrophobicity, hydrophilicy (Si-OH vs. Si-H)**
- **Texture: single crystal, microcrystalline, domains, orientation: Si (100) vs. (111)**
- **Form - supported or unsupported, nature of substrate**

Surface Energy

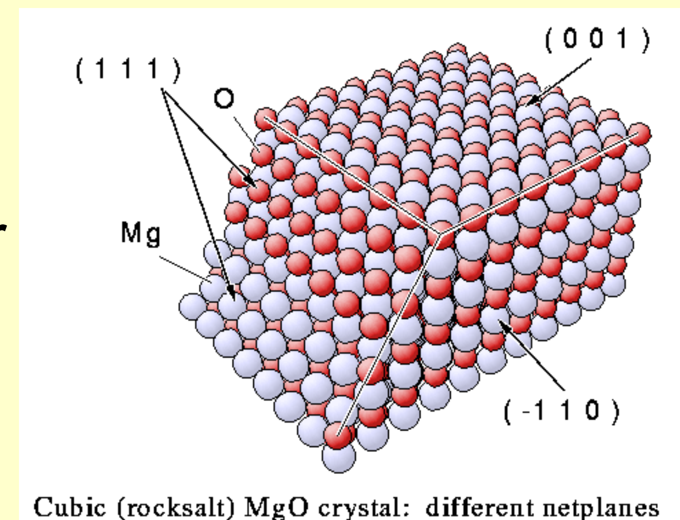
Surface energy [J m^{-2}] a scalar
Surface stress [J m^{-2}] a tensor

Same for liquids, different for solids

Surface tension [J m^{-2}] the work done in creating unit area of new surface (= Surface energy in one-component systems)

Surface energy [J m^{-2}] depends on:

- **The distance of the face from the center of the crystal**
- **Miller indices**
- **Surface roughness**
- **The radius of curvature**

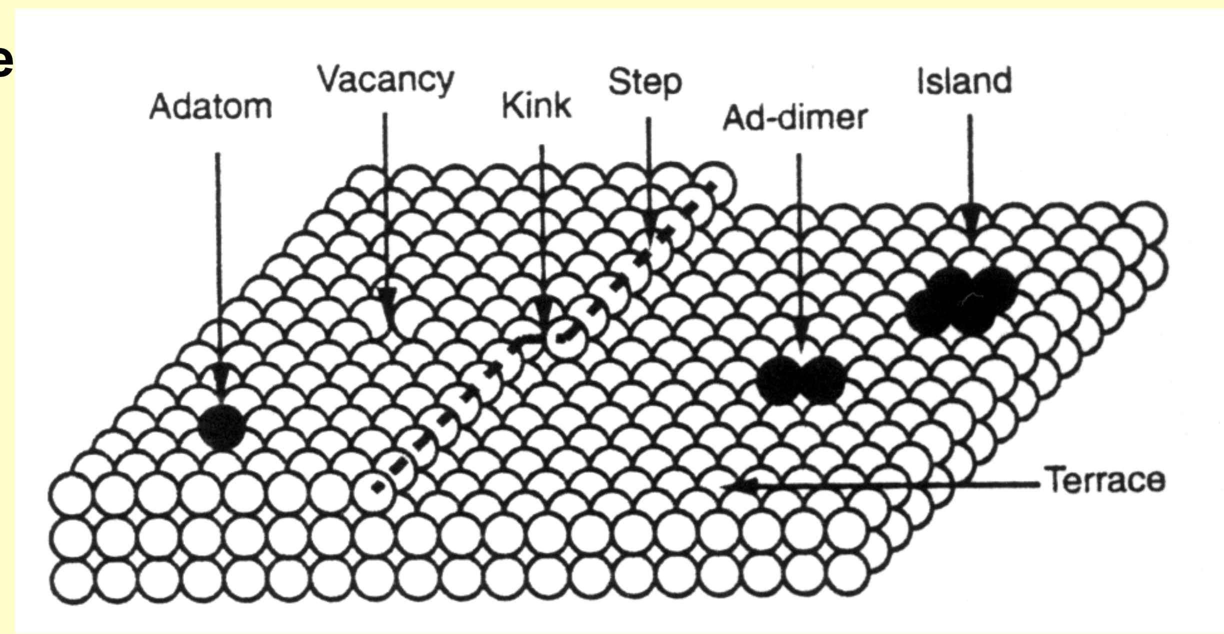


Cubic (rocksalt) MgO crystal: different netplanes

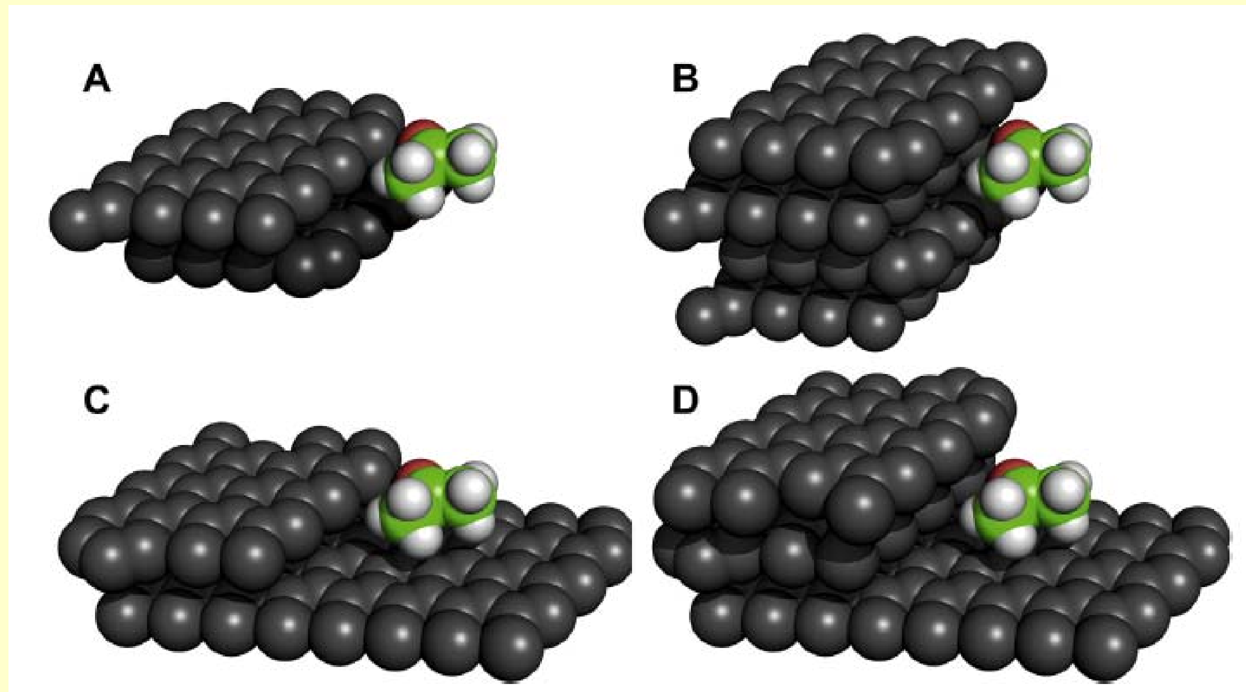
Surface Model

The Terrace-Step-Kink (TSK) Model of a Surface (Kossel/Stranski)

- **Terrace**
- **Step/Ledge**
- **Kink**
- **Vacancy**
- **Adatom**
- **Island**

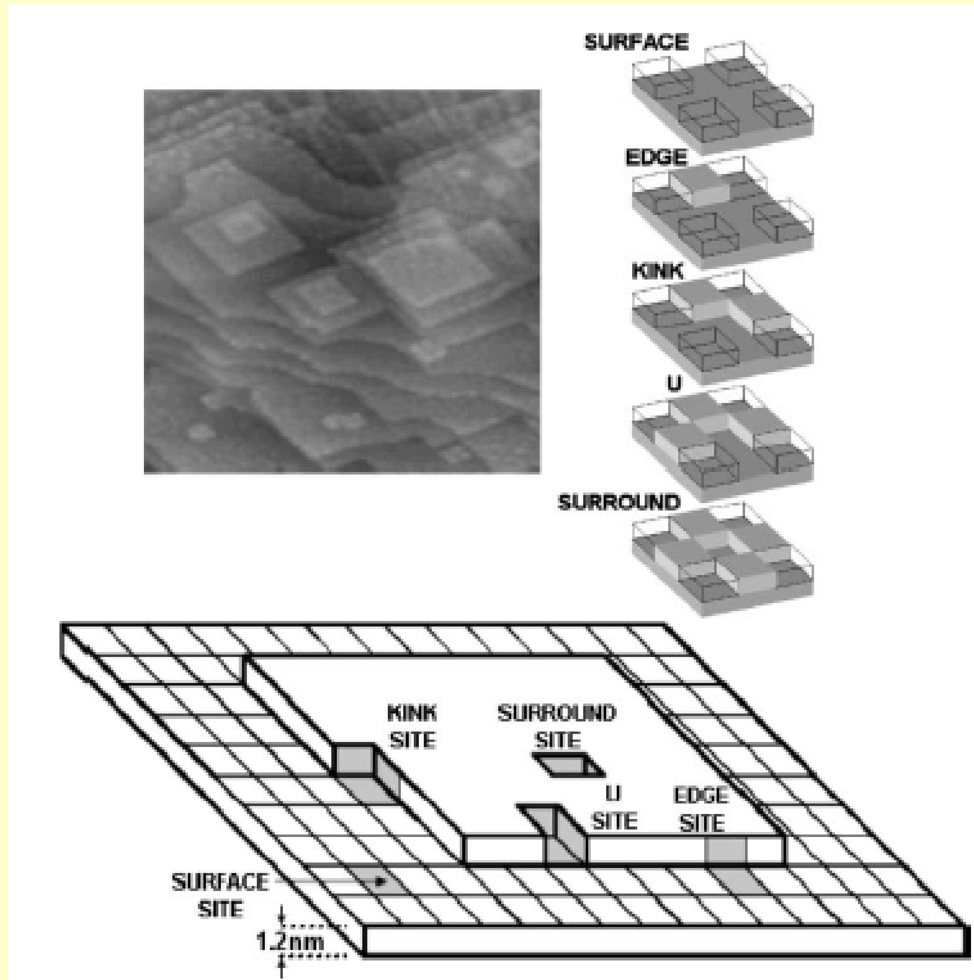


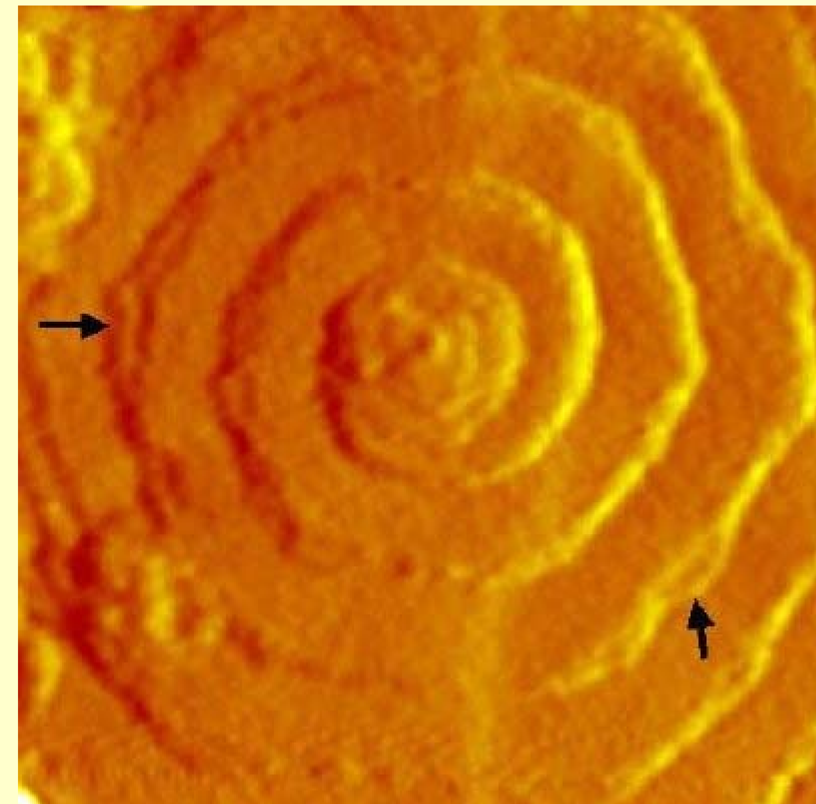
Surfaces



The acetone molecule (in colored spheres) attached to (A) the edge of bilayer graphene (carbon atoms are represented as black balls), (B) the edge of four layer graphene, (C) on a step formed from bilayer graphene, and (D) on a step formed from trilayer graphene

Surfaces





Screw dislocation on graphite
Spiral growth

Thin-Film Growth Mechanisms

The growth of epitaxial (homogenous or heterogeneous) thin films on a single crystal surface depends on **the interaction strength between adatoms and the surface**

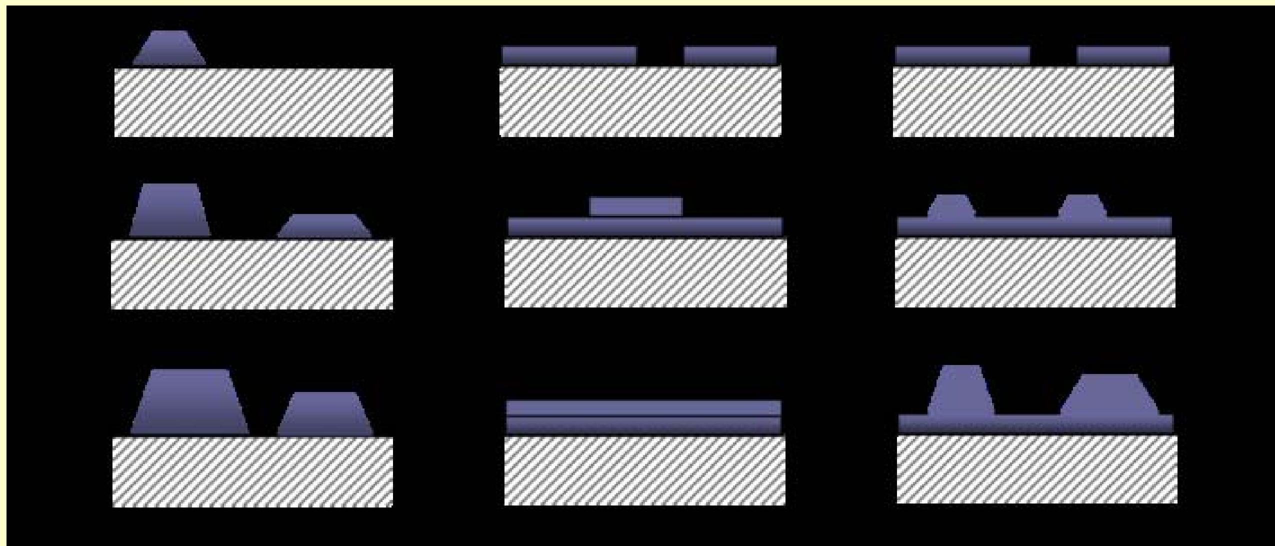
• **Volmer–Weber (VW) growth** - adatom-adatom interactions are stronger than those of the adatom with the surface, the formation of three-dimensional adatom clusters or **islands**, coarsening, rough multi-layer films

• **Frank–van der Merwe (FM) growth -** adatoms attach preferentially to surface sites, atomically **smooth layers**, layer-by-layer growth, epitaxy

• **Stranski–Krastanov growth** - an intermediary process, both 2D layer and 3D island growth, transition from the layer-by-layer (wetting layer) to island-based growth occurs at a critical layer thickness, dependent on the chemical and physical properties, such as surface energies and lattice parameters, of the substrate and film

Thin-Film Growth Mechanisms

VW (island) | **FM (layer-by-layer)** | **SK (layer-plus-island)**



Surface coverage, Θ

$\Theta < 1$ ML

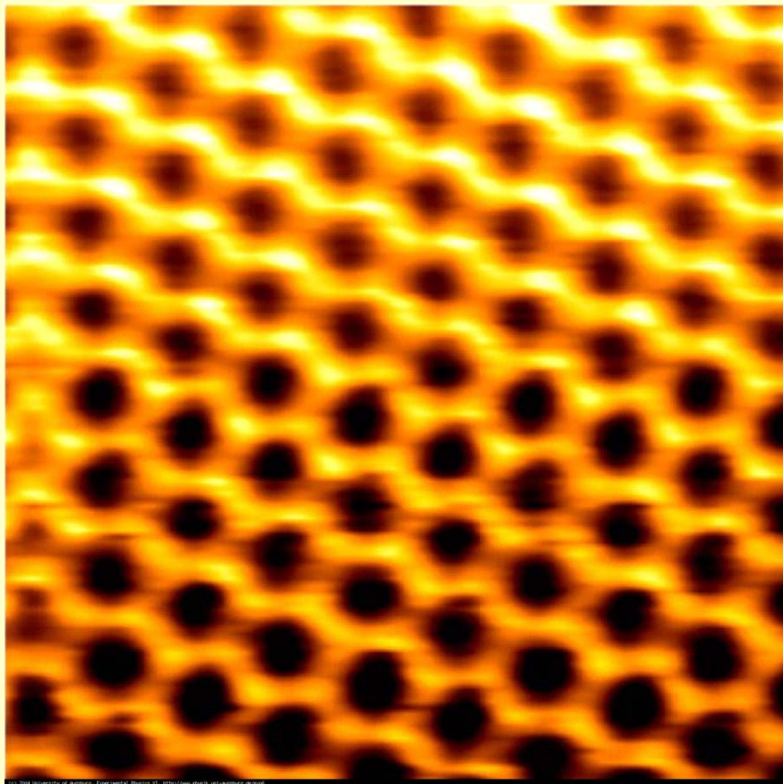
$1 < \Theta < 2$

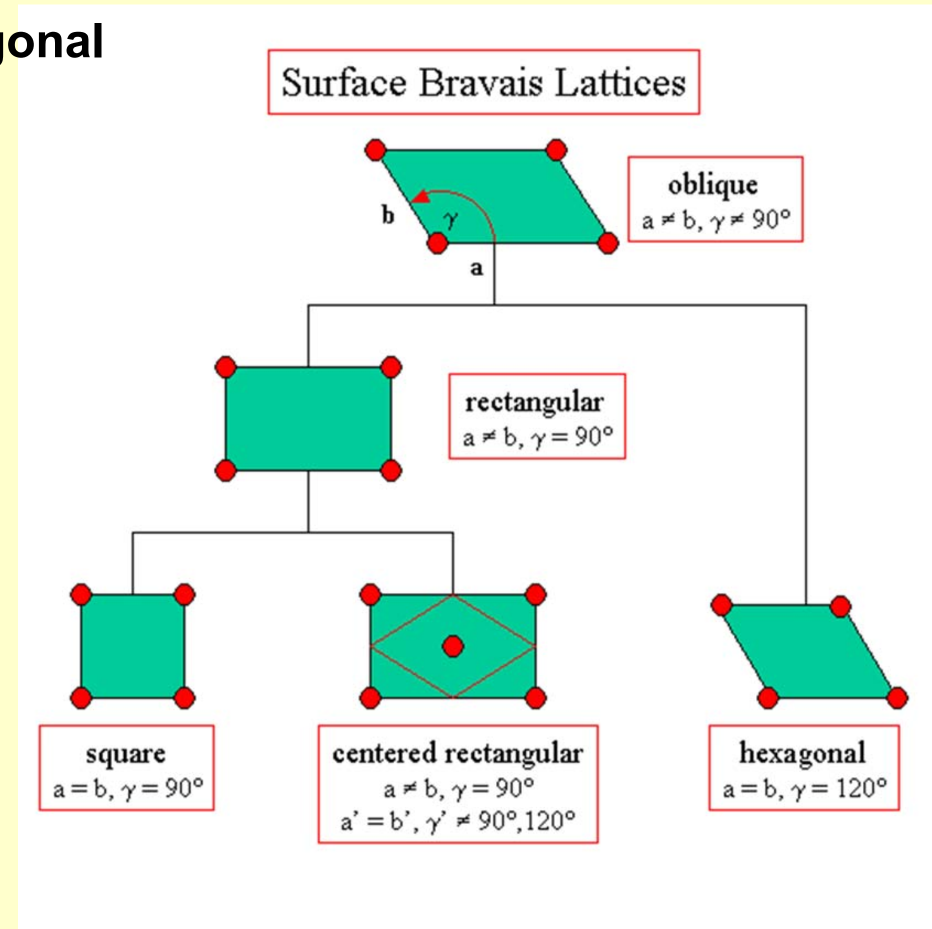
$\Theta > 2$

Symmetry at Surfaces

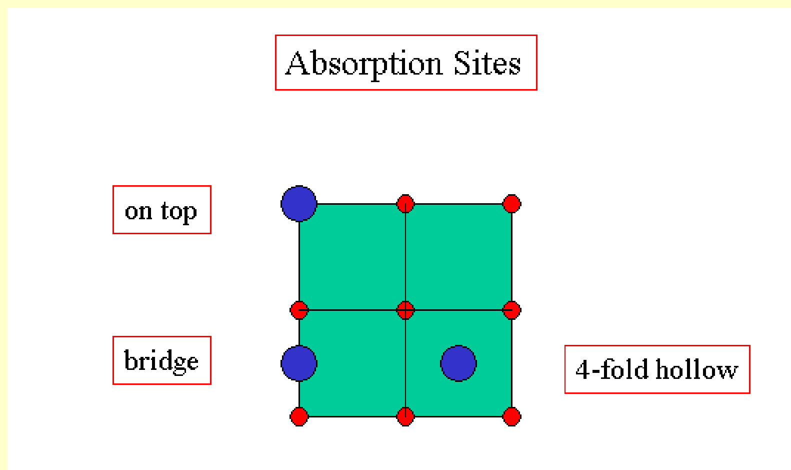
AFM of C atoms within the hexagonal graphite unit cells

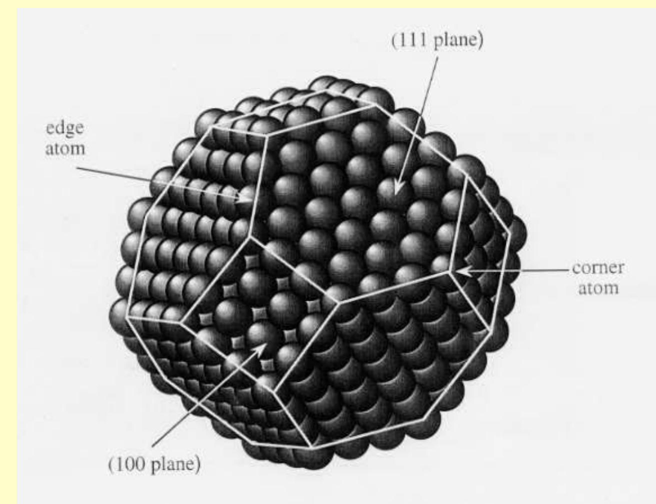
Image size 2×2 nm²

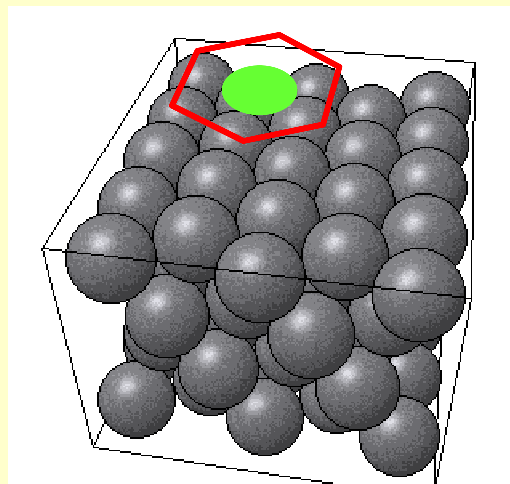




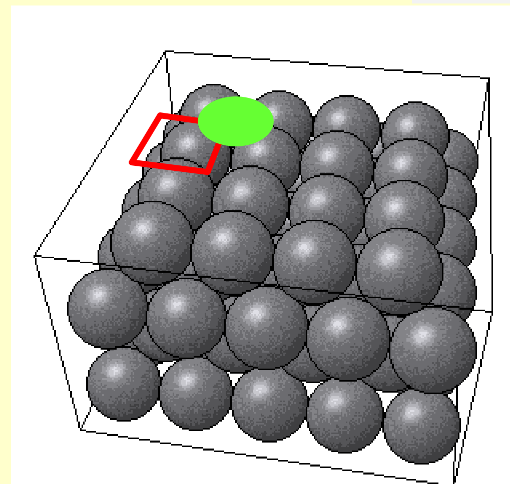
Symmetry at Surfaces



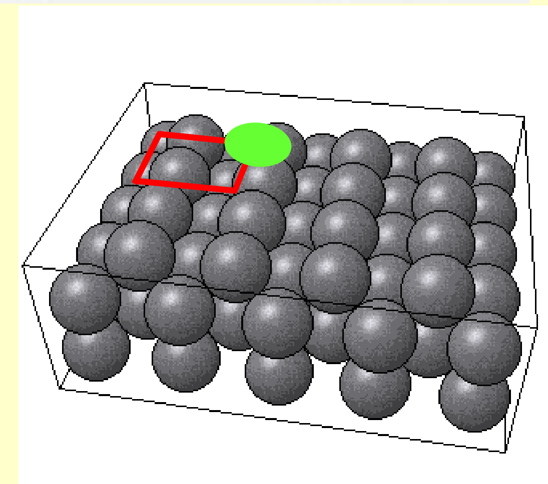




(111)



(100)



(110)

Surface Diffusion

Surface diffusion coefficient D

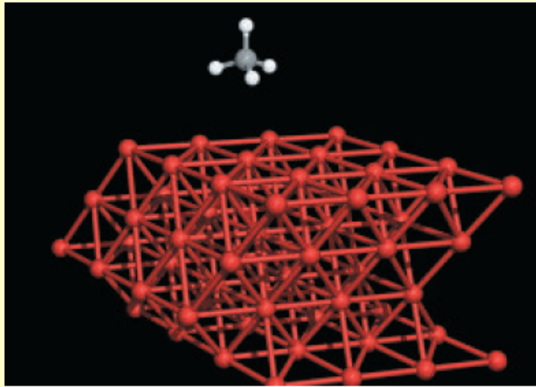
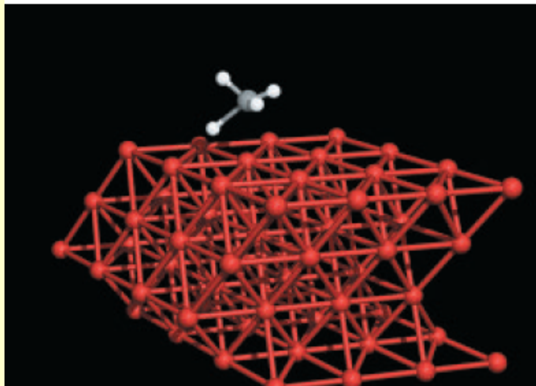
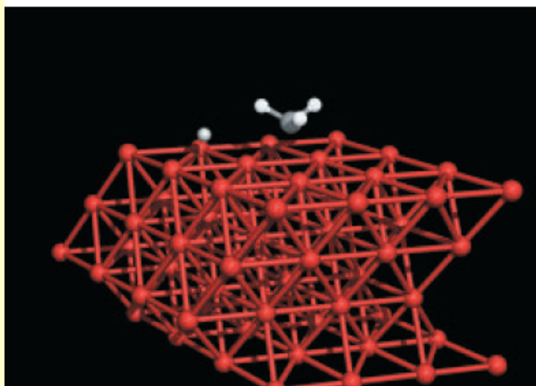
$D = a^2 k_s$

a … effective hopping distance between sites
k_s … site-to-site hopping rate of an adatom

$k_s = A \exp(-V_s/k_b T)$

V_s … energy barrier to hopping from site to site
T … substrate temperature

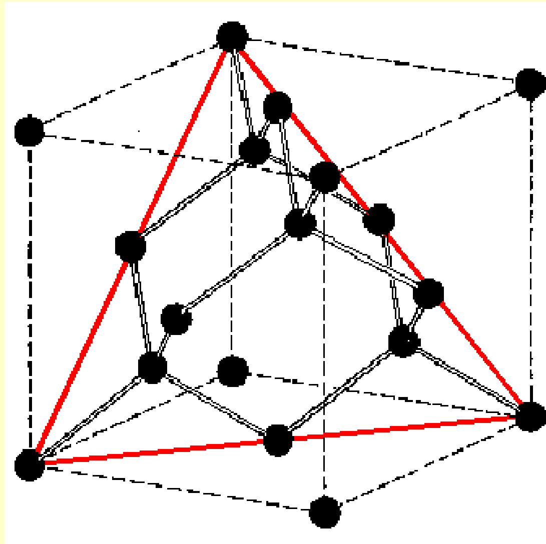
Higher temperature = Faster diffusion

Surface Diffusion

The dissociative collision of a CH_4 molecule with a nickel surface does not significantly perturb the nickel atom at the impact point

Si(111) Surface

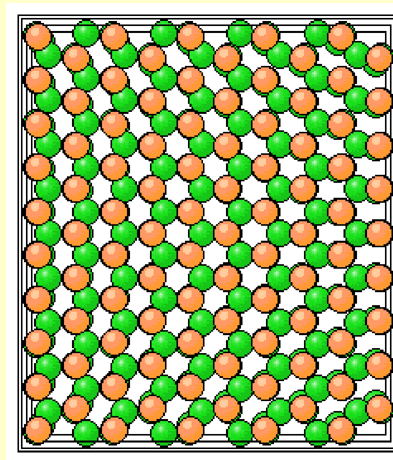


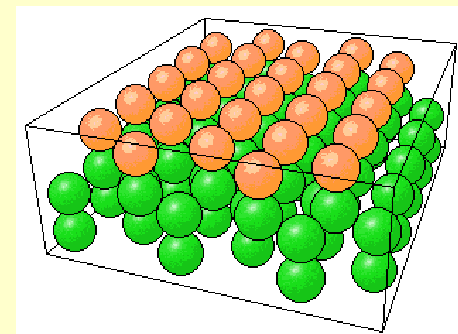
Silicon "diamond lattice" structure

a = 5.463 Å

Si(111) = a set of atomic planes
One plane outlined with red

A top view of the atomic arrangement for the (111) plane

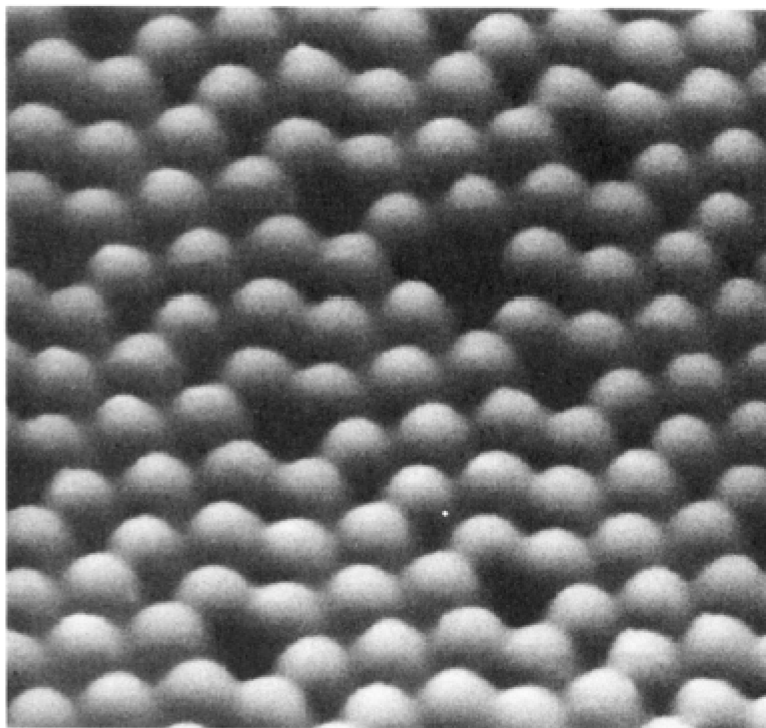




orange = the top layer
green = deeper layers

Si (111) etches more slowly than (001)
Si (111) oxidizes twice as rapidly as (001)

Si(111) Surface



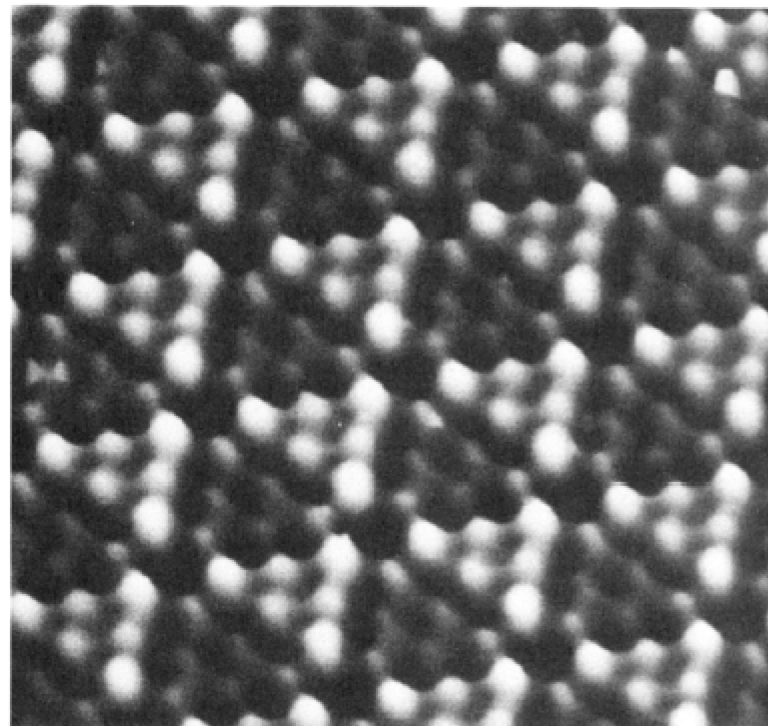


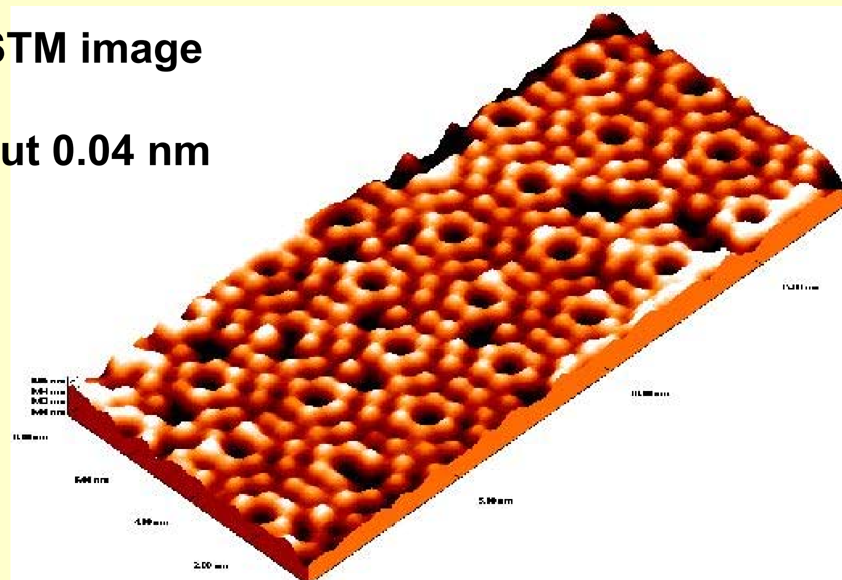
Figure 7. STM topographs of the clean Si(111)-(7×7) surface: (a) unoccupied states imaged at +2.0 V crystal bias, (b) occupied states imaged at −2.0 V crystal bias. The 12 adatoms are clearly visible in both images, and in the occupied state image the stacking fault and differences between corner and center adatoms are also seen. Courtesy of V. Ukraintsev, J. C. Camp, and J. T. Yates, Jr.

Reconstruction

Relaxation = energy lowering, no change in symmetry

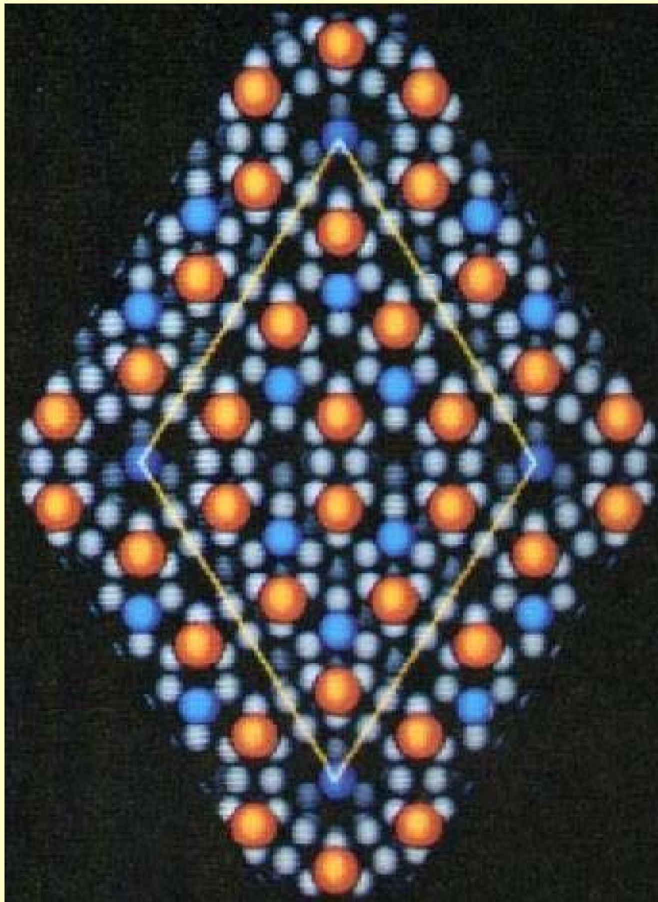
Reconstruction = the surface atoms rearrange to a more energetically stable configuration
Symmetry lowering
2D symmetry – 17 plane groups / 230 bulk space groups

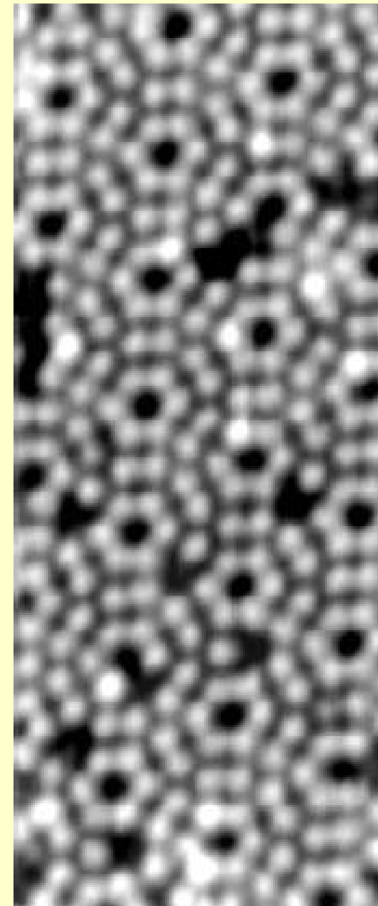
3D representation of the Si 7x7 STM image
The image area is 18 x 8 nm^2
the height of the "bumps" is about 0.04 nm



Si 7x7 Reconstruction

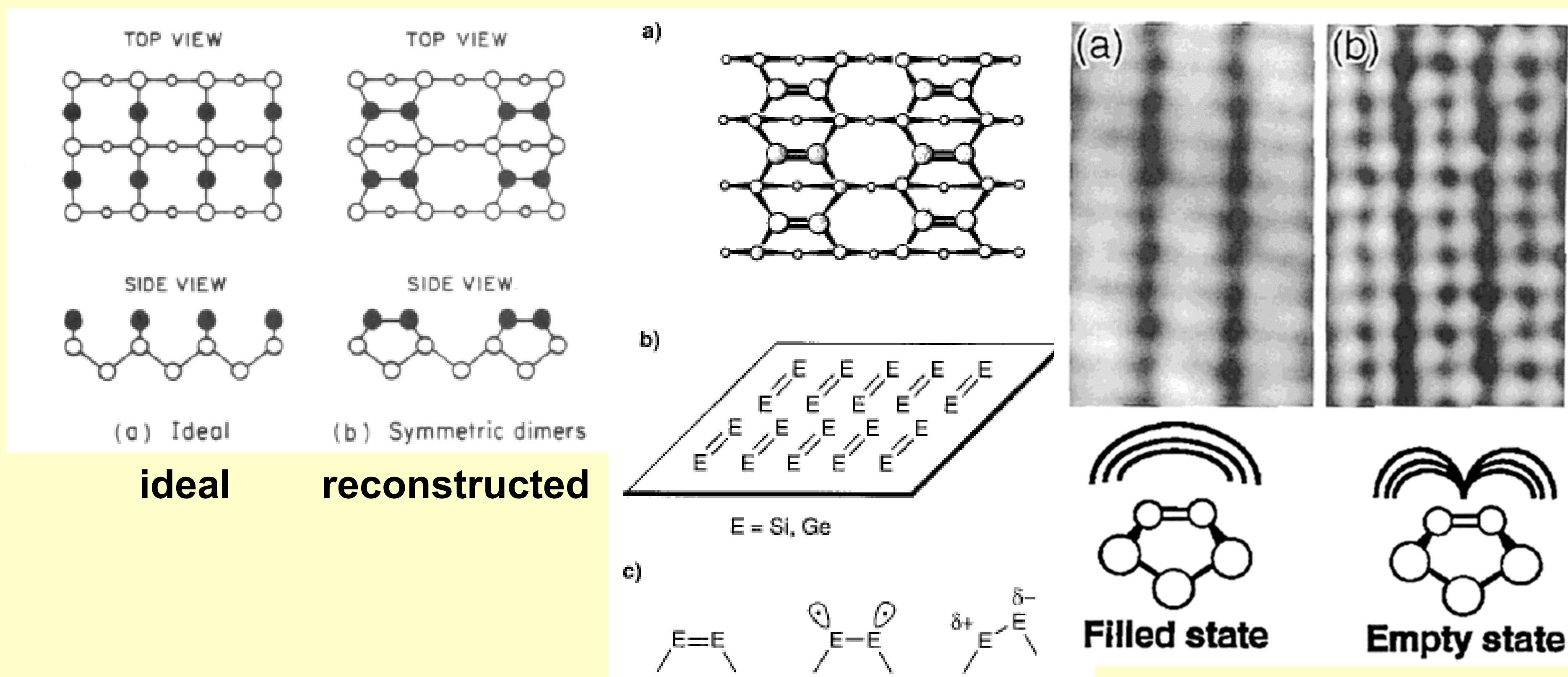
When (111) surface of Si is heated to high temperatures under the Ultra-High Vacuum conditions the surface atoms rearrange to a more energetically stable configuration called 7x7 reconstruction





STM image of Si(111) surface

Si(100) Surface



STM images of the silicon-silicon dimers imaged with
(a) V_{sample} = -2.0 V
(b) V_{sample} = 2.3 V
The filled and empty states of these highly ordered dimers can be probed by biasing the surface in the opposite directions
The dimensions of the figure are 2.3 nm x 7.7nm

Critical Parameters Synthesis of Thin Films

High-quality films for the electronics and optics industries

Chemical composition control - variety of materials to be deposited
Purity of precursors: usually less than 10^{-9} impurity levels
Challenge for chemistry - purifying and analyzing at the ppb level
Exceptionally clean growth systems
Impurities destroy controlled doping of films for device applications

Good film uniformity over large areas covered > 100 cm^2
Precise reproducibility
Precise control of film thickness = accurate control of deposition, film growth rate, 1 - 2000 nm layer thickness

Crystal quality, epitaxy - high degree of film perfection
Defects degrade device performance

Alternating composition and graded composition films
30 - 40 sequential layers
0.5 - 50 nm thickness required with atomic level precision
Interface widths - abrupt changes of composition and dopant concentration required, quantum confined structures

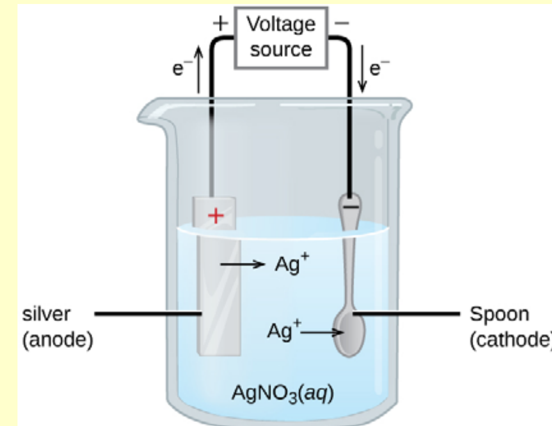
Synthesis of Thin Films

MAIN METHODS OF SYNTHESIZING THIN FILMS:

CHEMICAL, ELECTROCHEMICAL, PHYSICAL

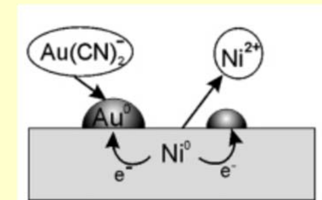
- **Cathodic deposition, Anodic deposition, Electroless deposition**
- **Thermal oxidation, nitridation**
- **Chemical vapor deposition (CVD)**
- **Metal organic chemical vapor deposition (MOCVD)**
- **Cathode sputtering, vacuum evaporation**
- **Molecular beam epitaxy, supersonic cluster beams, aerosol deposition**
- **Photoepitaxy**
- **Electrochemical deposition**
- **Laser ablation**
- **Plasma spraying**
- **Self-assembly, surface anchoring, SAM**
- **Dip coating**
- **Evaporation-Induced Self-Assembly**
- **Spin coating**

Electrochemical Synthesis of Thin Films



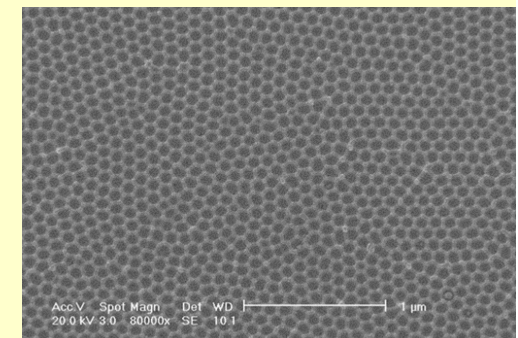
CATHODIC DEPOSITION
Two electrodes, dipped into electrolyte solution
External potential applied
Metal deposition onto the cathode as thin film
Anode metal slowly dissolves

ELECTROLESS DEPOSITION
Spontaneous, no applied potential, cementation
Depends on electrochemical potential difference between electrode and solution redox active species to be deposited



Both methods limited to metallic films on conducting substrates

ANODIC DEPOSITION
Formation of oxide films, such as alumina, titania
Oxide films grow on a metallic electrode in aqueous salts or acids



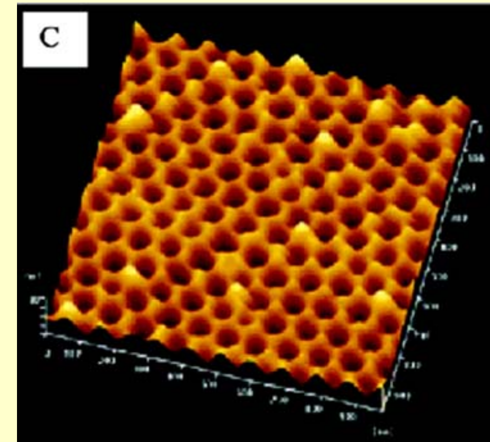
Deposition of conducting polymer films by oxidative polymerization of monomer, such as thiophene, pyrolle, aniline

Porous Alumina Films

Anodic oxidation of aluminum in oxalic or phosphoric acid

Al | H_3PO_4, H_2O | Pt electrolytic cell

AFM Image of Porous Alumina Film



$Al \rightarrow Al^{3+} + 3\,e^-$ anode = oxidation

$2\,Al^{3+} + 3\,O^{2-} \rightarrow \gamma\text{-}Al_2O_3$ (annealing) $\rightarrow \alpha\text{-}Al_2O_3$

$PO_4^{3-} + 2\,e^- \rightarrow PO_3^{3-} + O^{2-}$ cathode = reduction

Overall electrochemistry:
$2\,Al + 3\,PO_4^{3-} \rightarrow Al_2O_3 + 3\,PO_3^{3-}$

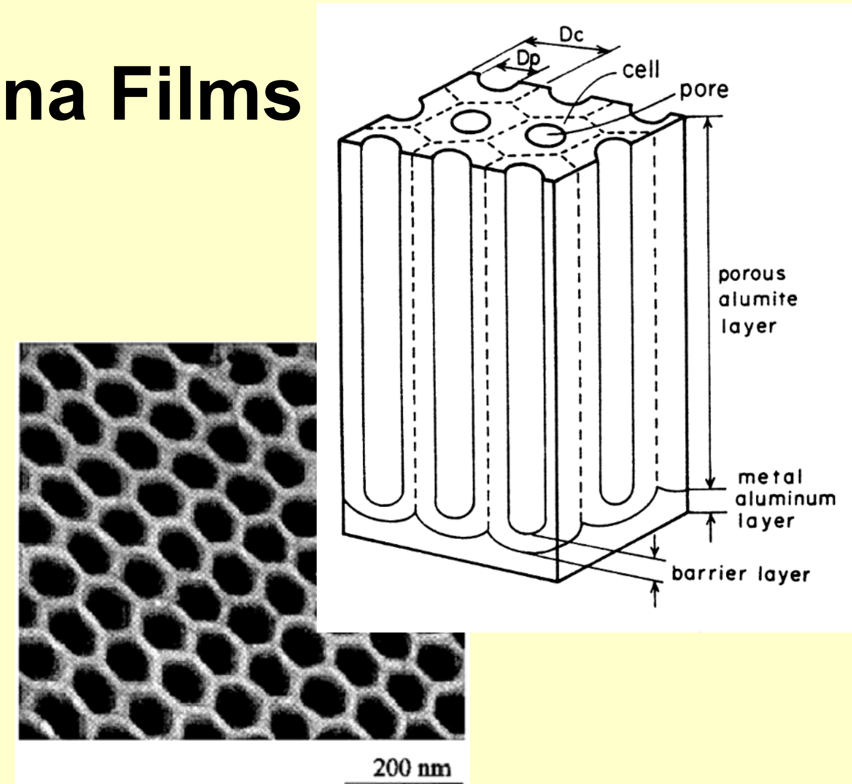
The applied potential controls the oxide thickness and the rate at which it forms, oxide anions from solution have to diffuse through an Al_2O_3 layer of growing thickness on the reacting Al substrate, to attain an equilibrium thickness of the alumina film

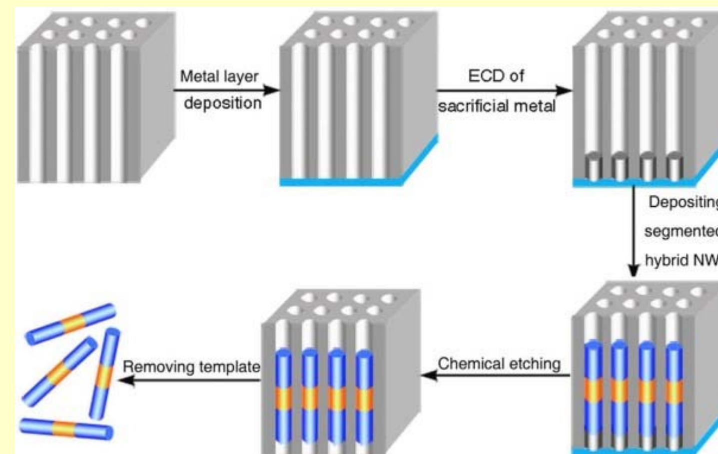
Porous Alumina Films

Self-organizing process observed
A regular array of size tunable hcp pores form and permeate orthogonally through the alumina film

Exceptionally useful process for creating

- **Controlled porosity membranes**
- **Photonic gap materials**
- **Hard template for synthesizing semiconductor/metal nanostructures**
- **Host for synthesizing and organizing aligned carbon nanotubes**
- **Fuel cell electrode materials**



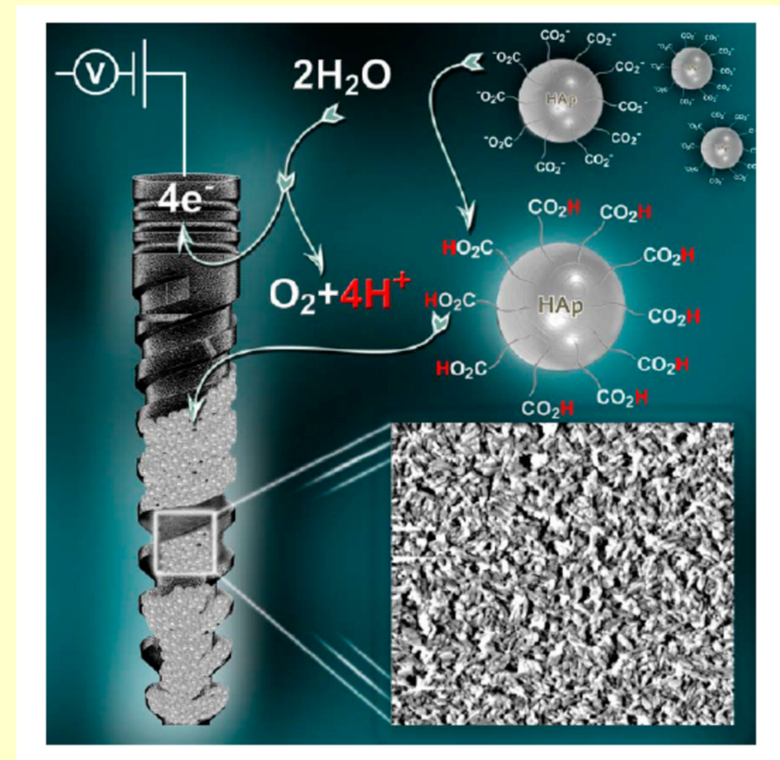


Electrochemical Deposition

HAp protective films on Ti implants
$Ca_5(PO_4)_3(OH)$
Ionic species as precursors: Ca^{2+}, PO_4^{3-}, may form undesired Ca/PO_4 phases

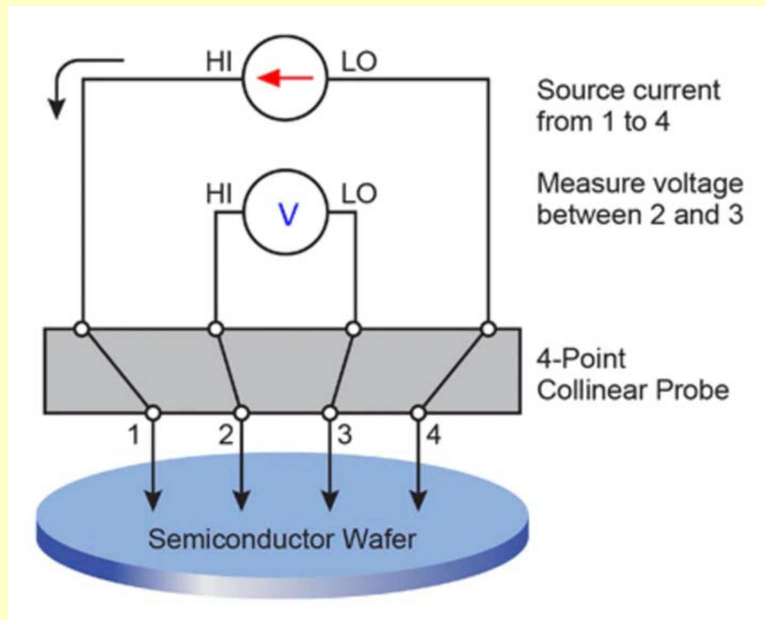
Nanoparticulate HAp dispersed in aqueous solution using stabilizing agents (tri-sodium citrate and sodium polyacrylate)

Oxidation of water, a reduction in the pH in vicinity of the implant surface, the protonation of the carboxylic residues of the dispersants, diminishes the repulsion interactions among the NPs
Irreversible aggregation of NPs on the surface



Resistivity Measurements in Thin Films

Four-Point Collinear Probe



The sheet resistance = surface resistivity

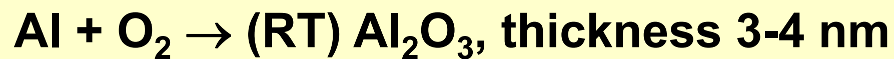
$$\sigma = \frac{\pi}{\ln 2} \times \frac{V}{I} \times k = 4.532 \times \frac{V}{I} \times k$$

V = the measured voltage (V)
I = the source current (A)
k = a correction factor based on the ratio of the probe to wafer diameter and on the ratio of wafer thickness to probe separation

Synthesis of Thin Films

THERMAL OXIDATION

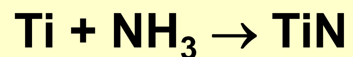
Oxides - metal exposed to a glow discharge in O_2



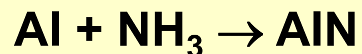
$Al + O_2 \rightarrow$ (RT) Al_2O_3, thickness 3-4 nm

Similar method applicable to other metals, Ti, V, W, Zr etc.

Nitrides, exceptionally hard, high temperature protective coating



$Ti + NH_3 \rightarrow TiN$



$Al + NH_3 \rightarrow AlN$

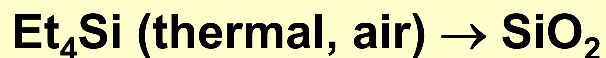
Synthesis of Thin Films

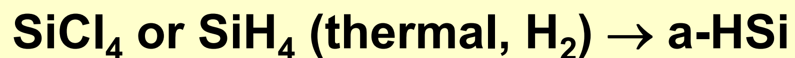
CHEMICAL VAPOR DEPOSITION

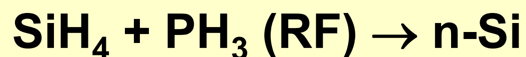
Pyrolysis, photolysis, chemical reaction, discharges, RF, microwave
Epitaxial films, correct matching to substrate lattice

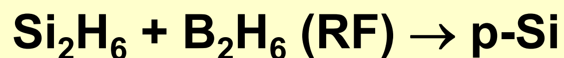
EXAMPLES OF CVD

$CH_4 + H_2$ (RF, MW) $\rightarrow$ C, diamond

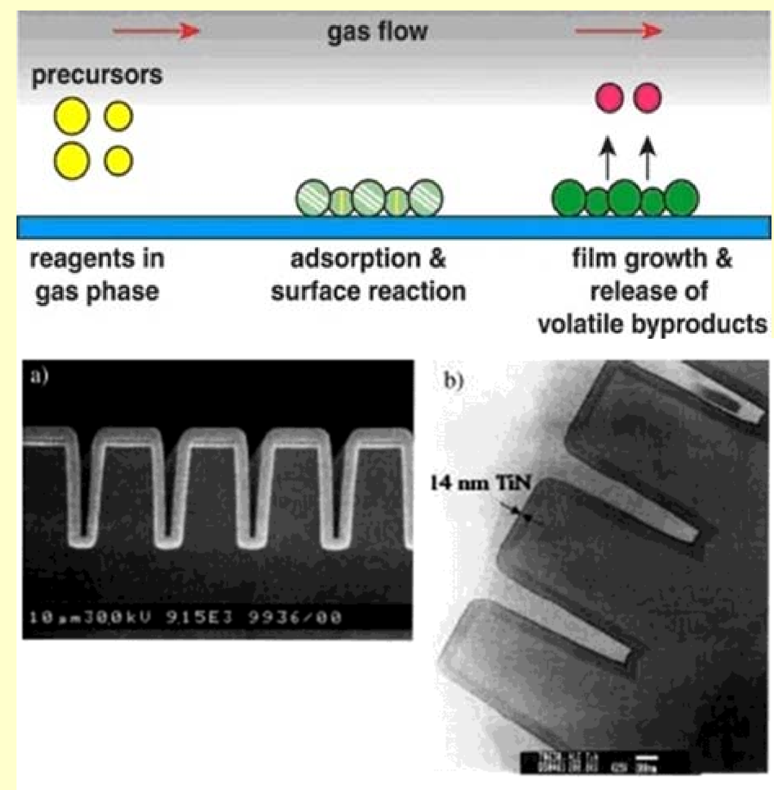

Et_4Si (thermal, air) $\rightarrow$ SiO_2


$SiCl_4$ or SiH_4 (thermal, H_2) $\rightarrow$ a-HSi


$SiH_4 + PH_3$ (RF) $\rightarrow$ n-Si


$Si_2H_6 + B_2H_6$ (RF) $\rightarrow$ p-Si

$SiH_3SiH_2SiH_2PH_2$ (RF) $\rightarrow$ n-Si



Synthesis of Thin Films

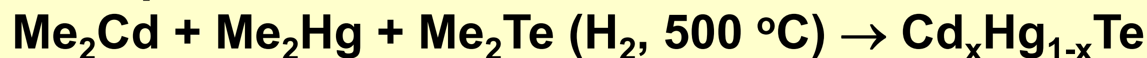
METAL ORGANIC CHEMICAL VAPOR DEPOSITION, MOCVD

Invented by Mansevit in 1968
Recognized high volatility of metal organic compounds as sources for semiconductor thin film preparations

MOCVD PRECURSORS, SINGLE SOURCE MATERIALS

Me_3Ga, Me_3Al, Et_3In
NH_3, PH_3, AsH_3
H_2S, H_2Se
Me_2Te, Me_2Hg, Me_2Zn, Me_4Pb, Et_2Cd
All toxic materials – a problem of safe disposal of toxic waste

Example - IR detectors:



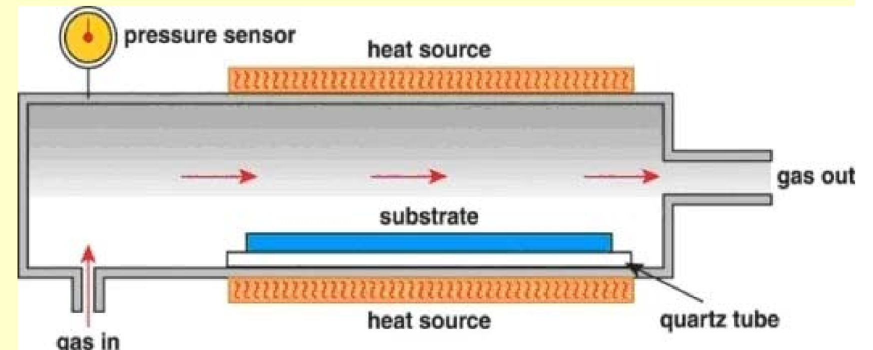
$Me_2Cd + Me_2Hg + Me_2Te\ (H_2,\ 500\ ^oC) \rightarrow Cd_xHg_{1-x}Te$

Synthesis of Thin Films

MOCVD reactors

Controlled flow of precursors to single crystal heated substrate
Most reactions occur in range 400 – 1300 ^{o}C
Hot-wall or cold-wall reactors
Photolytic processes (photoepitaxy) help to decrease the deposition temperatures

REQUIREMENTS OF MOCVD PRECURSORS

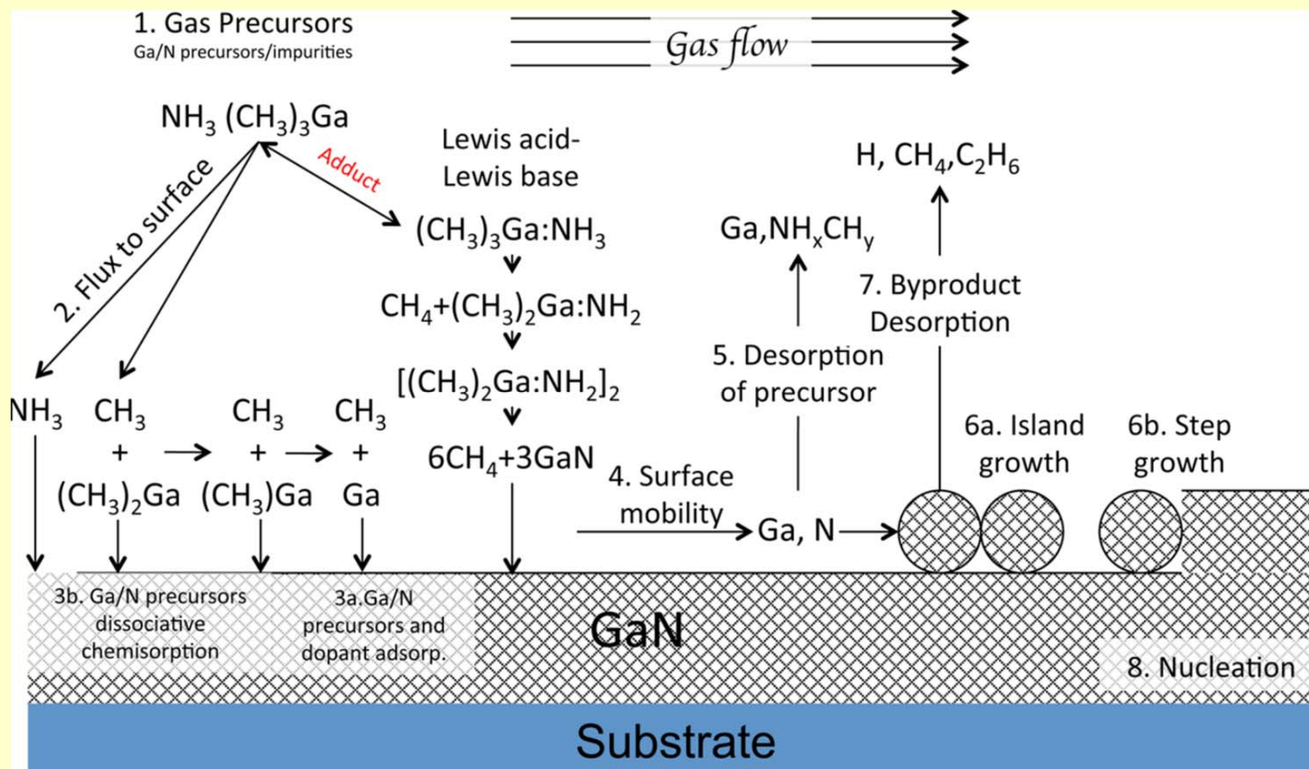


RT stable, no polymerization, decomposition
Easy handling, simple storage
Not too reactive
Vaporization without decomposition at modest T < 100 ^{o}C
Low rate of homogeneous pyrolysis (gas phase) wrt heterogeneous decomposition (surface)

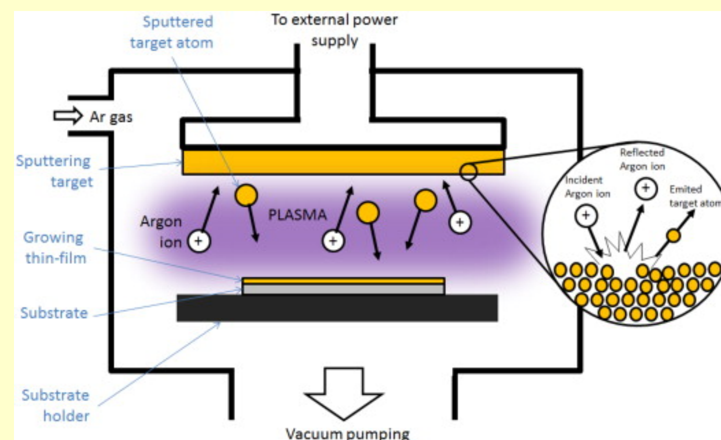
HOMO : HETERO rates ~ 1 : 1000

Synthesis of Thin Films

Gaseous precursor flow
Adsorption at the surface
Heterogeneous reaction on substrate
Surface diffusion, nucleation, film growth
Desorption of byproducts



Synthesis of Thin Films

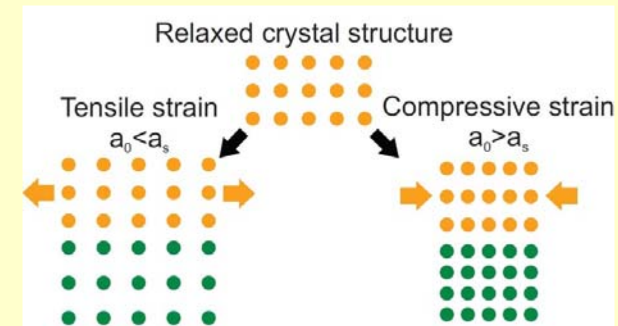


CATHODE SPUTTERING
Bell jar equipment
10^{-1} to 10^{-2} torr of Ar, Kr, Xe
Glow discharge created by high voltage
Positively charged rare gas ions
Accelerated by the electric field to cathode target
High energy ions collide with cathode
Sputter material from cathode
Deposits on substrate opposite cathode to form thin film
Multi-target sputtering creates composite or multilayer films

THERMAL VACUUM EVAPORATION
High vacuum bell jar - 10^{-6} torr = the mean free path > 1 m
Heating by e-beam, laser, joule heating of the resistive boat
Evaporation - gaseous material deposited on a substrate
Thin films nucleate and grow
Containers must be chemically inert:
W, Ta, Nb, Pt, BN, Al_2O_3, ZrO_2, Graphite
Substrates - insulators, metals, glass, alkali halides, silicon
Sources - metals, alloys, semiconductors, insulators, inorganic salts

Epitaxy

Epitaxial reactions = surface structure controlled reactions
Crystallographic orientation of the film is controlled by the substrate



Kinetic control – TD metastable phases
$YMnO_3$
- **hexagonal in bulk**
- **cubic perovskite film on $NdGaO_3$ substrates**

Homoepitaxy – same compound/orientation in substrate and film
Heteroepitaxy – different compounds in the substrate and film

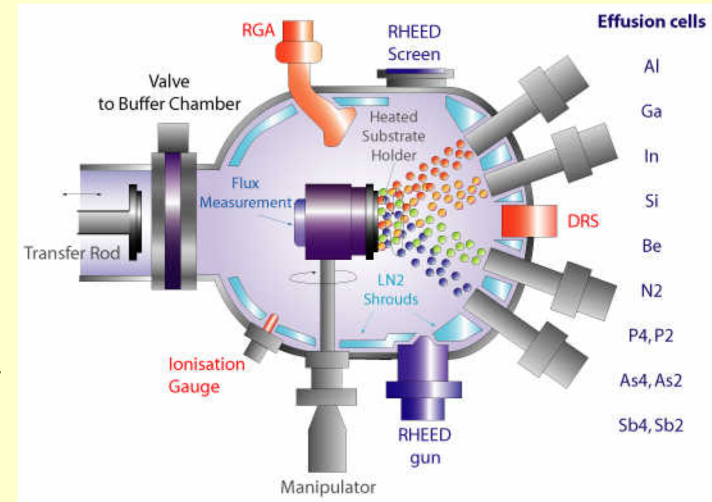
Strain engineering = the tuning of material properties via lattice distortions

Physical properties can be changed through lattice distortions (strain)
- the bond lengths, the electron density, the orbital overlap

Strain affects: the electronic bandgap, thermal conductivity, multiferroicity, catalytic properties, charge transport

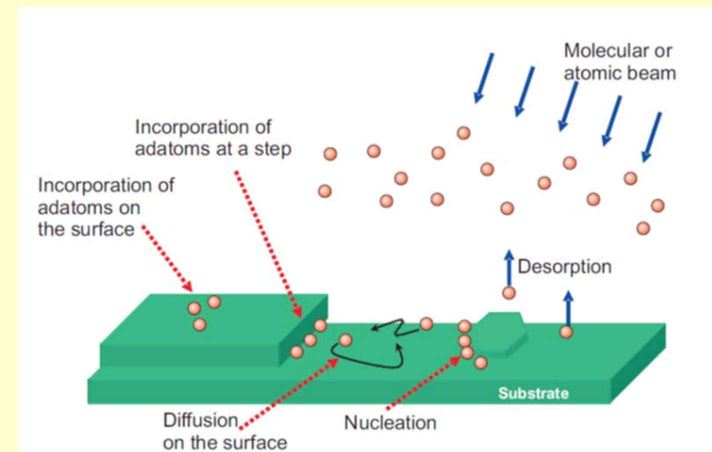
Synthesis of Thin Films

MOLECULAR BEAM EPITAXY
1968 Bell Laboratories
Ultrahigh vacuum system >10^{-12} torr
Elemental or compound sources in shutter controlled Knudsen effusion cells



Ar⁺ ion gun for cleaning substrate surface or depth profiling sample using Auger analyzer

Reflection high-energy electron diffraction (RHEED) for surface structure analysis
Mass spectrometer for control and detection of vapor species
Electron-gun for heating the substrate



Fabrication of high quality artificial semiconductor quantum superlattices, ferroelectrics, superconductors

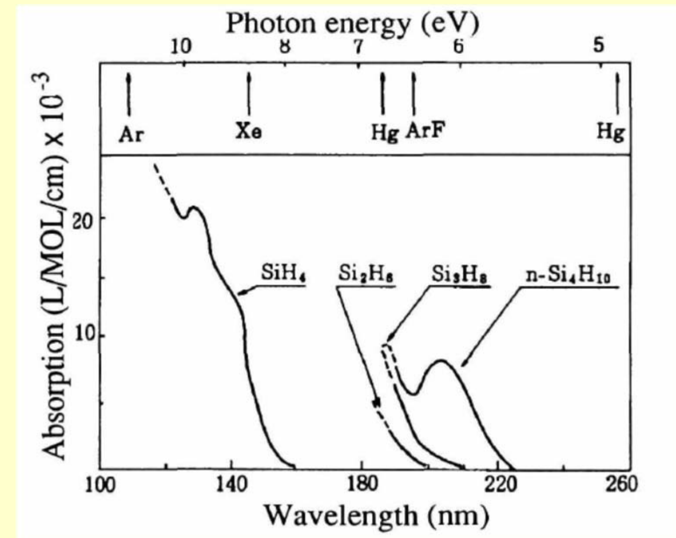
Synthesis of Thin Films

PHOTOEPITAXY

Making atomically perfect thin films under milder and more controlled conditions

Mullin and Tunnicliffe 1984

- **Photo chemical reaction**
- **Pyrolytic reaction due to hot substrate**



Coherent laser source

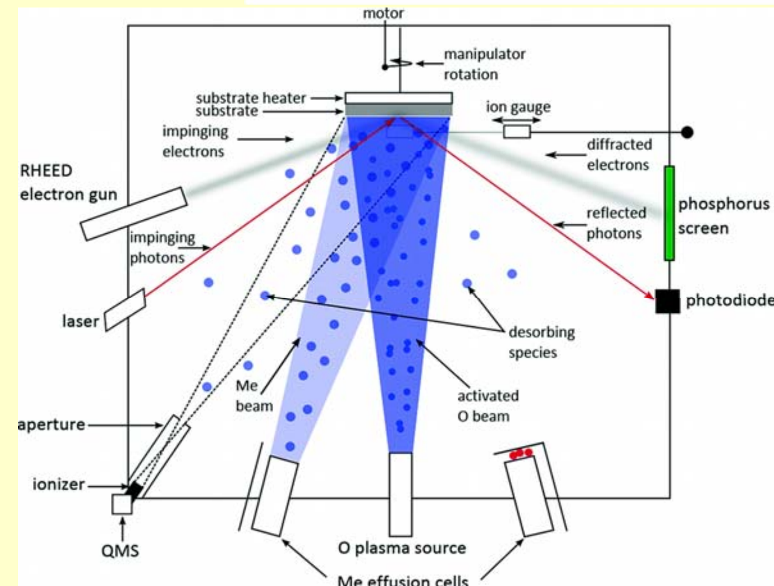
- **Excimer lasers 351 nm (XeF), 308 nm (XeCl), 248 nm (KrF), 193 nm (ArF) and 157 nm (F_2)**
- **Ar^+ ion laser**
- **CO_2 laser 9 -11 μm**

Incoherent light source

- **High pressure Hg lamp**
- **Xe, W, H_2, D_2 lamp**

Advantages of photoepitaxy

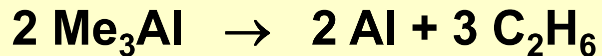
- **Lower temperature operation**
- **Multilayer formation**
- **Lower interlayer diffusion**
- **Easy to fabricate abrupt boundaries**
- **Less defects, strain, irregularities at interfaces**



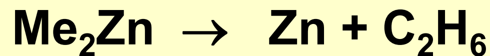
Synthesis of Thin Films

LASER DIRECT WRITING

Substrate GaAs
Me_3Al or Me_2Zn adsorbed layer or in (g)
UV laser beam focused on film
Photodissociation of organometallic precursors:

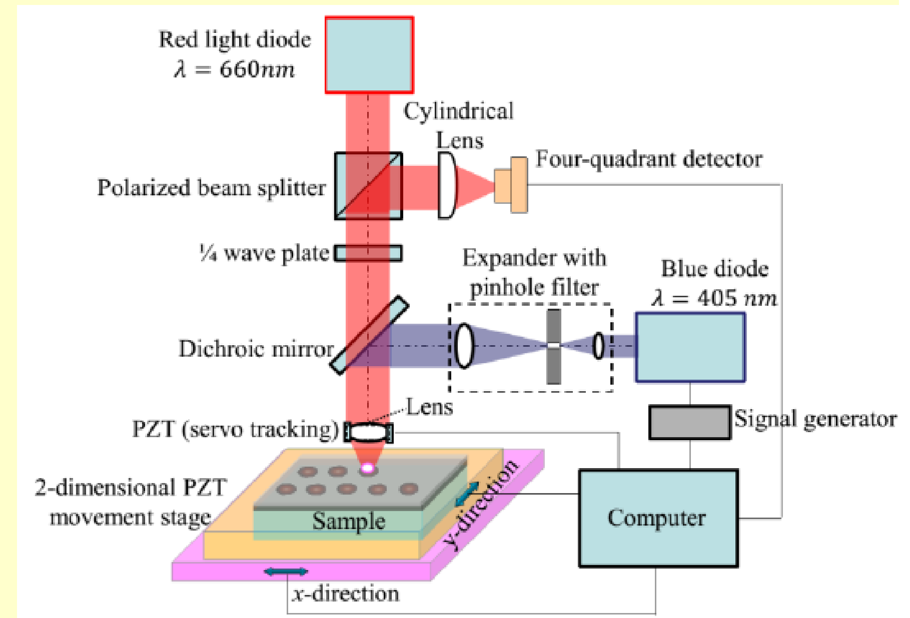


$$2\ Me_3Al \rightarrow 2\ Al + 3\ C_2H_6$$



$$Me_2Zn \rightarrow Zn + C_2H_6$$

Creates sub-micron lines of Al or Zn



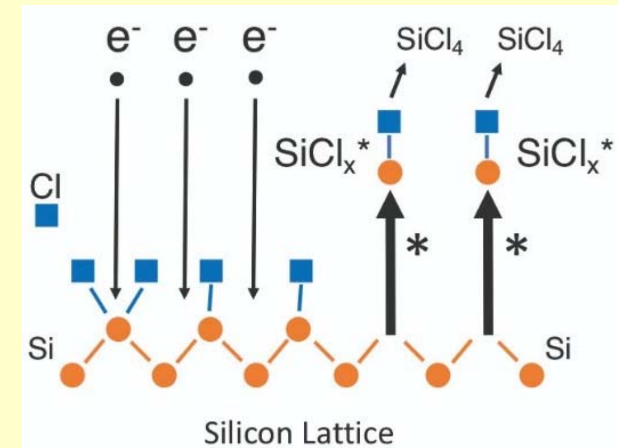
ZnO epitaxial films on (0112) sapphire
Temperature 350-500 °C, KrF excimer laser
Me_2Zn and NO_2

Polymerization

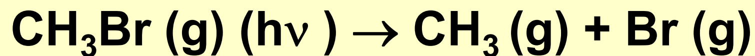
Quantum dots sintering

Synthesis of Thin Films

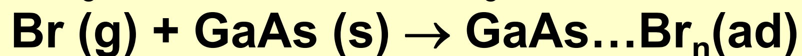
LASER ETCHING



GaAs substrate
Gaseous or adsorbed layer of CH_3Br
Focused UV laser creates reactive Br atoms

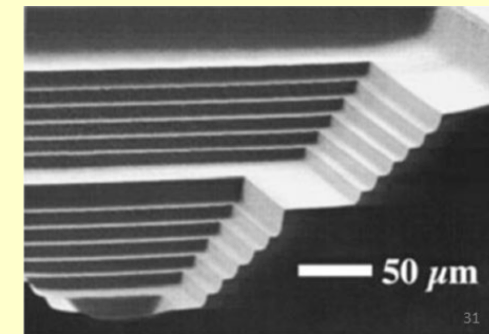


$CH_3Br\ (g)\ (h\nu) \rightarrow CH_3\ (g) + Br\ (g)$



$Br\ (g) + GaAs\ (s) \rightarrow GaAs\ldots Br_n(ad)$

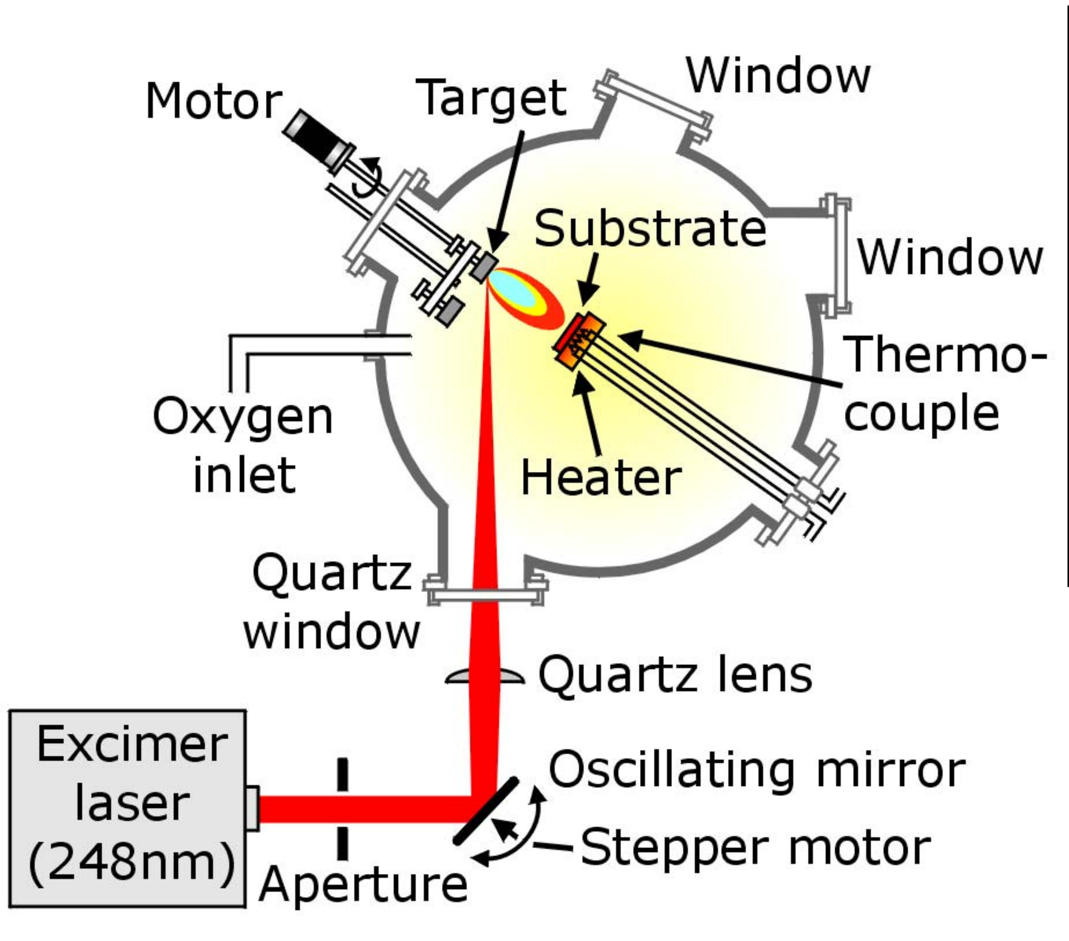
$GaAs\ldots Br_n(ad) \rightarrow GaBr_n\ (g) + AsBr_n\ (g)$

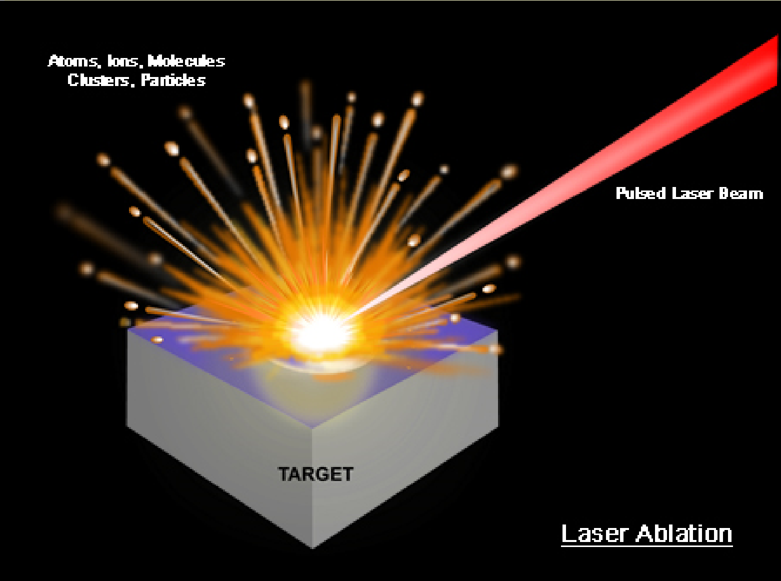


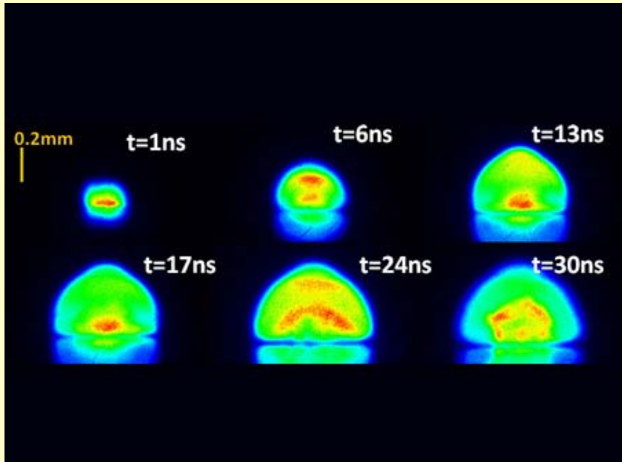
Adsorbed reactive surface Br atoms erode surface regions irradiated with laser
Vaporization of volatile gallium and arsenic bromides from surface creates sub-micron etched line

(100) Si, excimer laser 308 nm or focused e-beam, Cl_2
Surface chlorination due to photodissociation of Cl_2 in the gas phase
Induced etching of silicon to $SiCl_4$

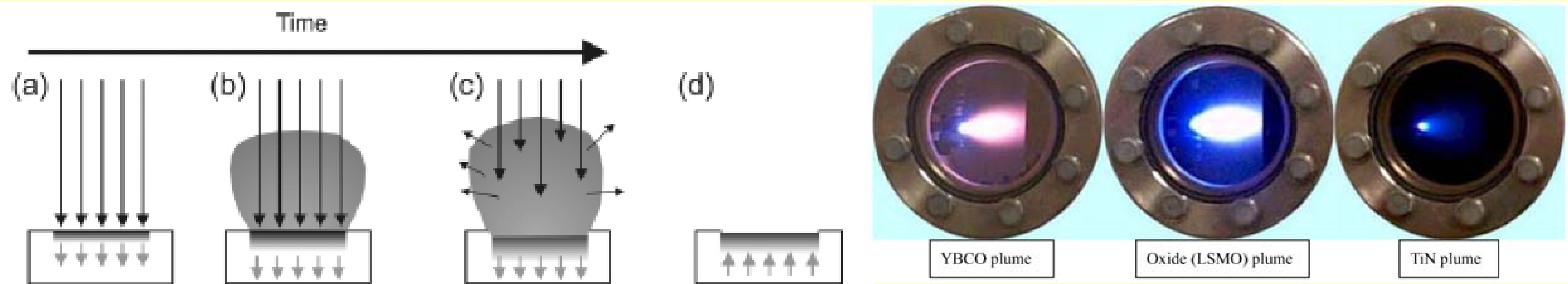
Pulsed Laser Ablation







Pulsed Laser Ablation



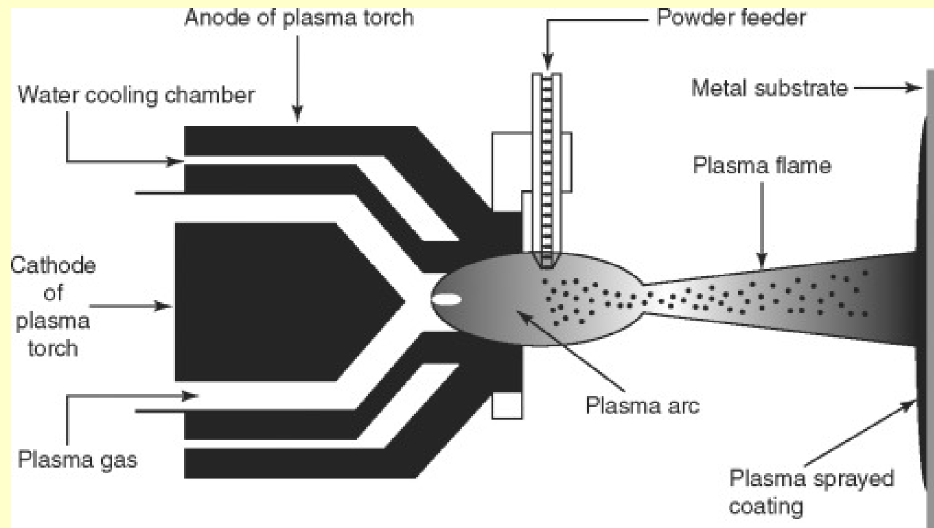
(a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid–liquid interface)

(b) Melt front propagates into the solid, vaporization continues and laser-plume interactions start to become important

(c) Absorption of incident laser radiation by the plume, and plasma formation

(d) Melt front recedes leading to eventual re-solidification

Plasma Spraying



The plasma spray gun

Cu anode, W cathode, water cooled
Plasma gas (Ar, N_2, H_2, He) flows around the cathode and through the anode nozzle (50 l min^{-1})
The plasma initiated by a high voltage discharge (70 V, 400 A)
Localized ionisation and a conductive path for a DC arc to form between cathode and anode

The resistance heating from the arc causes the gas to reach extreme temperatures (10 000 to 30 000 K), dissociate and ionise to form a neutral plasma flame (does not carry electric current)

Powder/suspension is fed into the plasma flame (40 g min^{-1})
Particles are melted and accelerated onto a prepared surface
Upon impact, droplets cool down and solidify instantly by heat transfer to the underlying substrate and form a coating consisting of lamellae

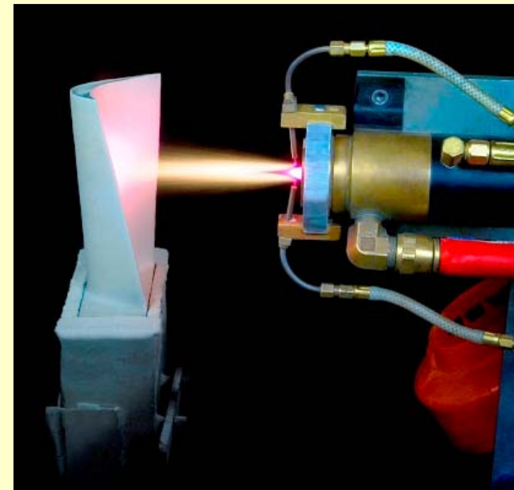
Plasma Spraying

Coatings applied with plasma spraying:

- **Pure metals (Cu, Al, Zn, Ni, Mo, W,…)**
- **Alloys (NiCr, NiAl, NiMoAl, NiCrSiB, Tribaloy, Inconel, Stellite, …)**
- **Carbides (WC/Co, CrC/NiCr, …)**
- **Ceramics (Al_2O_3, TiO_2, Cr_2O_3, ZrO_2/Y_2O_3, …)**
- **Abradables (Ni/Graphite, AlSi/Polyester, …)**

Vast variety of material combinations allow plasma spraying to be used in wide spectrum of industrial applications providing:

- **wear resistance**
- **corrosion resistance**
- **oxidation resistance**
- **thermal and electrical insulation**
- **electrical conductivity**

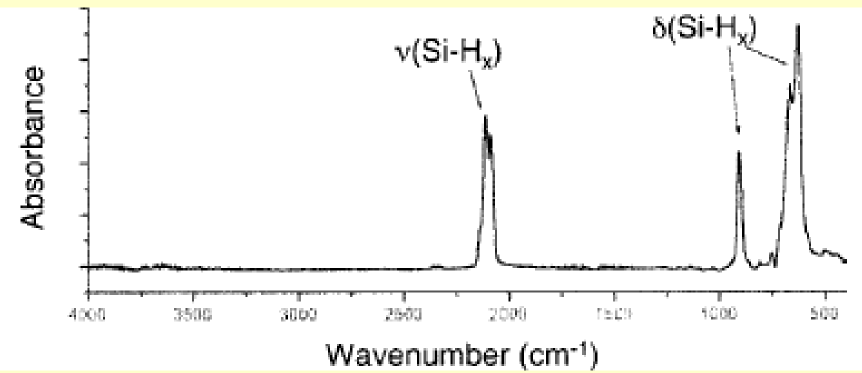


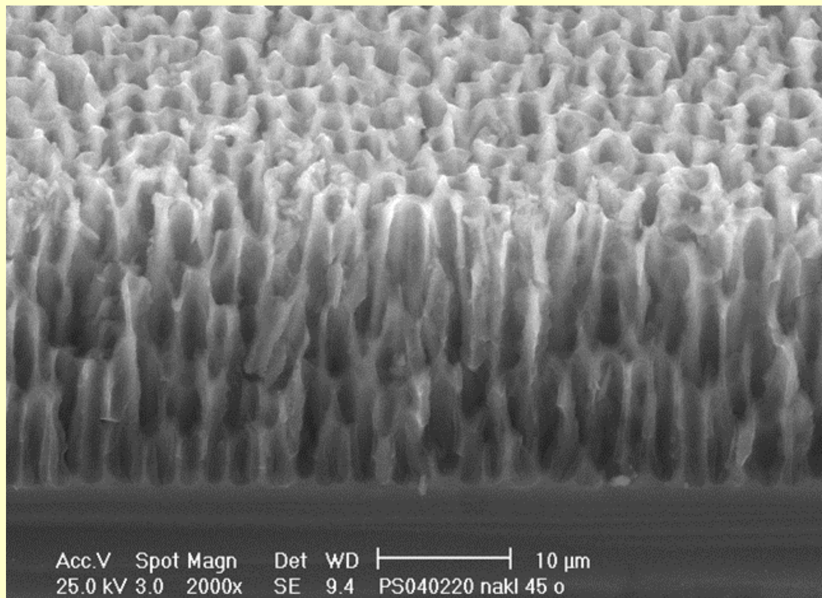
Porous Si

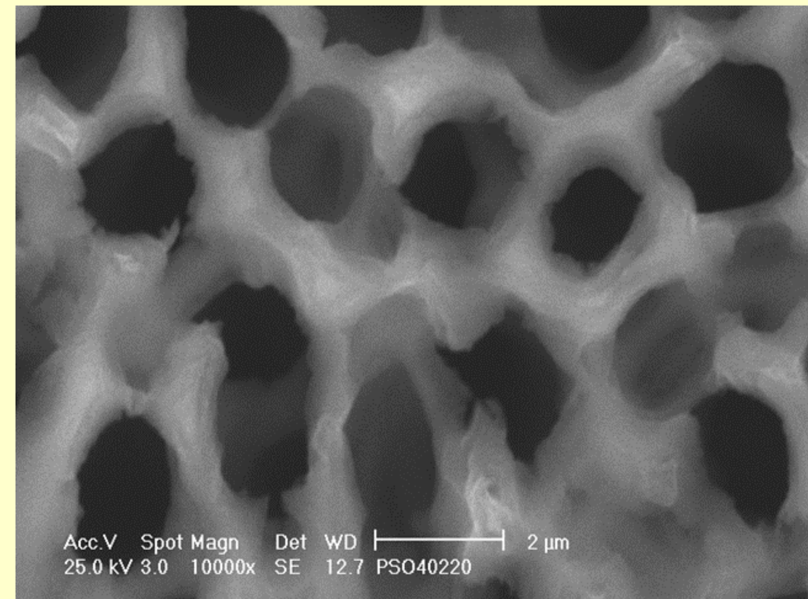
Electrochemical etching

HF:EtOH = 1 : 2.5
j = 10 mA/cm^2
t = 30 min

IR spectrum of porous Si



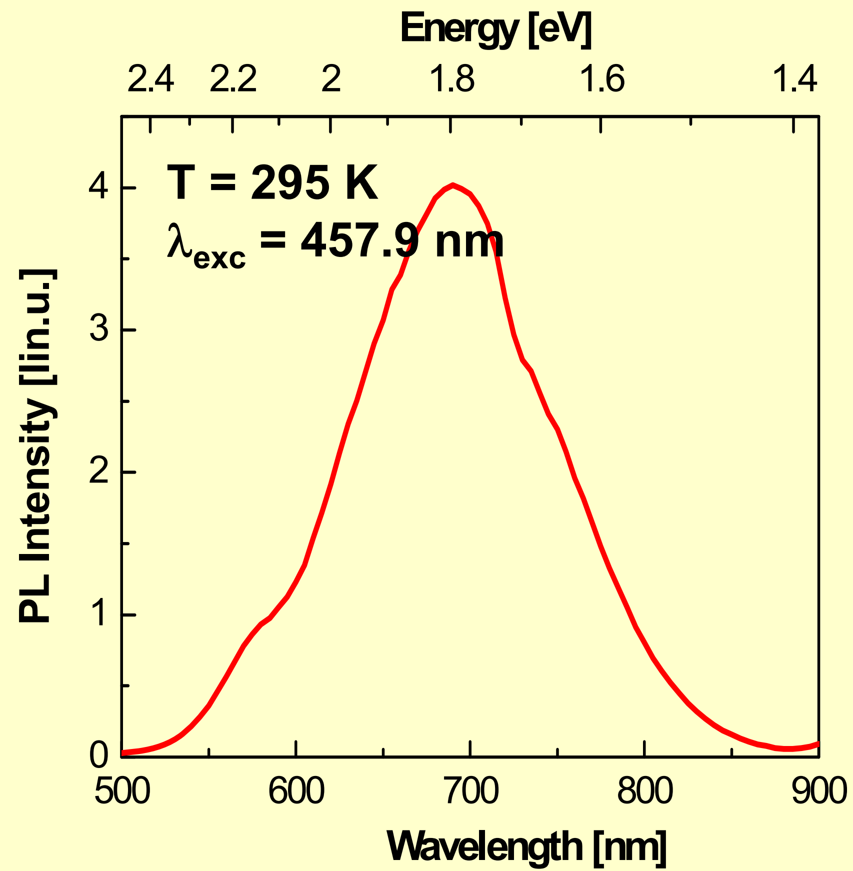


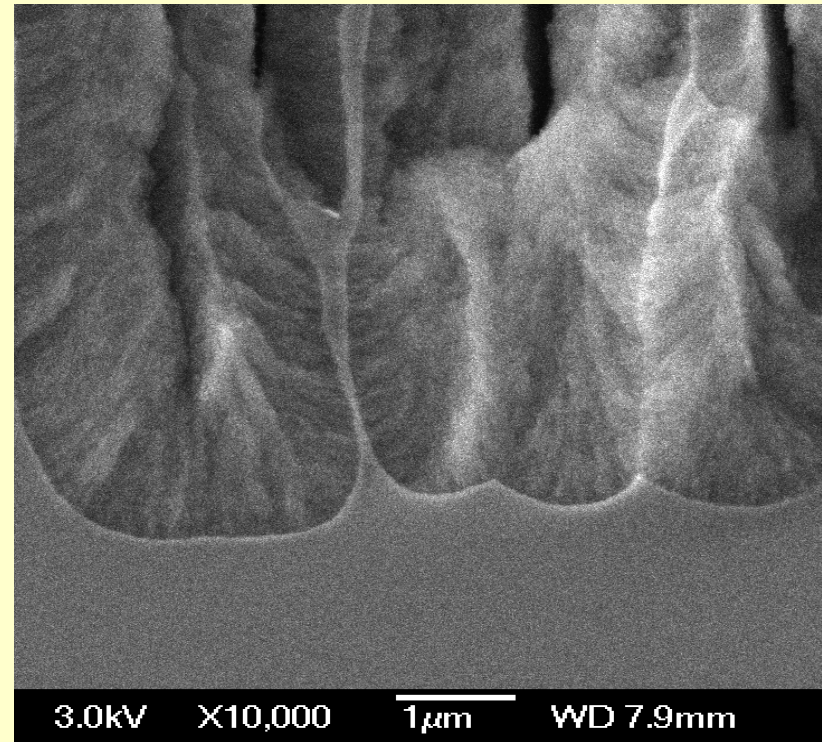


SEM of a porous silicon

Porous Si

Luminiscence of p-Si

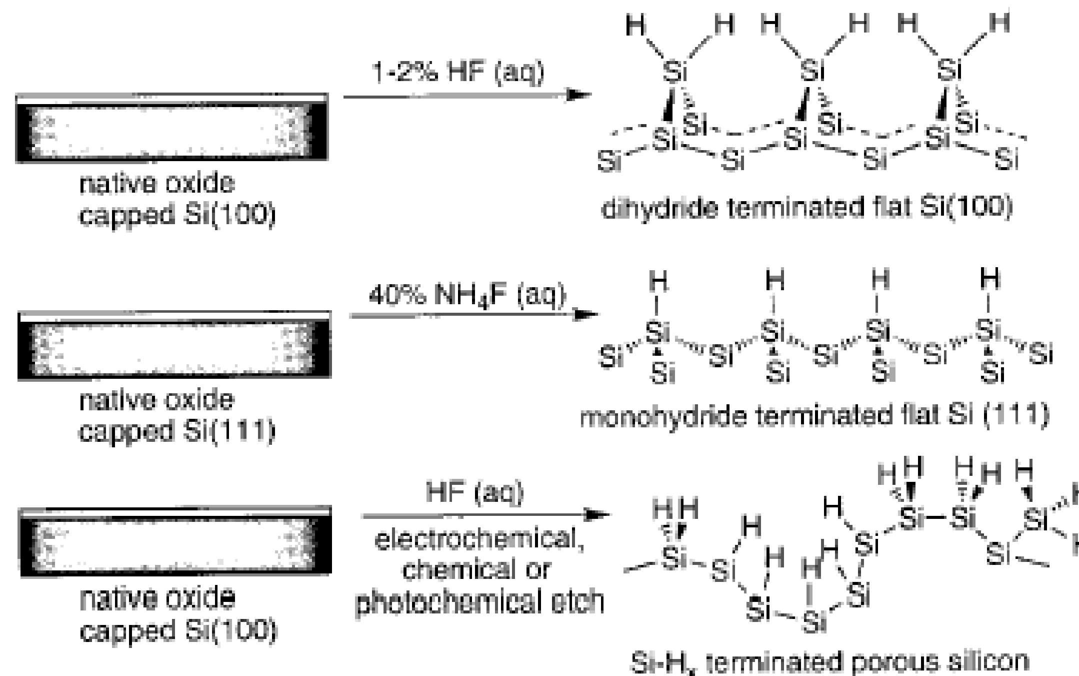




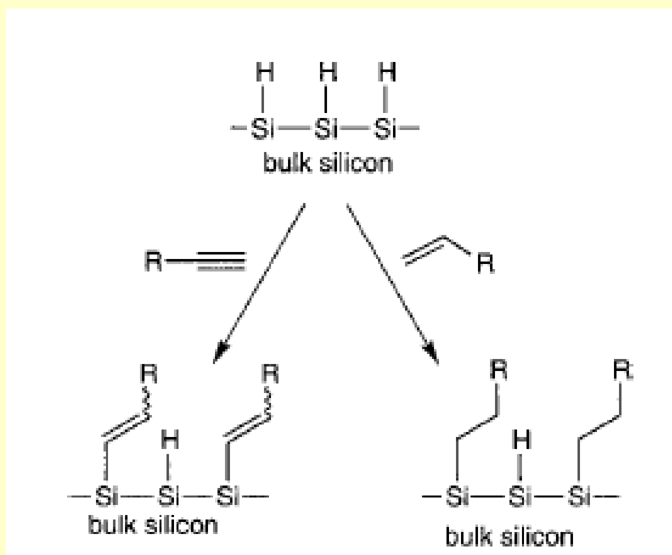
Chemistry on Si Surface

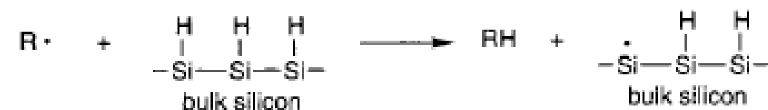
Table 1. Typical Bond Energies for Various Groups Related to Group(IV) Elements (kJ mol^{-1})

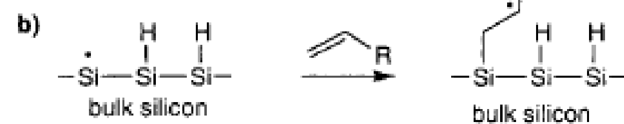
element	self	H	C	O	F	Cl	Br	I
C	292–360	416		336	485	327	285	213
Si	210–250 (bulk)	323	369	368	582	391	310	234
	310–340 (disilane)							
	105–126 (disilene)							
Ge	190–210 (bulk)	290	255		465	356	276	213
	256 (digermane)							

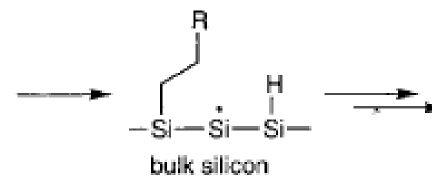


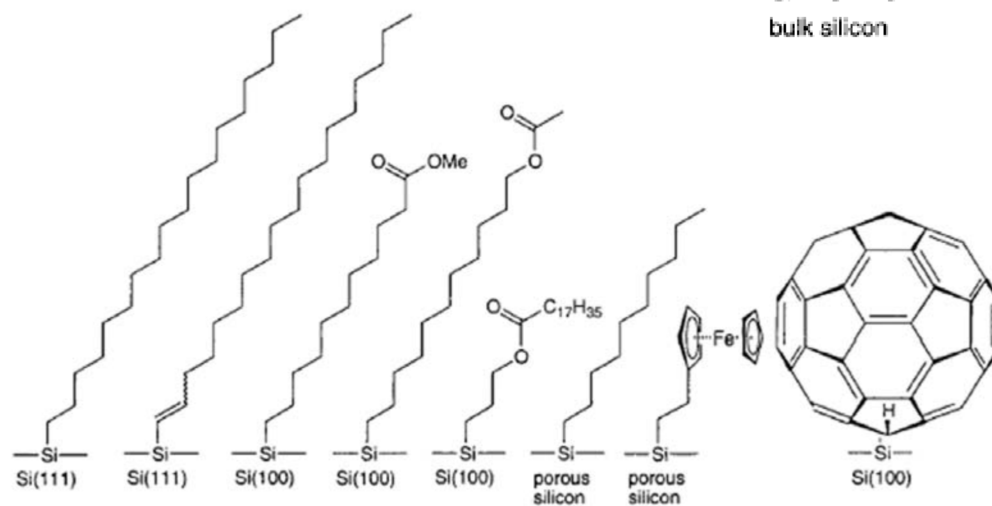
Hydrosilylation



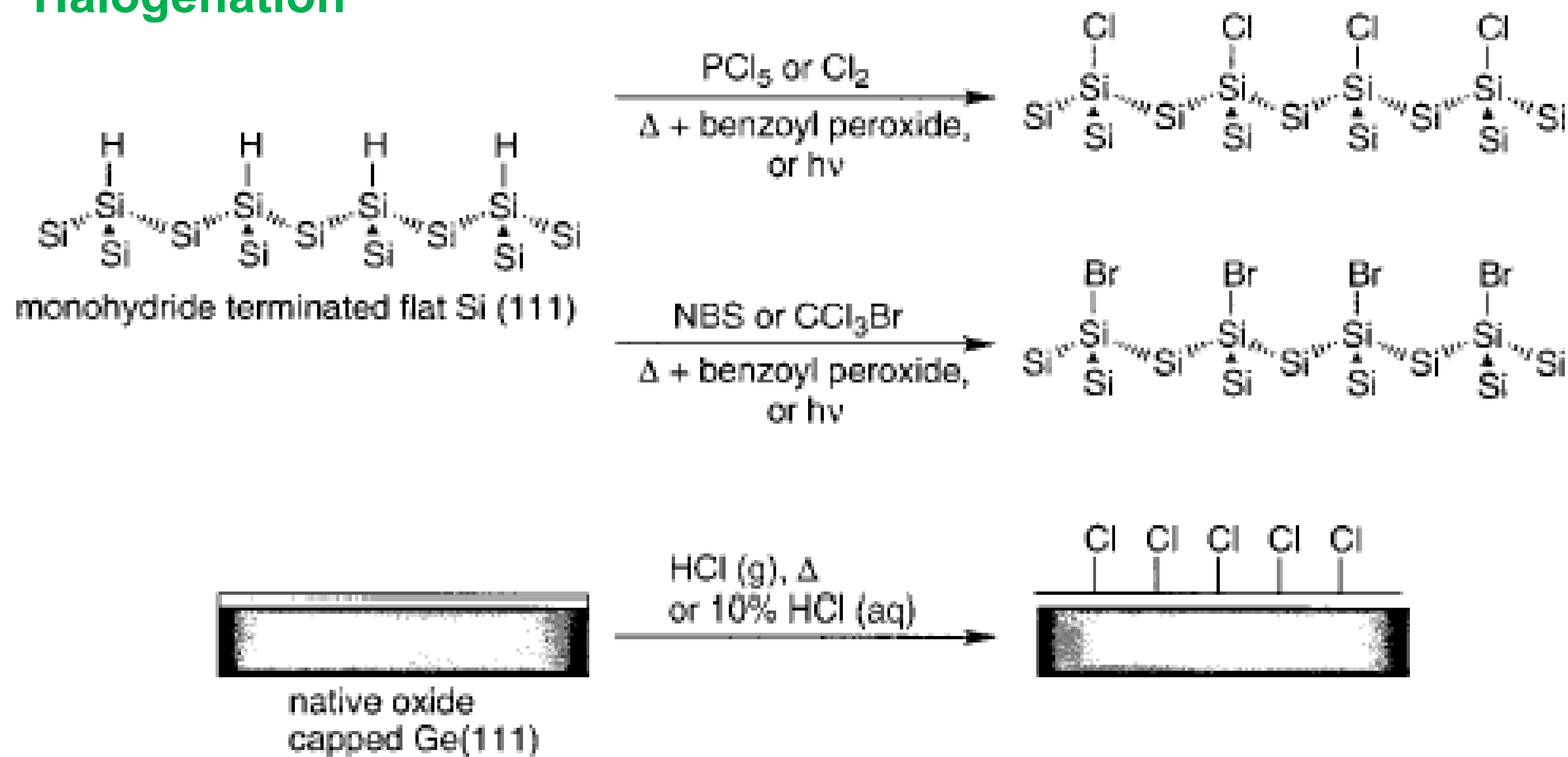






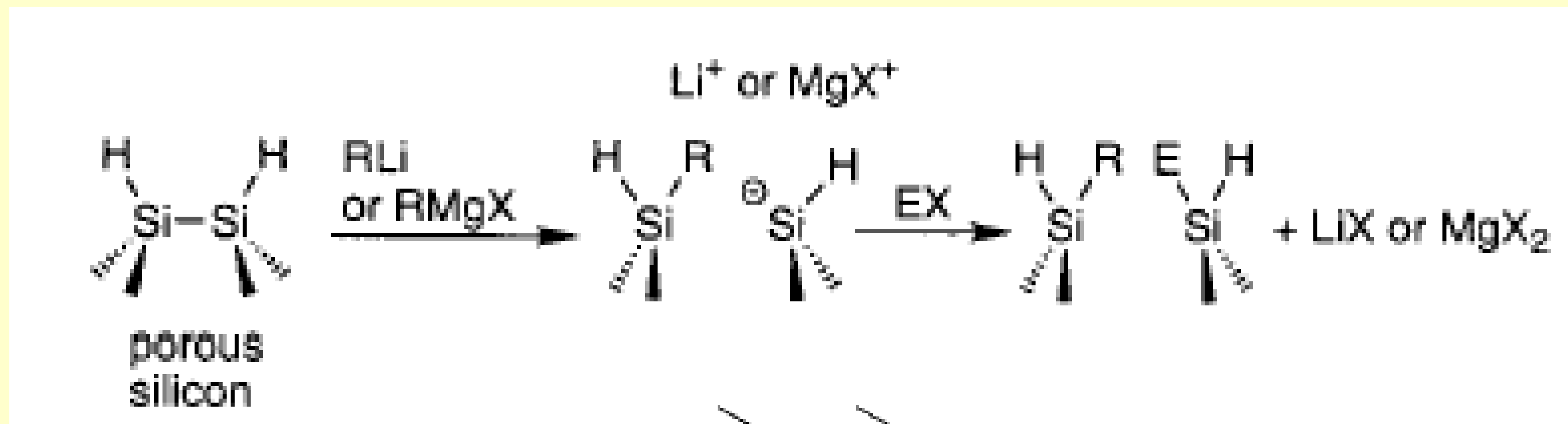


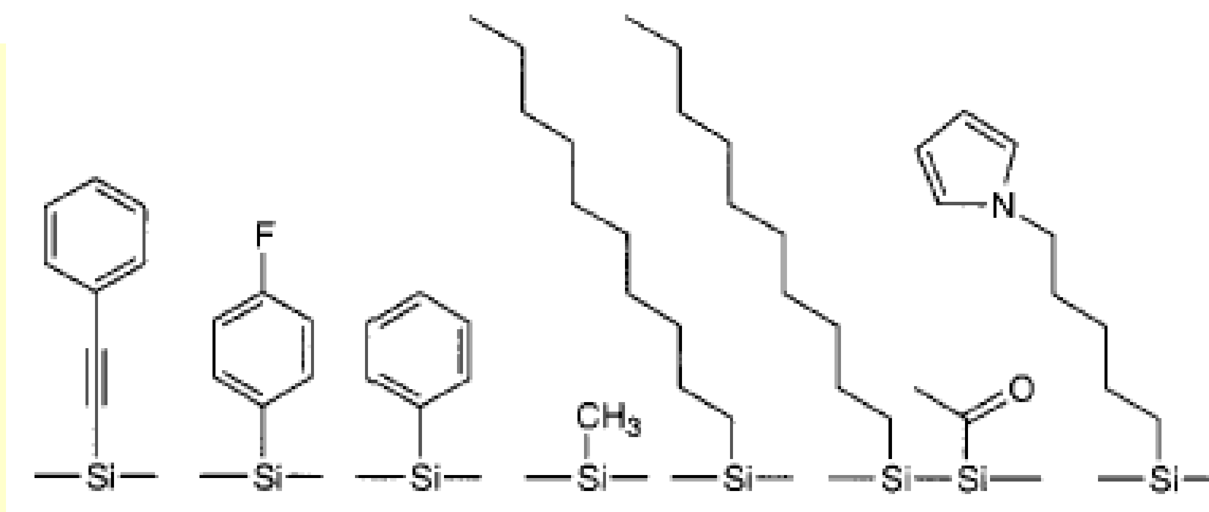
Chemistry on Si Surface



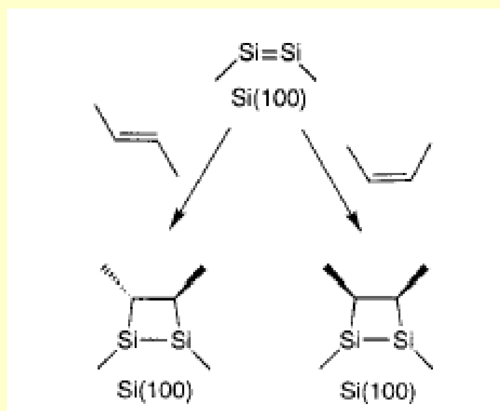
NBS = N-Bromo Succinimide

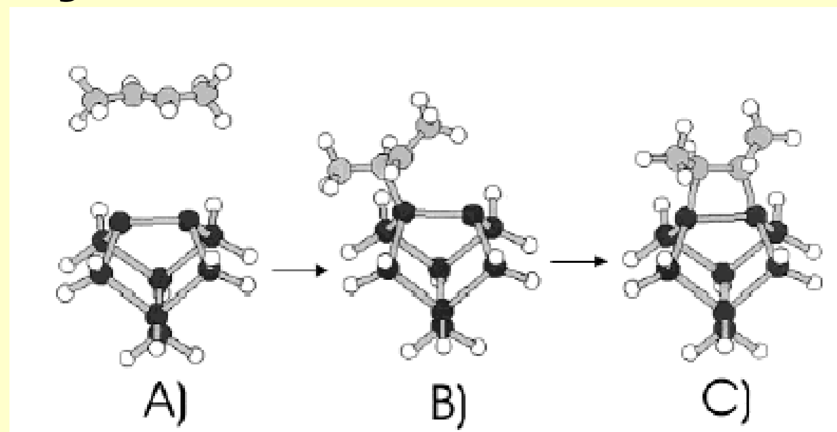
Carbaanion LiR, RMgX

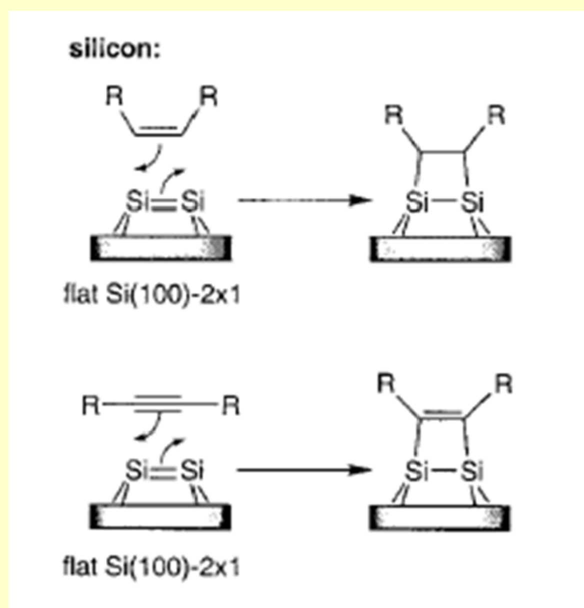


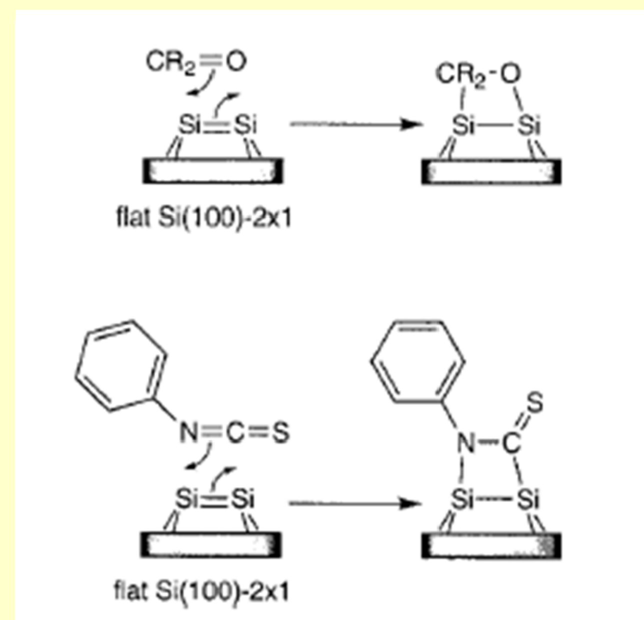


2+2 Cycloaddition

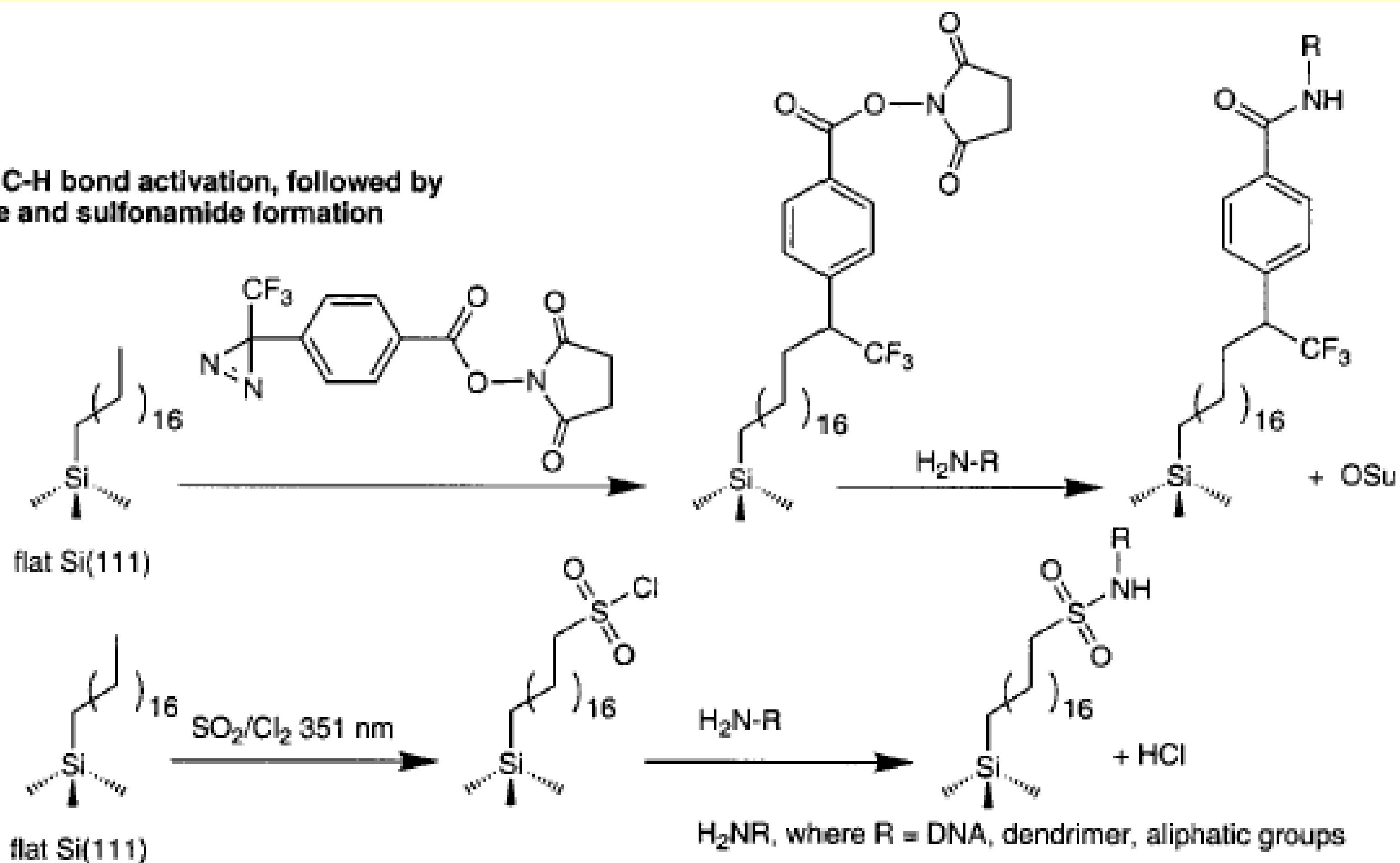




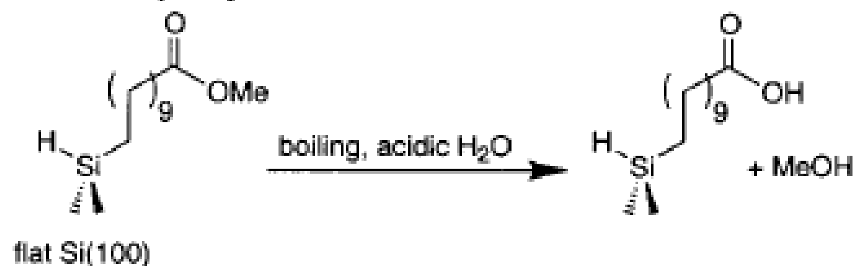


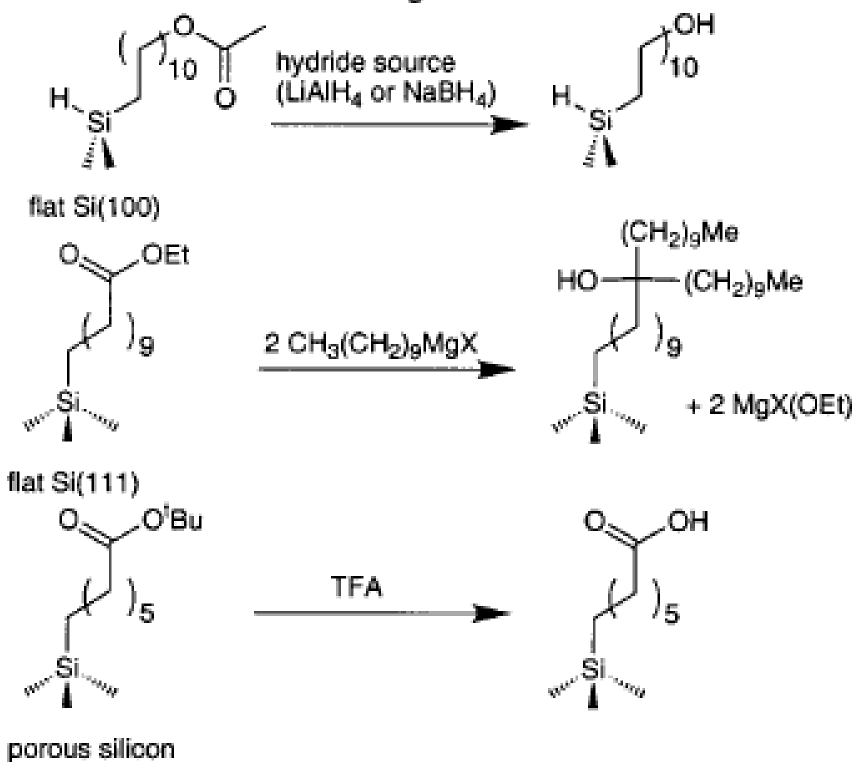


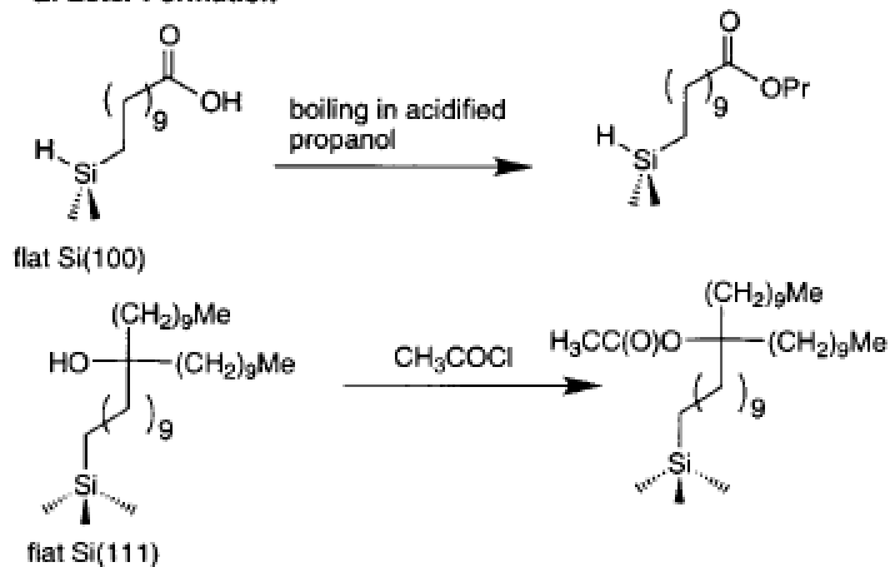
Secondary Chemistry



Secondary Chemistry





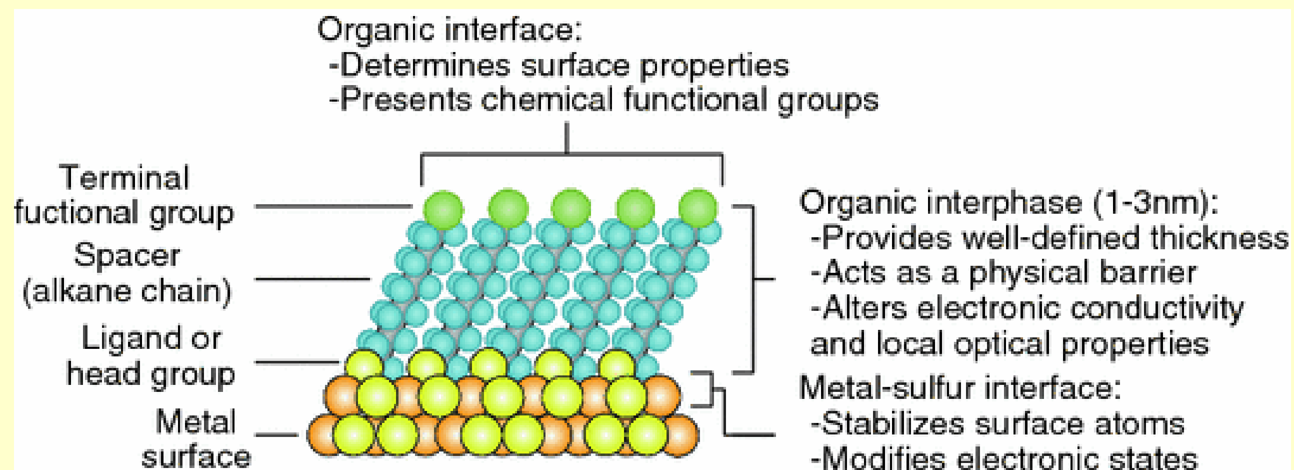


Self-Assembled Monolayers

Self-assembly: spontaneous organization of molecules into stable, structurally well-defined aggregates

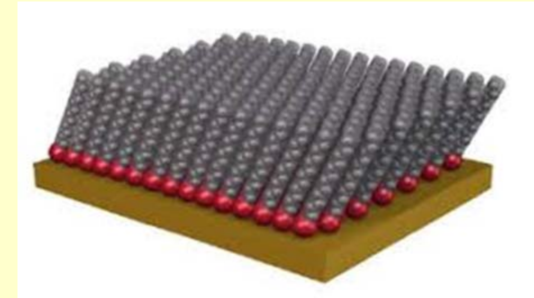
Self-assembled monolayers (SAM): two-dimensional ordered assemblies of long hydrocarbon chains anchored through chemical bonds to surfaces of solid inorganic substrates

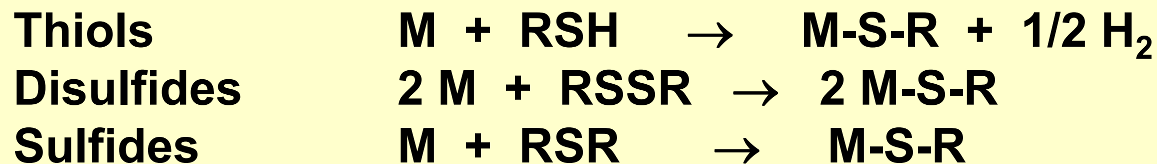
Alkanethiolates on gold and alkylsiloxanes on silicon dioxide belong the most notoriously studied SAM systems



Self-Assembled Monolayers

Metal surfaces Au, Ag, Cu, Pt, Hg, Fe,…
react with



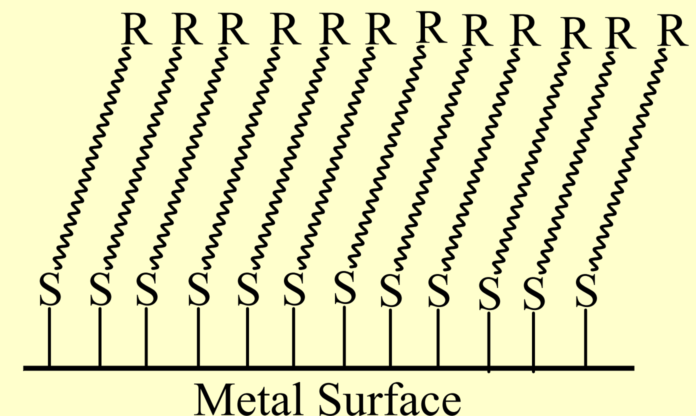


Same products formed in all three reactions: thiolates
RSH are more soluble and react 10^3 faster with Au than RSSR

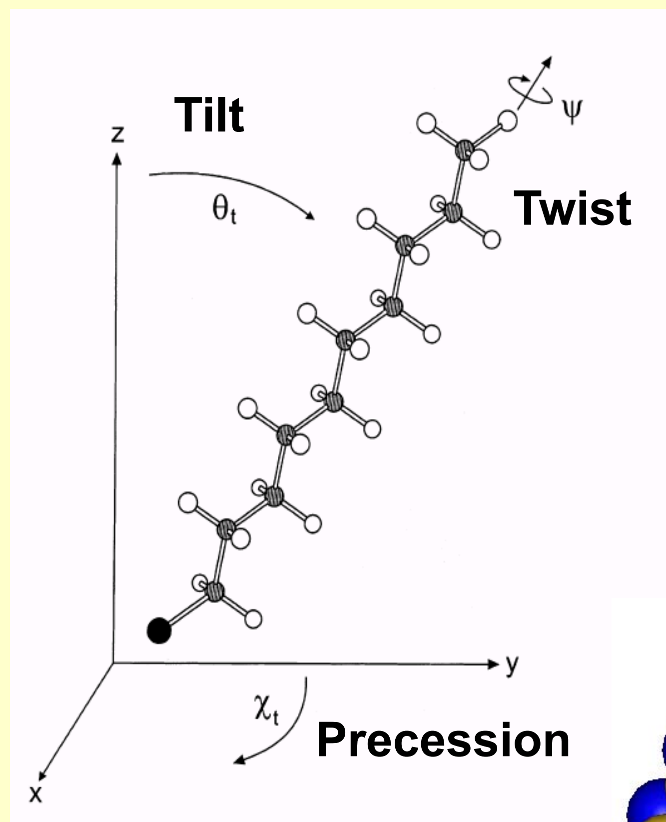
Substrates: gold polycrystalline films
on Si(SiO_2), glass, mica

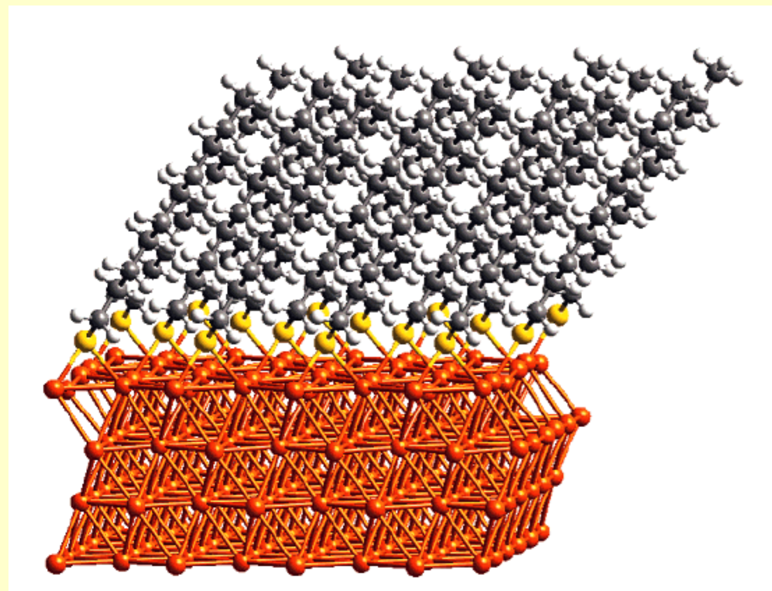
Thickness 5-300 nm, sputtering, evaporation

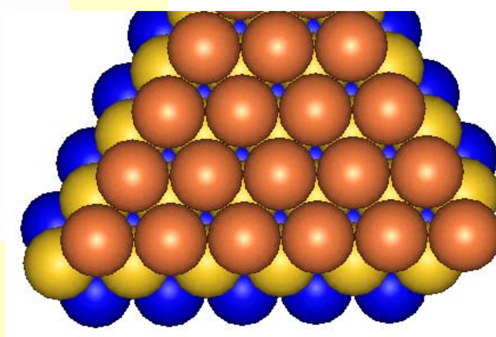
Anealed to atomically flat surface

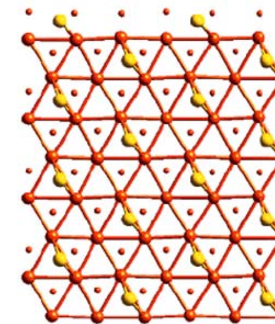


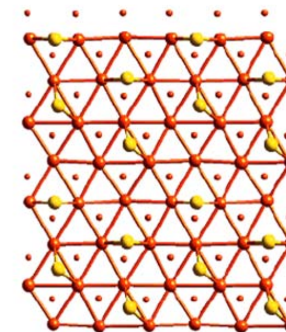
Self-Assembled Monolayers











Au surface = ccp

Self-Assembled Monolayers

Thermodynamics

Au does not form surface oxide layer

Reaction driving force:

- **Au-S bond energy 160-185 kJ mol^{-1}**
- **van der Waals attraction between alkyl chains 6-8 kJ mol^{-1} per CH_2**

In $^{t}BuSH$ and $n\text{-}C_{18}SH$ competition reaction, the linear alkyl thiol binds 300 – 700 times better

Surface coverage 10^{14} molecules per cm^2

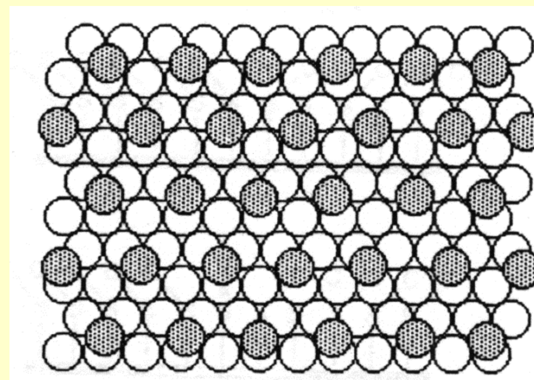
C_{16} chain length ~2.2 nm, 32-40° tilted, all-trans

Chemical stability: $Cu/C_{18}SH$ sustains HNO_3

Thermal stability: Au/RSH loses sulfur at 170-230 °C

Self-Assembled Monolayers

Binding modes on Au(111)
- ✧ **On-top sites**
- ✧ **Hollow sites – threefold, more stable by 25 kJ mol^{-1}**
- ✧ **Bridging sites – the most stable!! (QM calculations)**



Au–S–C = 180°, sp
Au–S–C = 104°, sp^3, more stable by 1.7 kJ mol^{-1}
barrier to interconversion 10.5 kJ mol^{-1}

Au(111)
Hexagonal array of S, S….S distance 4.97 Å, interchain distance in crystalline paraffins 4.65 Å, tilt angles 25 - 30° to reestablish alkyl chain contacts, hollow site binding, 21.4 $Å^2$ per molecule

Ag(111)
Hexagonal array of S, S….S distance 4.41 Å, on-top site binding, more tightly packed alkyl chains, no tilt

Self-Assembled Monolayers

Kinetics

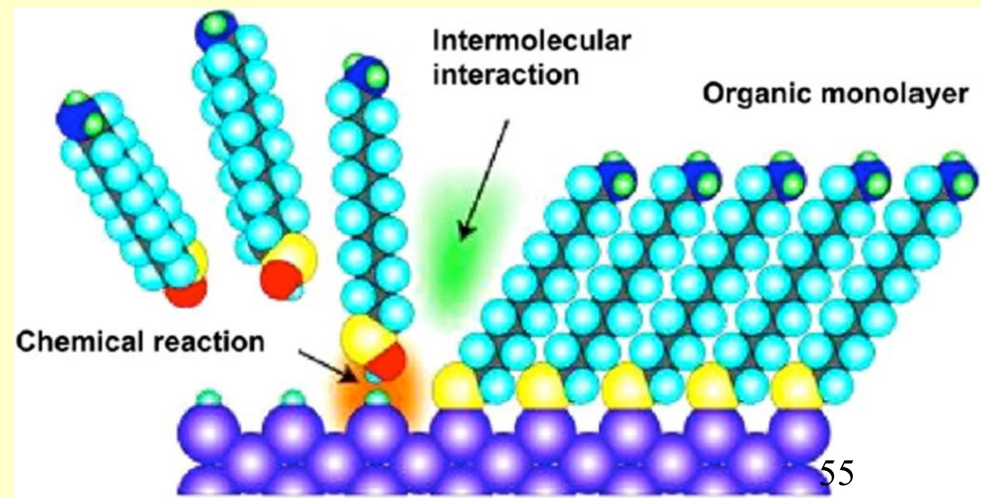
Au(111) + RSH reactions proceed in two steps:

1. First step, fast (minutes), diffusion controlled Langmuir adsorption, concentration dependent (1 mM ~ 1 min, 1 μM ~ 100 min)

2. Second step, slow (hours), disordered film orders to a 2D crystal, surface crystallization, defect healing, trapped solvent expulsion

Mechanisms: alkyl chain flipping, RS^- lateral diffusion, equilibrium with dissolved RSH, Au atom diffusion, Au in solution

Better crystallinity of films in polar solvents: MeOH, EtOH,…



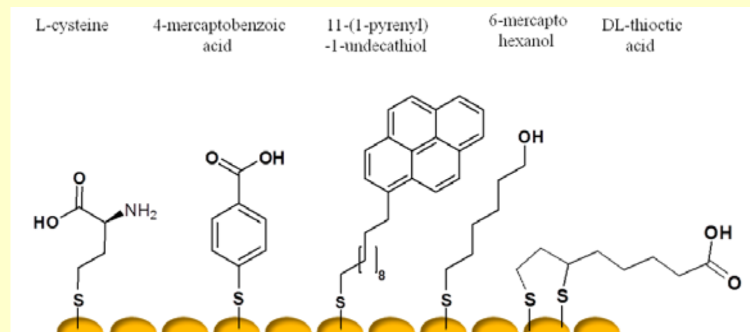
Self-Assembled Monolayers

Surface chemical derivatization

$HS–(CH_2)_n–X$
X = CH_3, CF_3, OH, NH_2, SH, COOH, COOR, CN, $CH=CH_2$, $C\equiv CH$, Cl, Br, OCH_3, SO_3H, $SiMe_3$, ferrocenyl, ….

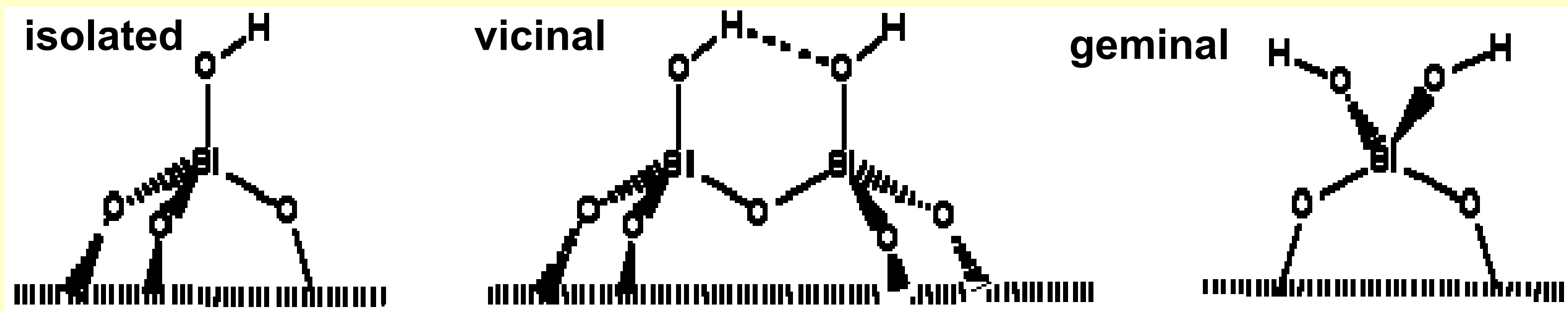
Microfabrication

♠ **Self-assembly, at thermodynamic minima, rejects defects, high degree of perfection**
♠ **Dimension in the range 1 nm to 1000 μm, too large for chemical synthesis, too small for microlithography**
♠ **High efficiency, spontaneous**

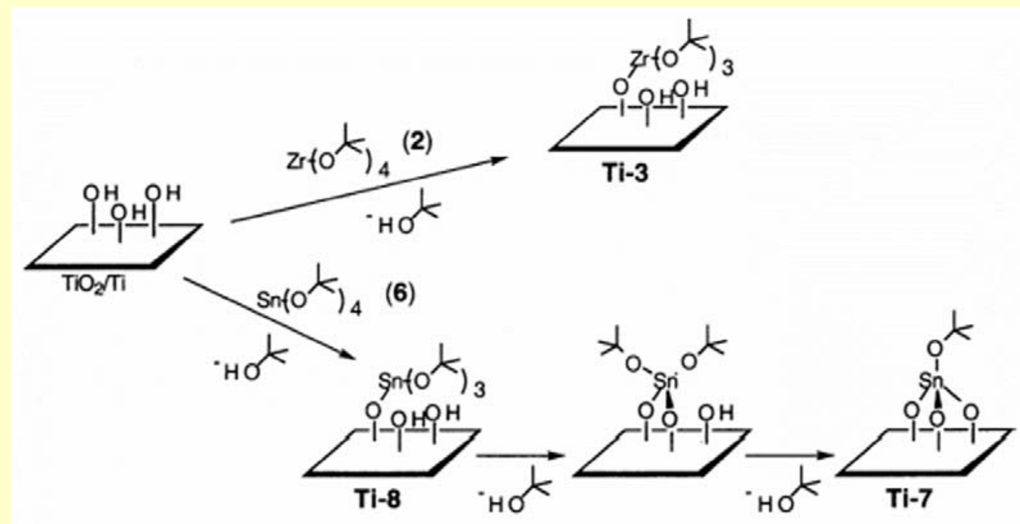


SiO_2 Surfaces

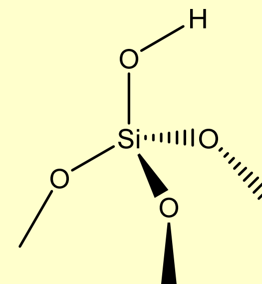
- Native oxide on Si
- Silicagel



Chemical derivatization methods are based on the reactivity of the surface hydroxyl groups with various reagents



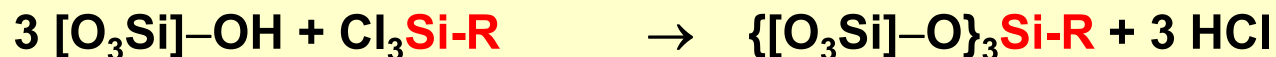
SiO_2 Surfaces



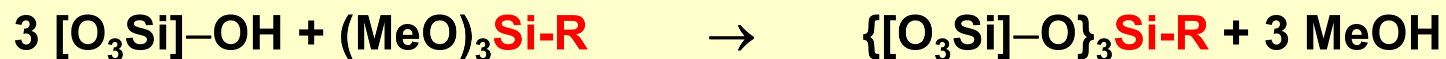
[O3Si]–OH stands for the siliceous surface

1. Grafting

Reactions with trifunctional reagents, such as alkyltrichlorosilanes and trialkoxyalkylsilanes, lead to the three-fold attachment of the Si-R groups

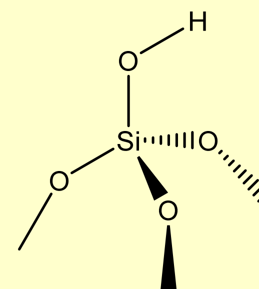


$3\ [O_3Si]\text{–}OH + Cl_3Si\text{-}R \rightarrow \{[O_3Si]\text{–}O\}_3Si\text{-}R + 3\ HCl$



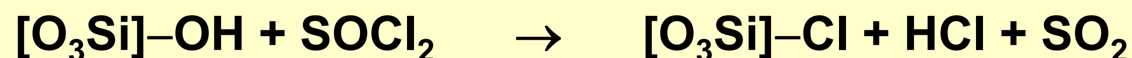
$3\ [O_3Si]\text{–}OH + (MeO)_3Si\text{-}R \rightarrow \{[O_3Si]\text{–}O\}_3Si\text{-}R + 3\ MeOH$

SiO_2 Surfaces

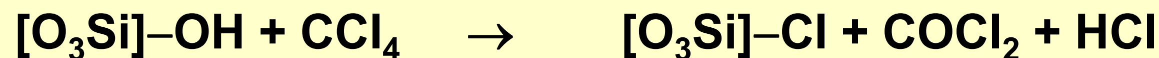


2. Chlorination/Displacement Method

The first step is the replacement of the Si-OH groups by more reactive Si-Cl bonds by chlorination

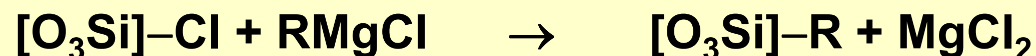


$$[O_3Si]–OH + SOCl_2 \rightarrow [O_3Si]–Cl + HCl + SO_2$$

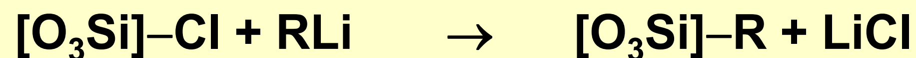


$$[O_3Si]–OH + CCl_4 \rightarrow [O_3Si]–Cl + COCl_2 + HCl$$

In the subsequent step, the surface is treated with a Grignard or organolithium reagent with the formation of strong Si-C bonds



$$[O_3Si]–Cl + RMgCl \rightarrow [O_3Si]–R + MgCl_2$$

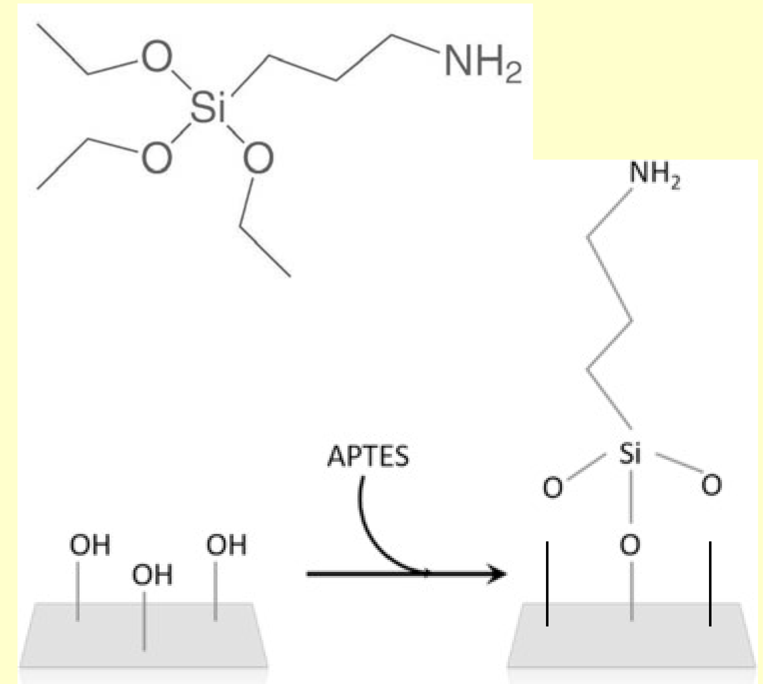


$$[O_3Si]–Cl + RLi \rightarrow [O_3Si]–R + LiCl$$

SiO_2 Surfaces

3. Post Modification Method

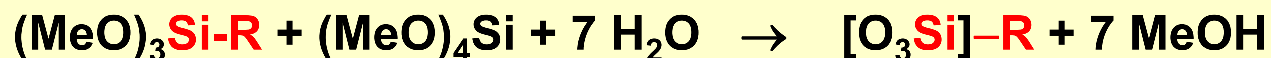
The organic groups (Si-R) covalently anchored to the siliceous surface by the two previous methods can be subsequently chemically modified



APTES (3-aminopropyl(triethoxy)silane)
Large number of chemical transformations of the amino moiety to other functional groups are known

4. Hybrid sol-gel method (co-condensation)

A thin layer of a hybrid (organically modified) silica gel can be deposited on the silica surface from a solution of TEOS and $(MeO)_3Si\text{-}R$ by controlled hydrolysis and condensation

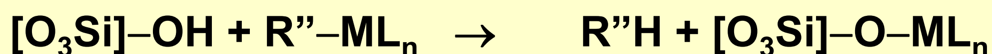


$$(MeO)_3Si\text{-}R + (MeO)_4Si + 7\,H_2O \rightarrow [O_3Si]\text{–}R + 7\,MeOH$$

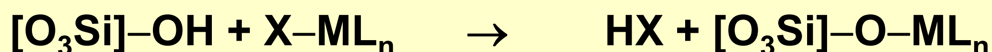
SiO_2 Surfaces

5. Organometallic modification method

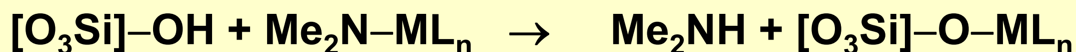
Organometallic reagents, such as metal alkyls, halides, amides, and alkoxides can be used to deposit a monolayer of metal complexes on the surface (ML_n stands for an organometallic group, M for a metal, L for a ligand, R” for a short alkyl chain, X for halogen)



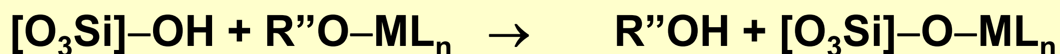
$$[O_3Si]{-}OH + R''{-}ML_n \rightarrow R''H + [O_3Si]{-}O{-}ML_n$$



$$[O_3Si]{-}OH + X{-}ML_n \rightarrow HX + [O_3Si]{-}O{-}ML_n$$

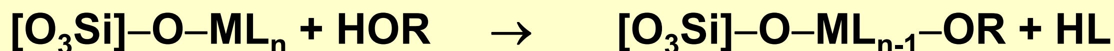


$$[O_3Si]{-}OH + Me_2N{-}ML_n \rightarrow Me_2NH + [O_3Si]{-}O{-}ML_n$$

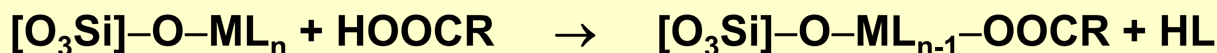


$$[O_3Si]{-}OH + R''O{-}ML_n \rightarrow R''OH + [O_3Si]{-}O{-}ML_n$$

These organometallic moieties can serve as attachment points for further modification with long chain alcohols, thiols, carboxylic acids, phosphates, and diketonates



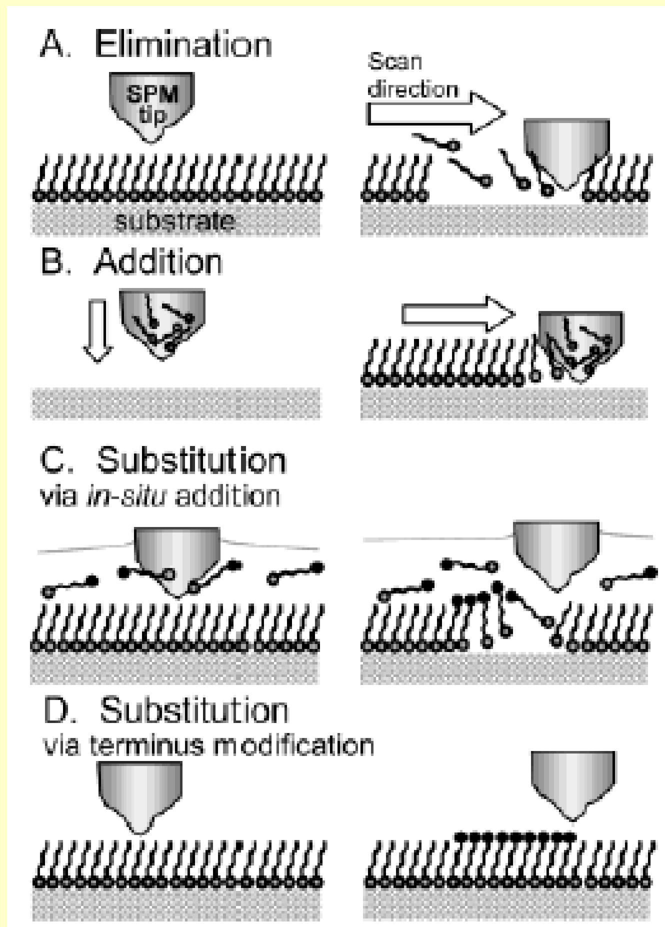
$$[O_3Si]{-}O{-}ML_n + HOR \rightarrow [O_3Si]{-}O{-}ML_{n-1}{-}OR + HL$$

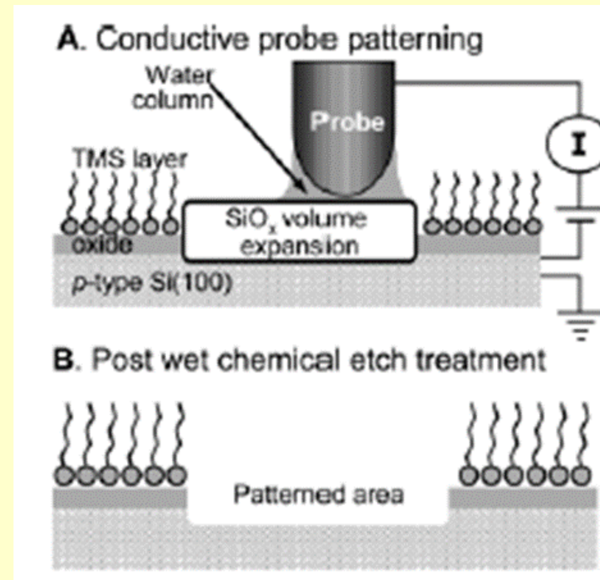


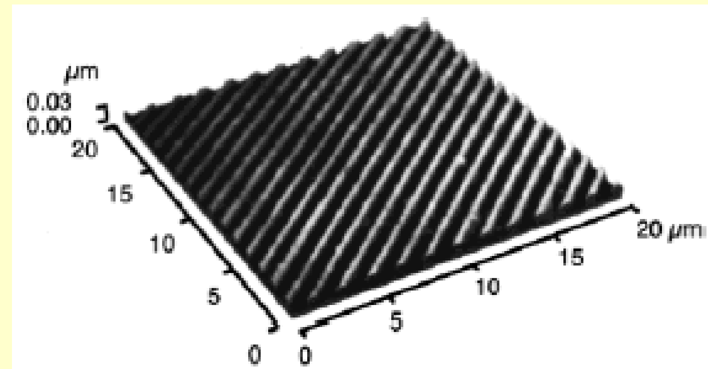
$$[O_3Si]{-}O{-}ML_n + HOOCR \rightarrow [O_3Si]{-}O{-}ML_{n-1}{-}OOCR + HL$$

Manipulations with SAM

STM or AFM probe tips – mechanical or electrochemical

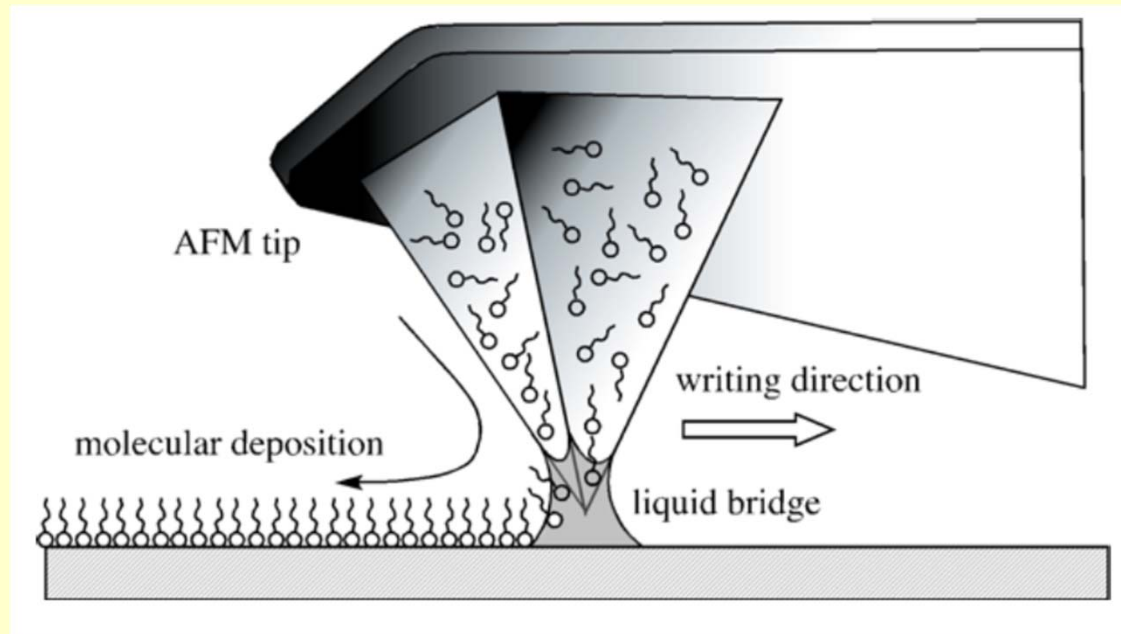






Manipulations with SAM

Dip-pen nanolithography



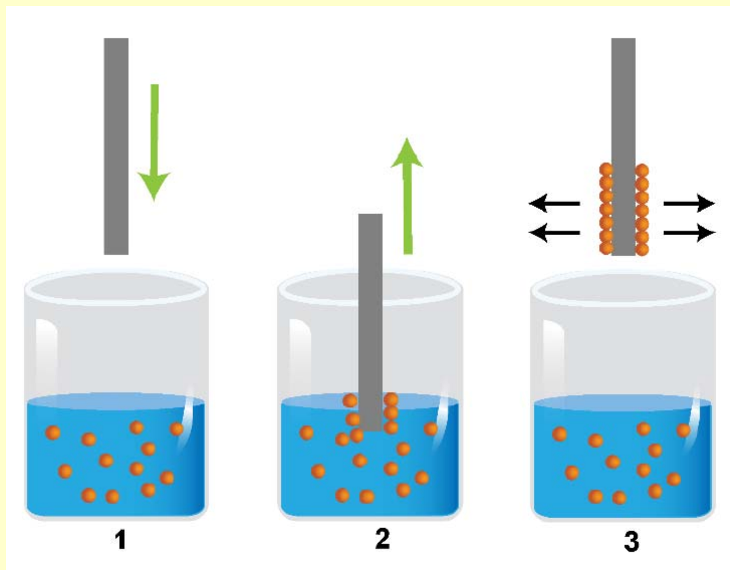
Dip Coating

Schott 1939
The substrates are dipped into a precursor solution - a sol or a slurry
Withdrawal from the sol - a wet film is formed
Solution viscosity, gravity force, surface tension gradient, particle size

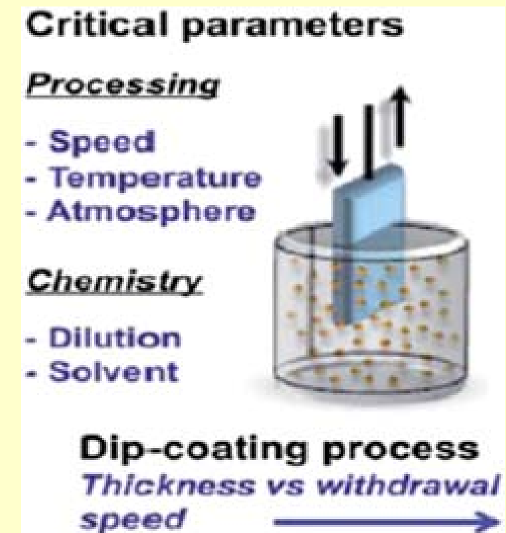
Drying atmosphere - the produced film is transformed into a xerogel
Heat treatment - crystallization

Control of the thickness:

- **Number of depositions**
- **Loading of the slurry**
- **Concentration of the sol**
- **Withdrawal speed**



Dip Coating



The substrate pretreatment process

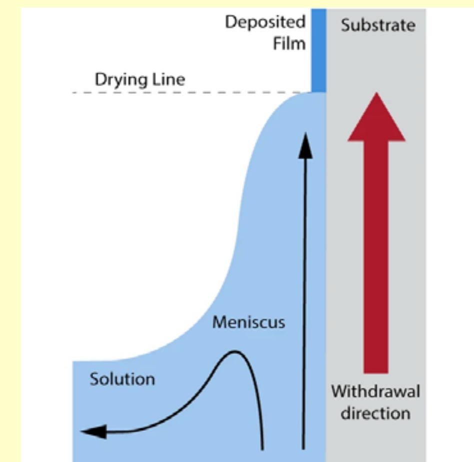
Immersion - at a constant speed, the substrate is dipped into the coating solution

Startup - the substrate remains in the solution for a designated time, and then it starts to be pulled out

Deposition - while the substrate is being pulled out, the thin film coating starts to be deposited on it, the thickness of the coating is directly dependent on the speed by which the substrate is being pulled out

Drainage - excess liquid is drained from the substrate surface

Evaporation - solvent starts to evaporate from the surface of the substrate to form a thin film



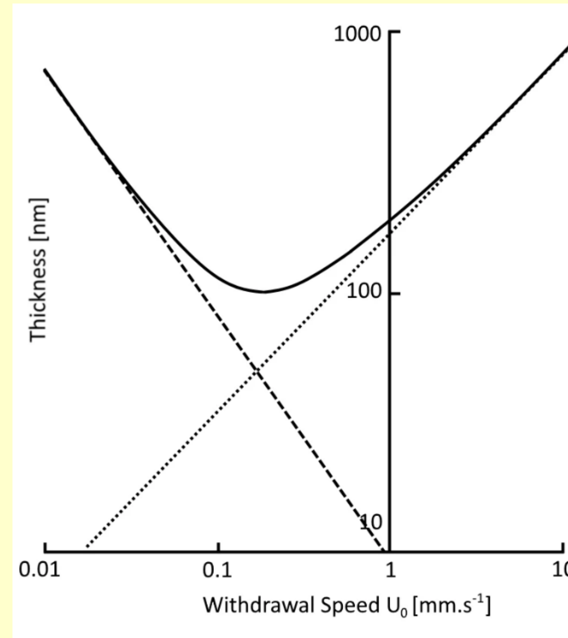
Coating Thickness

The capillarity regime

Very low withdrawal speeds

The solvent evaporation faster than the movement of the drying line

$$h_f = \frac{c_i M_i E}{\alpha_i \rho_i L U_0}$$



The viscous flow regime

High velocities and viscous solutions

$$h_0 = c\left(\frac{\eta U_0}{\rho g}\right)^{\frac{1}{2}}$$

The drainage regime

Low withdrawal speeds

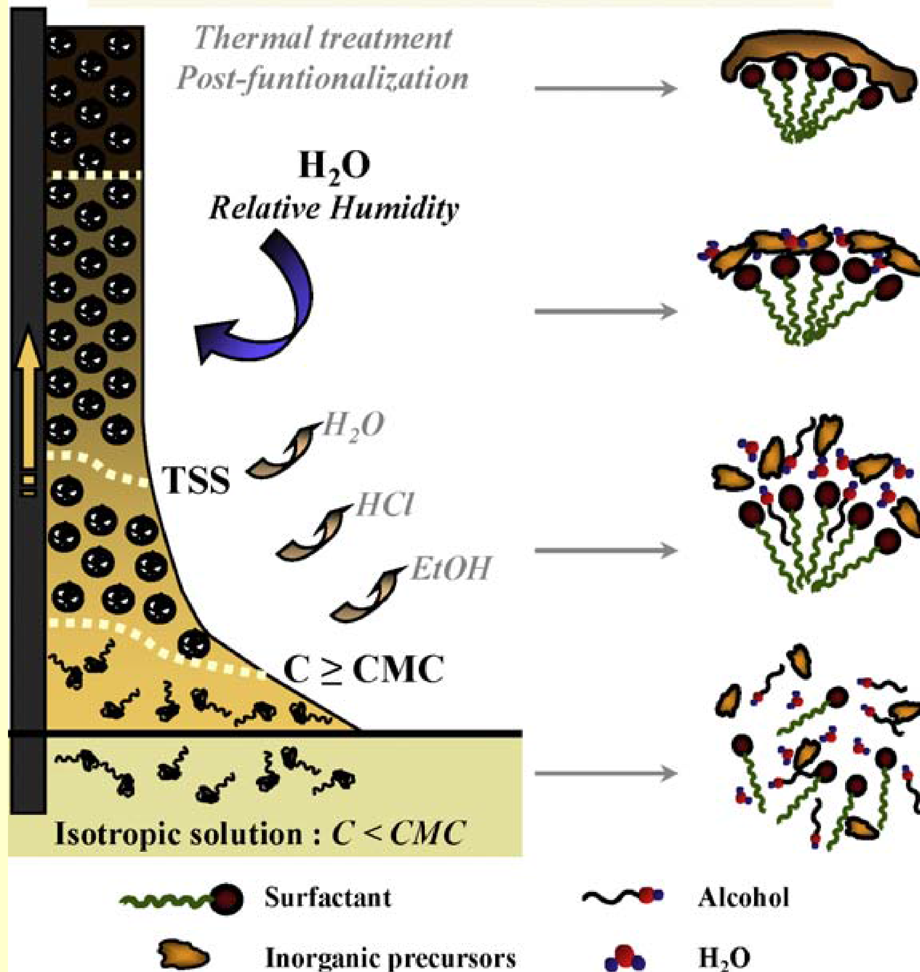
The Landau-Levich equation

$$h_0 = c\frac{(\eta U_0)^{\frac{2}{3}}}{\gamma_{LV}^{\frac{1}{6}}(\rho g)^{\frac{1}{2}}}$$

E = evaporation rate, L = the width of the film, h_f = the final dry film thickness, c_i = concentration of the solute, M_i = the molar weight of the solute, α_i = porosity of the final film

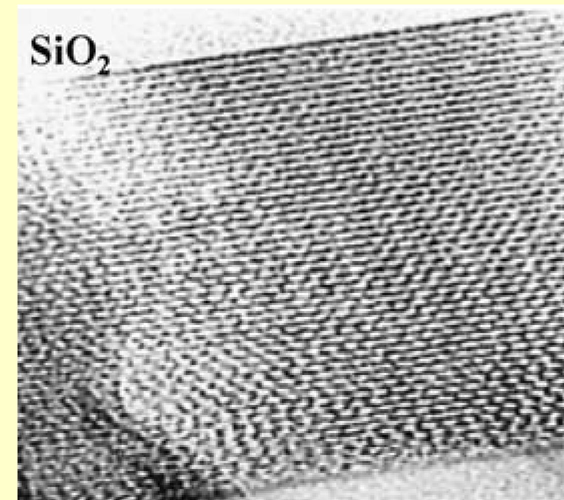
h_0 = wet coating thickness, η = viscosity, γ_{LV} = liquid-vapor surface tension, ρ = density, g = gravity, U_0 = withdrawal velocity, c = the curvature of the dynamic meniscus

Evaporation-Induced Self-Assembly (EISA)



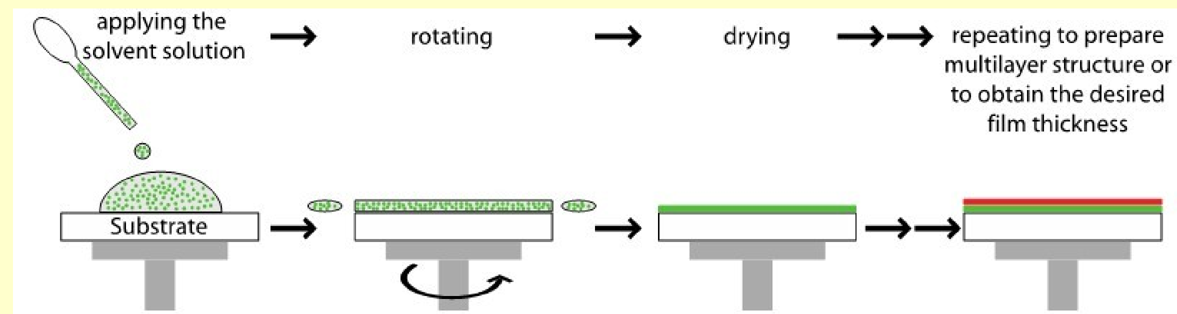
Critical parameters of EISA process:

- Molar ratio Surfactant / Inorganic precursor
- H_2O amount
- Volatile solvent content (Ethanol/THF)
- Temperature
- Relative Humidity



Spin-Coating

Four stages:



- **Deposition**

- **Spin-up**

the liquid flows radially outward, driven by centrifugal force

- **Spin-off**

the excess of liquid is ejected as drops on the perimeter

- **Evaporation**

Surface tension coating (2 - 50 μm)

Doctor-blade coating - solution deposition onto the surface of the substrate, moving the coating tool to spread the solution, drying of the deposited coating (below 5 μm)