SYNTHESIS OF THIN FILMS

THIN FILMS ARE VITAL IN MODERN TECHNOLOGY:

Protective coatings
Optical coatings
Filters, mirrors, lenses
Microelectronic devices
Optoelectronic devices
Photonic devices
Electrode surfaces
Photoelectric devices, photovoltaics, solar cells
Xerography
Photography
Lithography
Catalyst surfaces
Information storage, magnetic, magneto-optical, optical memories
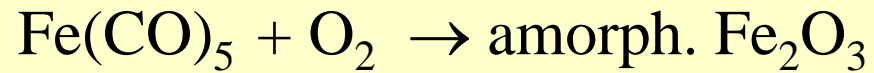
SYNTHESIS OF THIN FILMS

Crystalline, Amorphous, Microcrystalline

Monolayer, multilayer, superlattice, junctions

Free-standing, supported

Epitaxial (commensurate), incommensurate

Free-standing films

$Fe(CO)_5 + O_2 \rightarrow$ amorph. Fe_2O_3

Prepared on as a film on a NaCl crystal support

Dissolution of NaCl in water = Free-standing film

SYNTHESIS OF THIN FILMS

FILM PROPERTIES DEPEND ON NUMEROUS CONSIDERATIONS:

Thickness
Surface : volume ratio
Structure, surface versus bulk, surface reconstruction, surface roughness
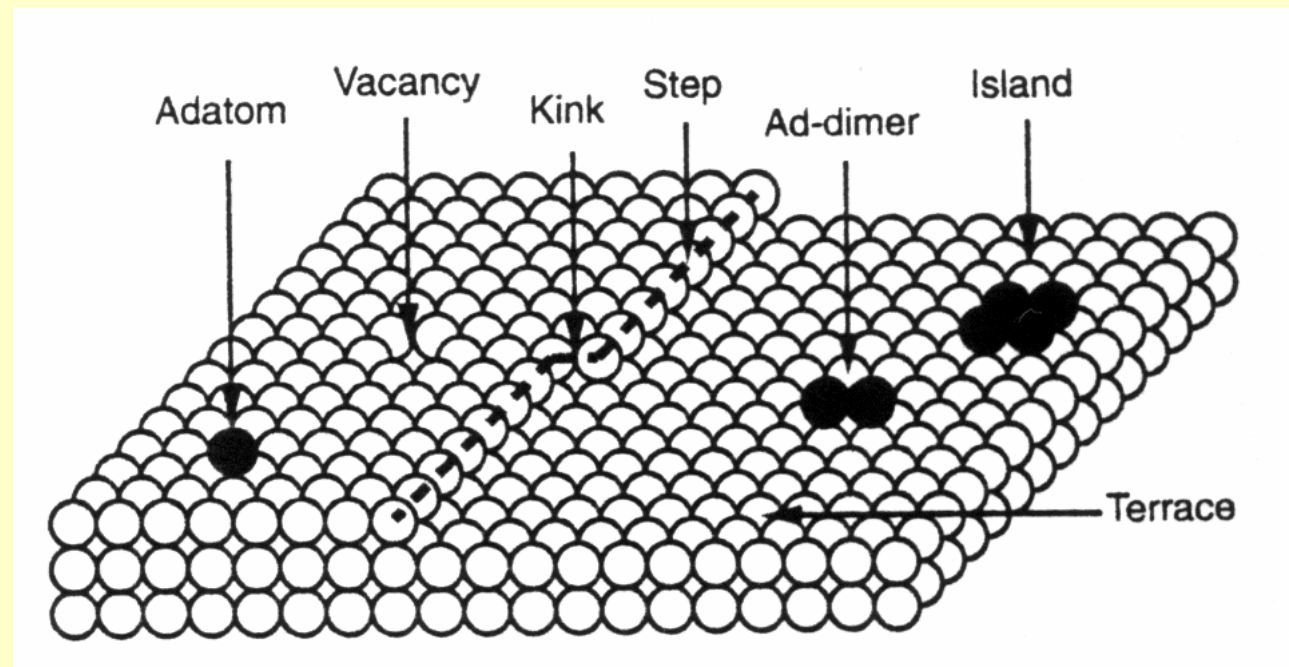**Hydrophobicity, hydrophilicy (Si-OH vs. Si-H)**
Composition
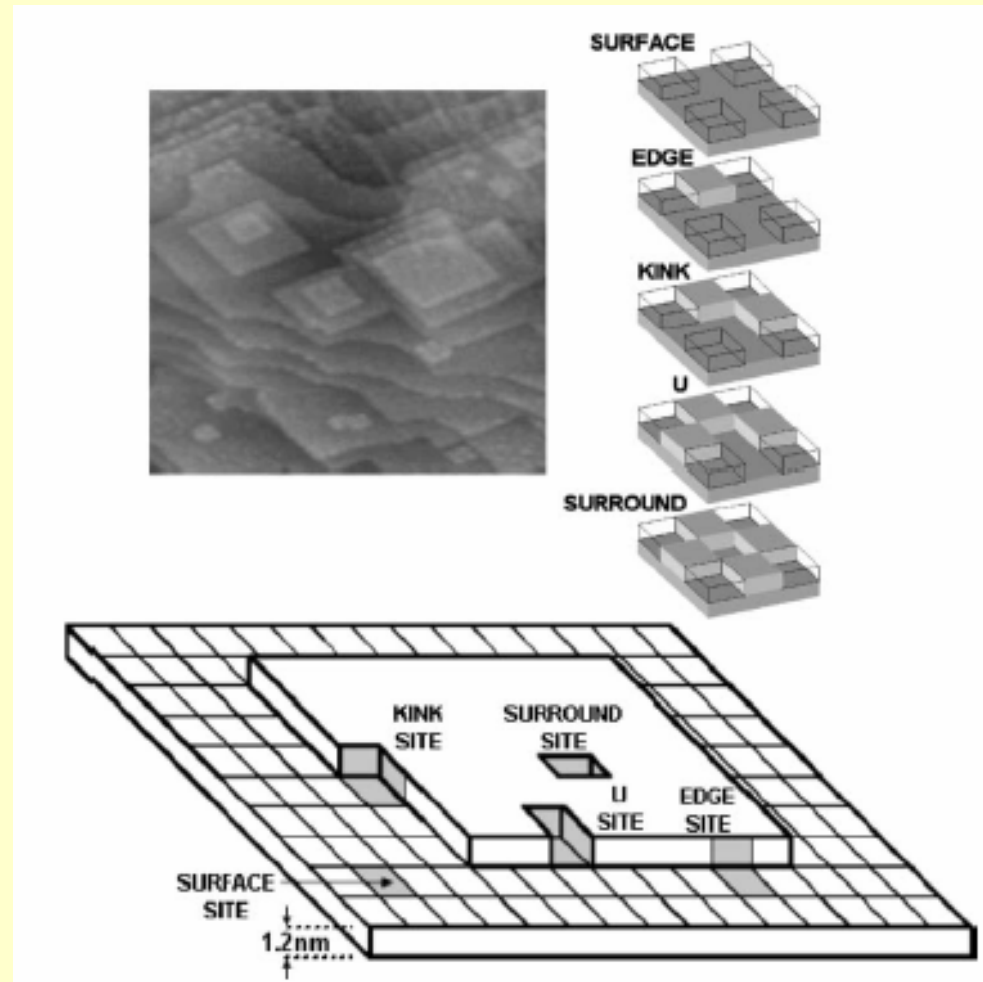**Texture: single crystal, microcrystalline, domains, orientation**
Form: supported or unsupported, nature of substrate

SYNTHESIS OF THIN FILMS

The TSK Model of a Surface

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

SURFACE

EDGE

KINK

U

SURROUND

KINK SITE

SURROUND SITE

U SITE

EDGE SITE

SURFACE SITE

1.2nm

Thin Films

6

SYNTHESIS OF THIN FILMS

Surface diffusion coefficient D

$D = a^2 k_s$ **a … effective hopping distance between sites**
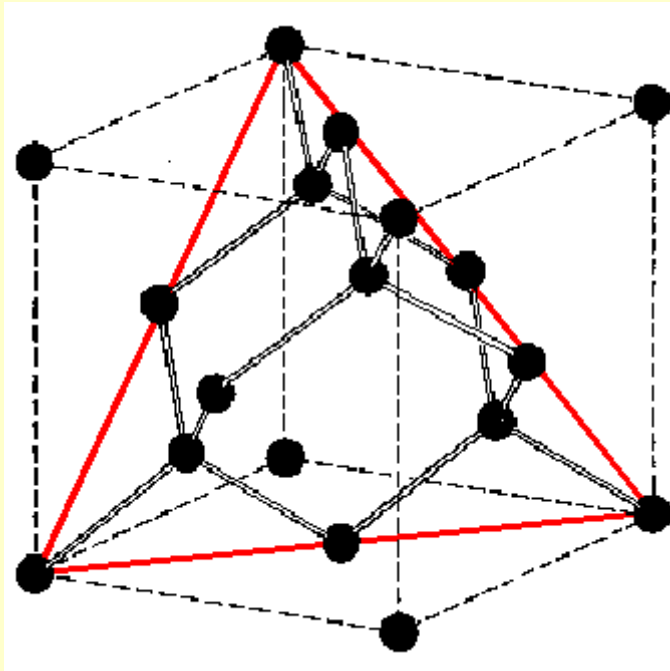
                              k_s **… site-to-site hopping rate of an adatom**

$k_s = A \exp(-V_s/k_b T)$ V_s **… potential-energy barrier to hopping from site to site**

                              T … substrate temperature

Higher temperature =   Faster diffusion

Si(111) Surface

Silicon "diamond lattice" structure
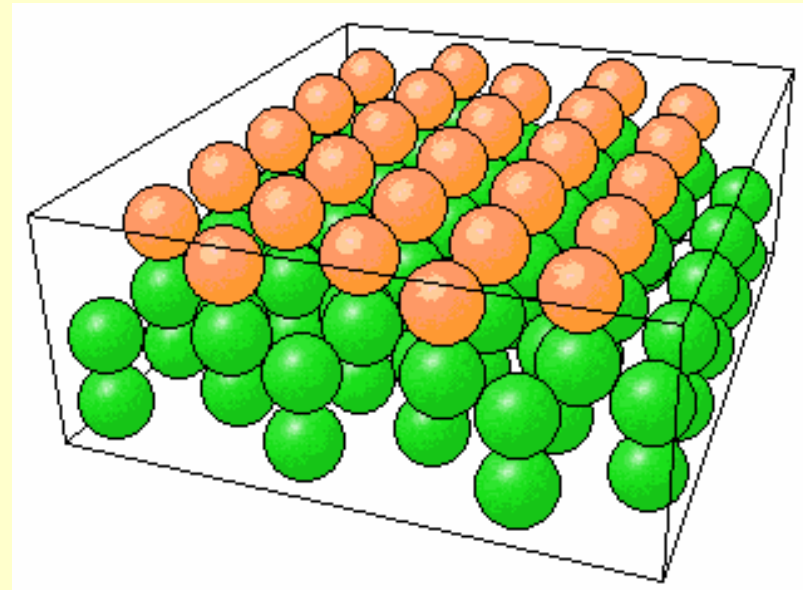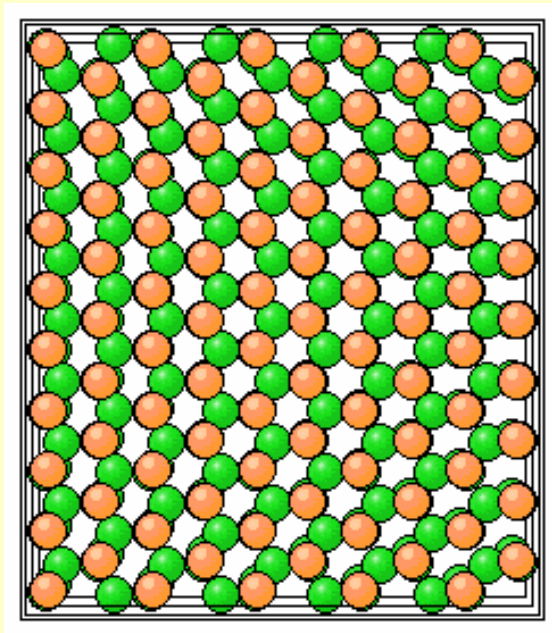
$$a = 5.463 \ \text{Å}$$

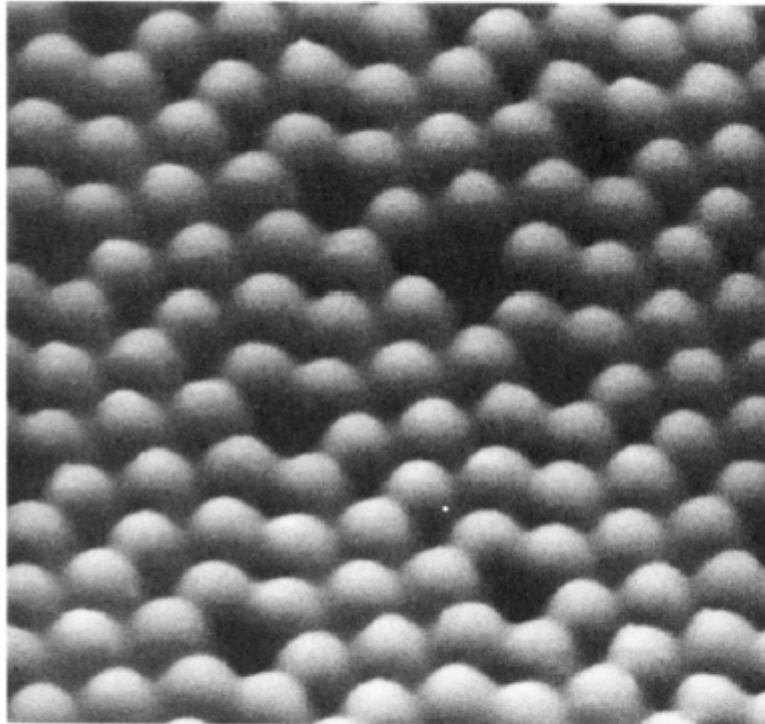**Si(111) = a set of atomic planes**

One plane outlined with red

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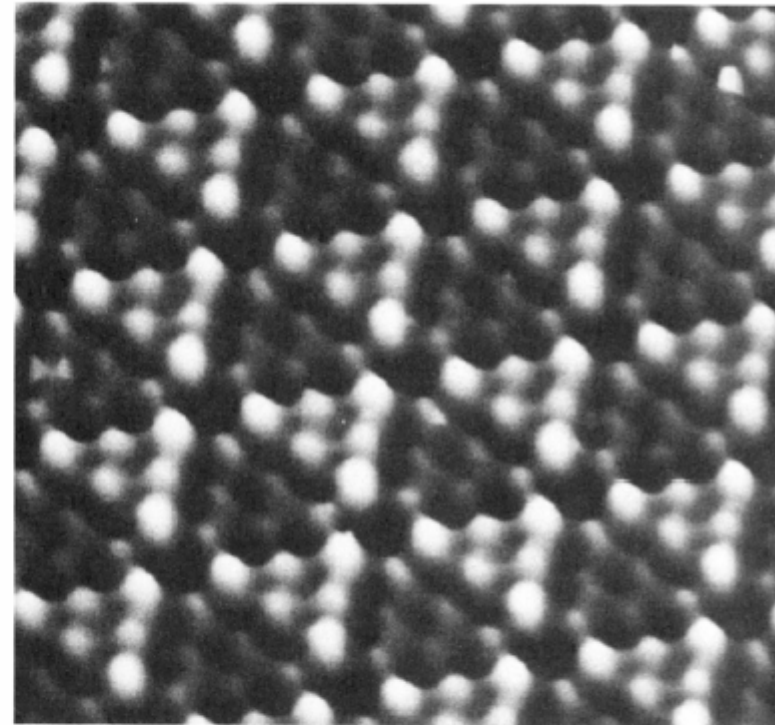
A top view of the atomic arrangement for the (111) plane

orange = the top layer
green = deeper layers

a) Unoccupied states

b) Occupied states

⊢⎯⎯⎯⎯⎯⊣
20 Å

⊢⎯⎯⎯⎯⎯⊣
20 Å

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.

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.
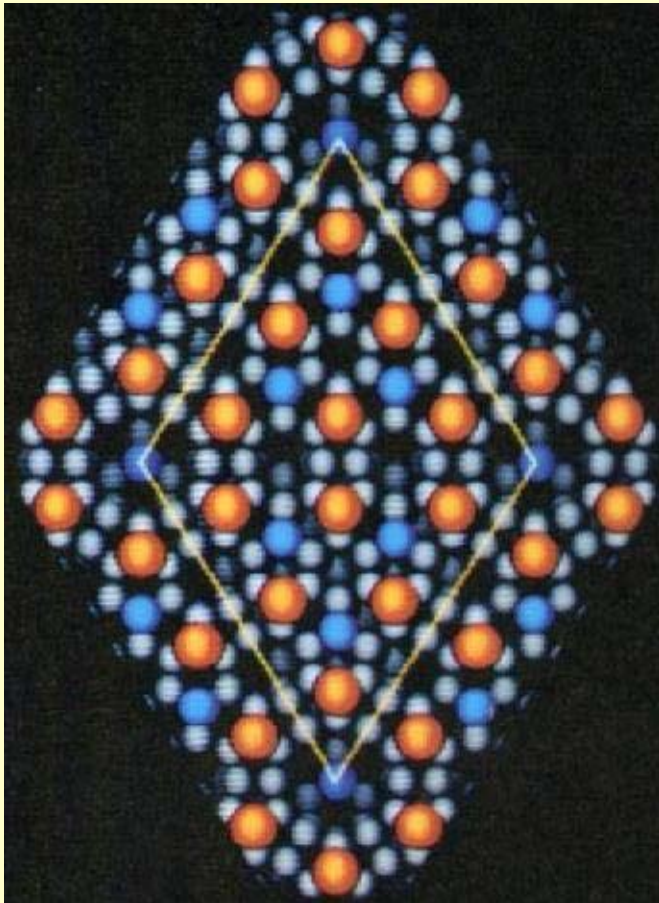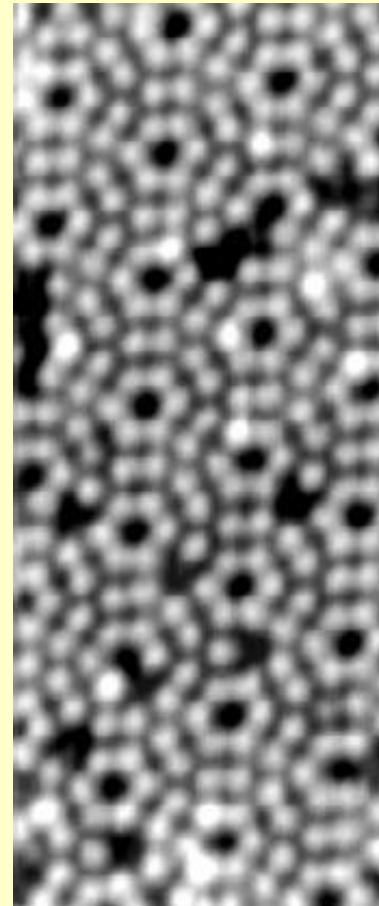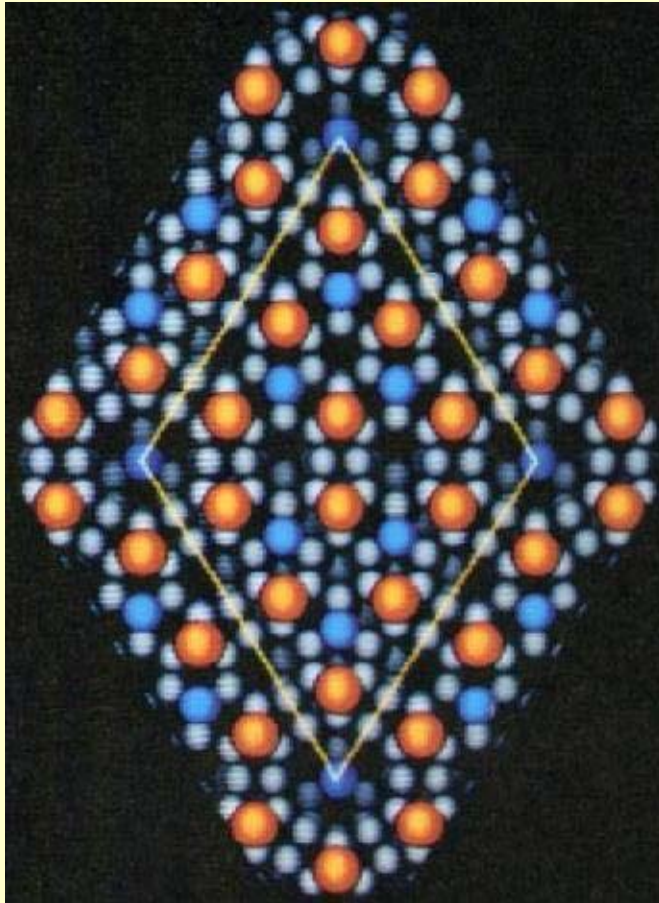

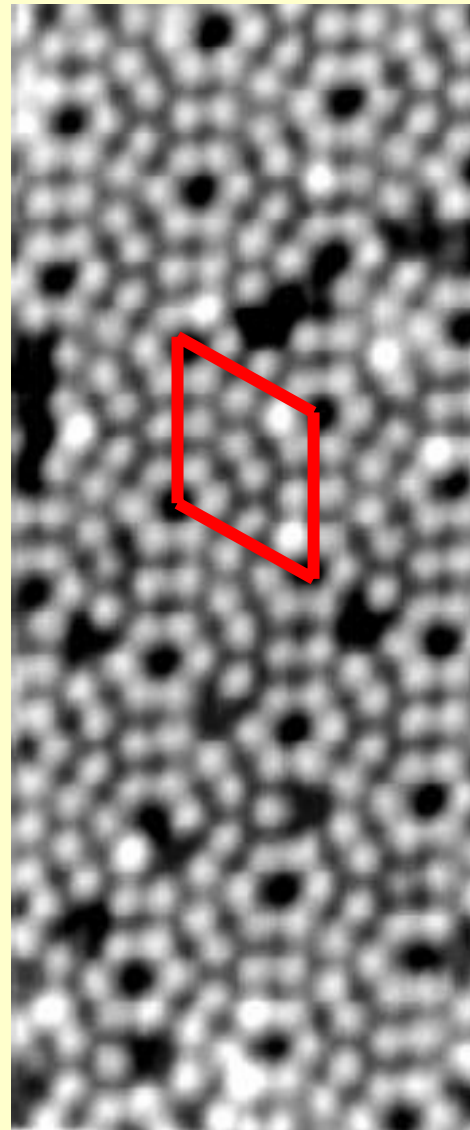**STM image of Si(111) surface**
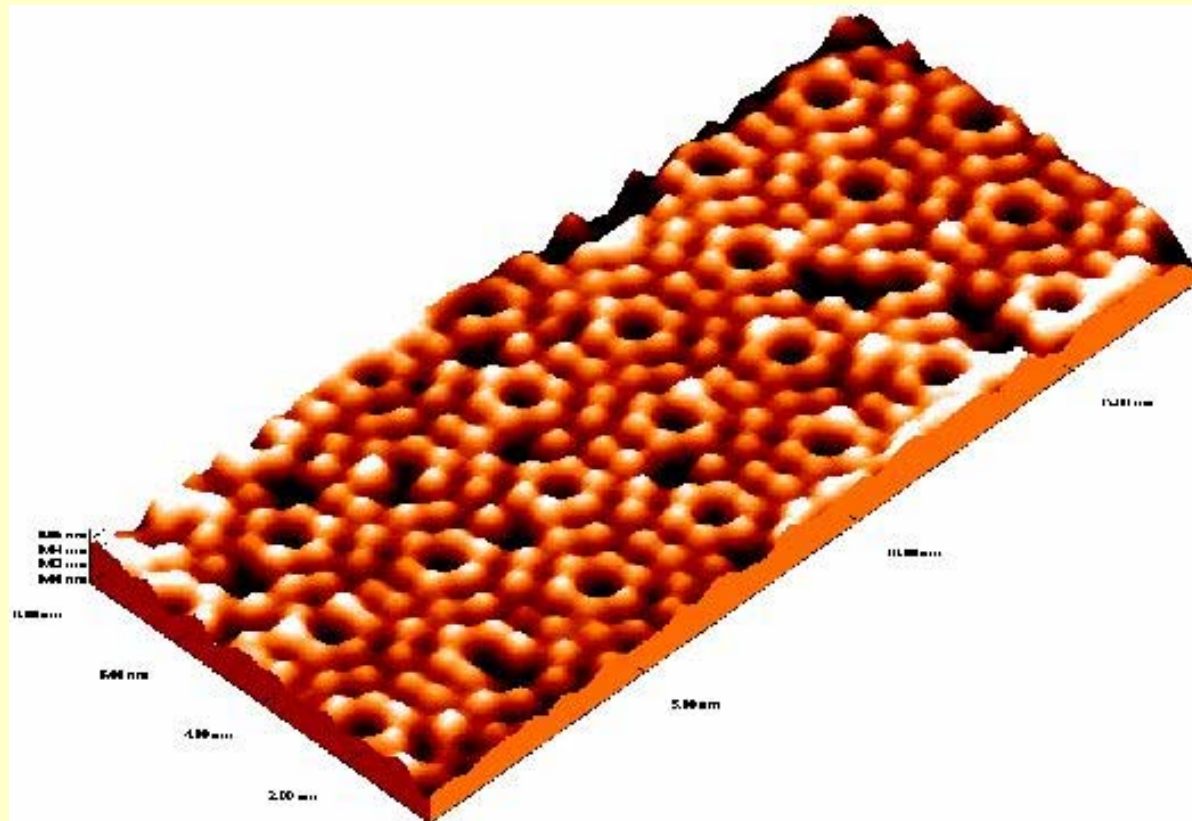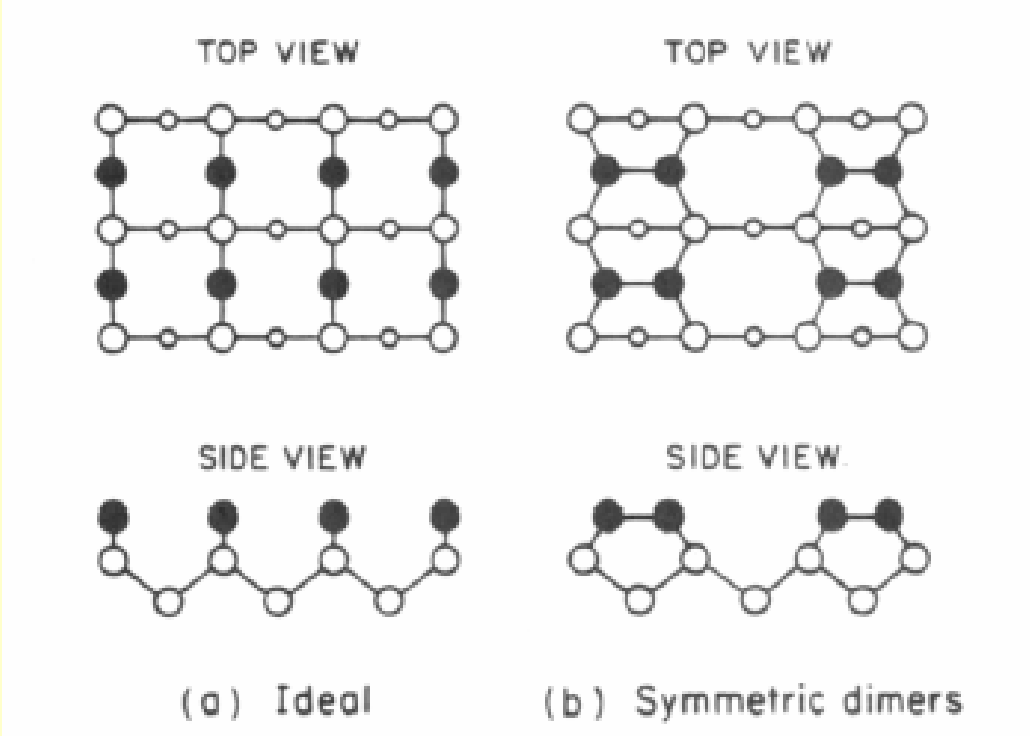
Thin Films

7x7 reconstruction

7x7 reconstruction

3D representation of the 7x7 STM image
The image area is 18x8 nm^2, the height of the "bumps" is only about 0.04 nm
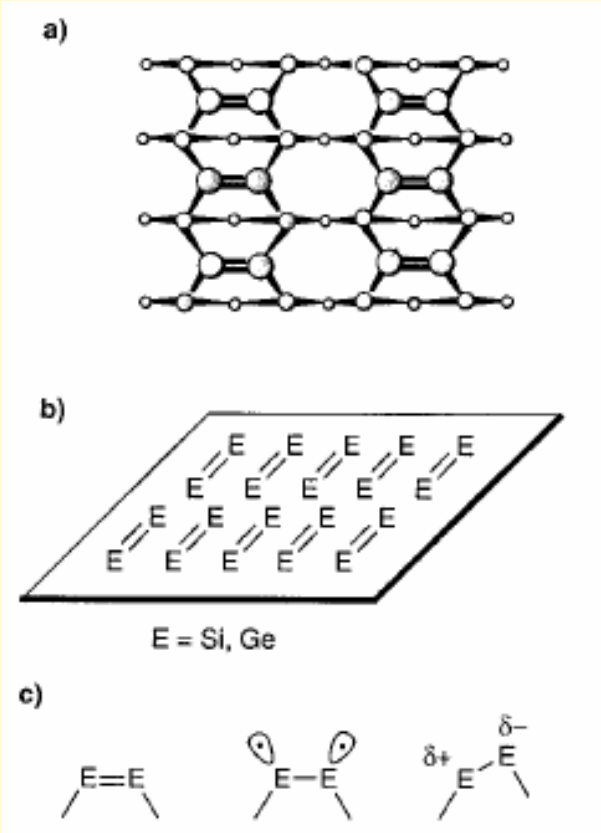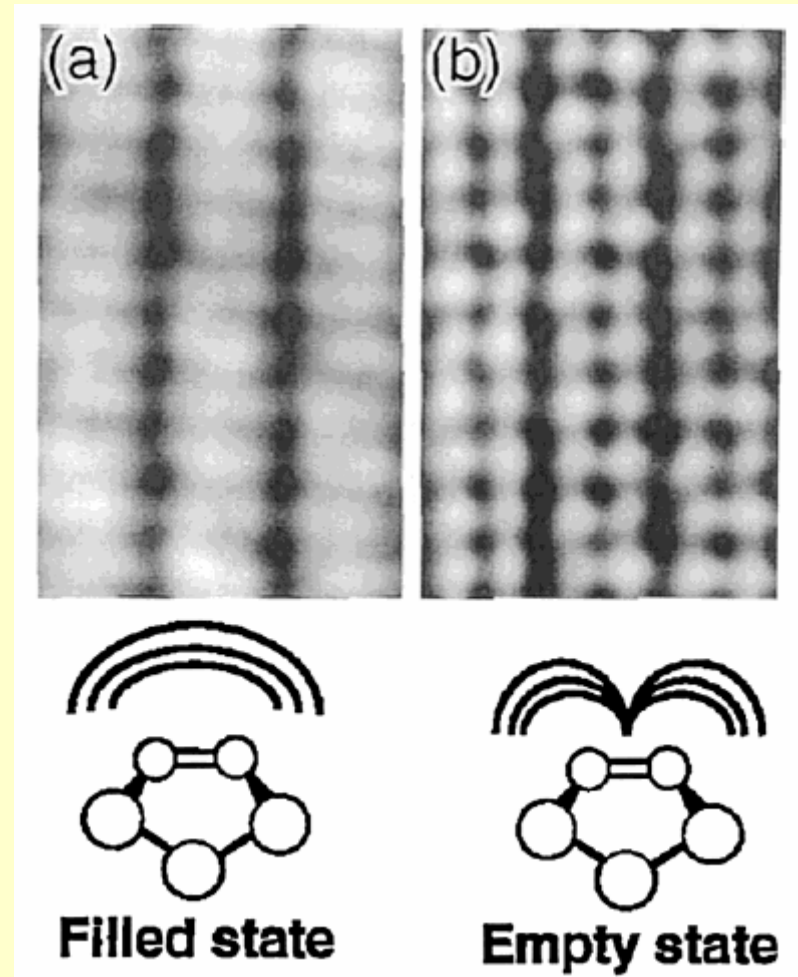
Si(100) Surface

TOP VIEW   TOP VIEW

SIDE VIEW   SIDE VIEW

(a) Ideal   (b) Symmetric dimers

a)

b)

E = Si, Ge

c)

$E=E$ $E-E$ $\overset{\delta-}{\underset{\delta+}{E}}E$

ideal   reconstructed

STM images of the silicon-silicon dimers imaged with
(a) V_{sample} = -2.0 V and (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.

(a) (b)

Filled state   Empty state

H-terminated Si(100) Surface

a)

Si(100)-(2x1)   monohydride

b)

Si(100)-(1x1)   dihydride

c)

Si(100)-(3x1)   mono- and dihydride
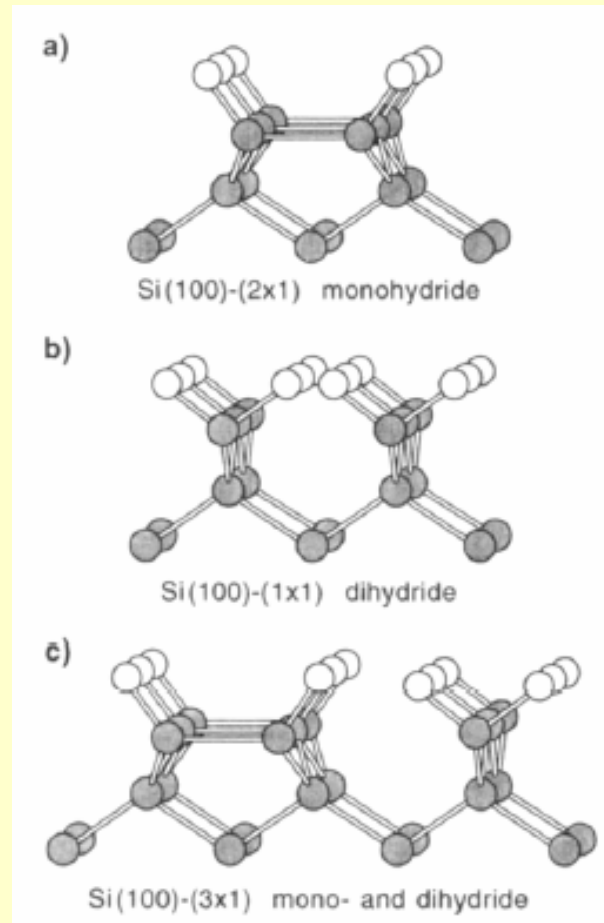
SYNTHESIS OF THIN FILMS

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)
Molecular beam epitaxy, supersonic cluster beams, aerosol deposition
Liquid phase epitaxy
Self-assembly, surface anchoring, SAM
Discharge techniques, RF, microwave
Laser ablation
Cathode sputtering, vacuum evaporation

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
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**

Deposition of oxide films, such as alumina, titania
Deposition of conducting polymer films by oxidative polymerization
of monomer, such as thiophene, pyrolle, aniline
Oxide films formed from metallic electrode in aqueous salts or acids

SYNTHESIS OF THIN FILMS

Example:
Anodic oxidation of aluminum in oxalic or phosphoric acid

$Pt|H_3PO_4, H_2O|Al$

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

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

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

overall electrochemistry:

$2Al + 3PO_4^{3-} \rightarrow Al_2O_3 + PO_3^{3-}$

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
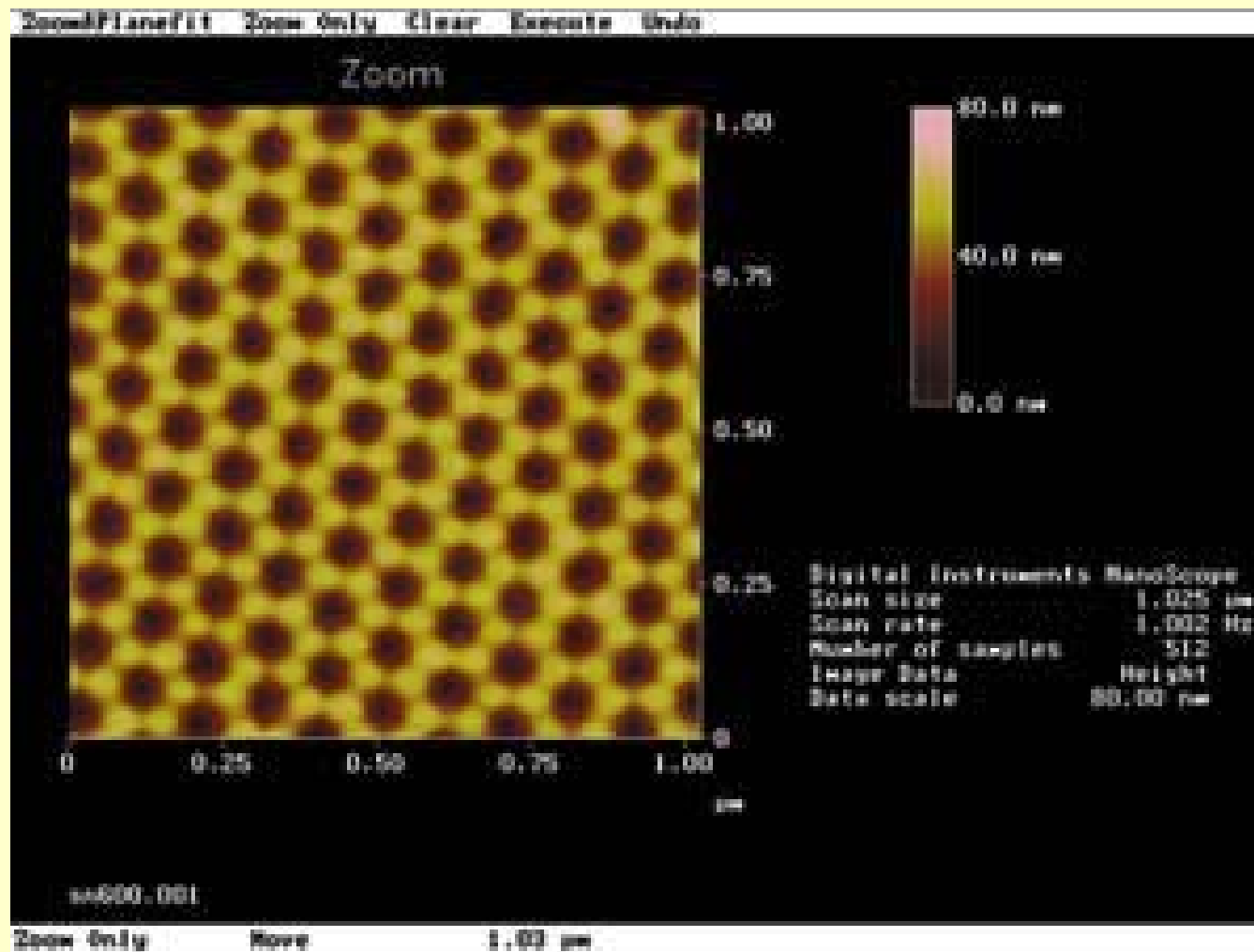
SYNTHESIS OF THIN FILMS

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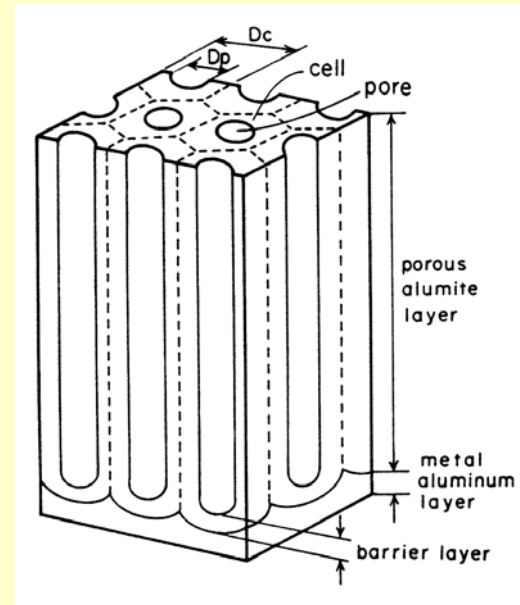

Exceptionally useful process for creating controlled porosity membranes, photonic gap materials, template for synthesizing semiconductor nanostructures, host for synthesizing and organizing aligned carbon nanotubes for high intensity electron emission displays, and last but not least, fuel cell electrode materials

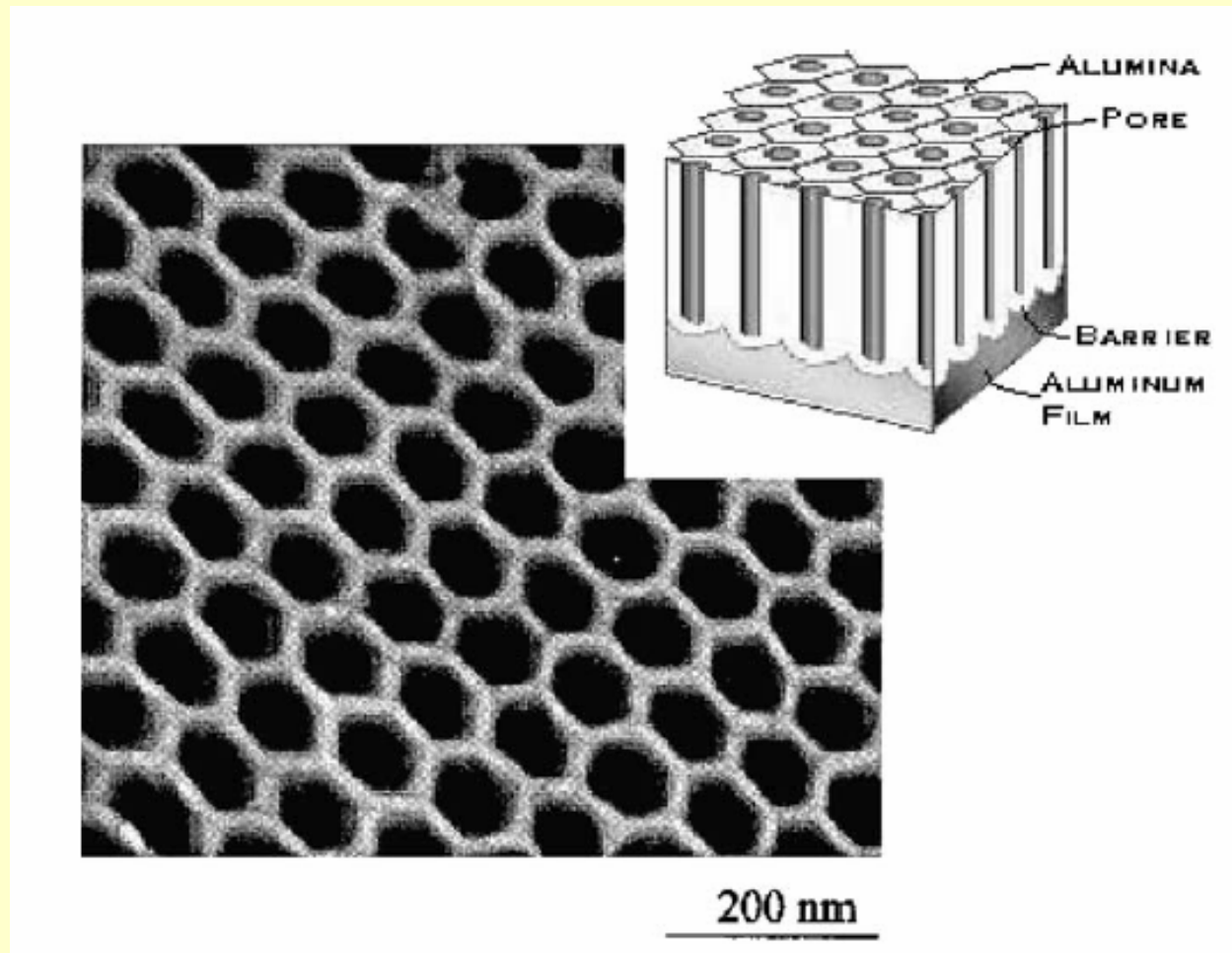# AFM picture of porous alumina film
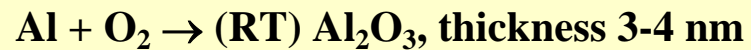
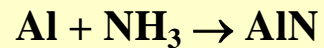# AFM picture of porous alumina film

Porous Alumina Films

ALUMINA
PORE
BARRIER
ALUMINUM FILM

200 nm
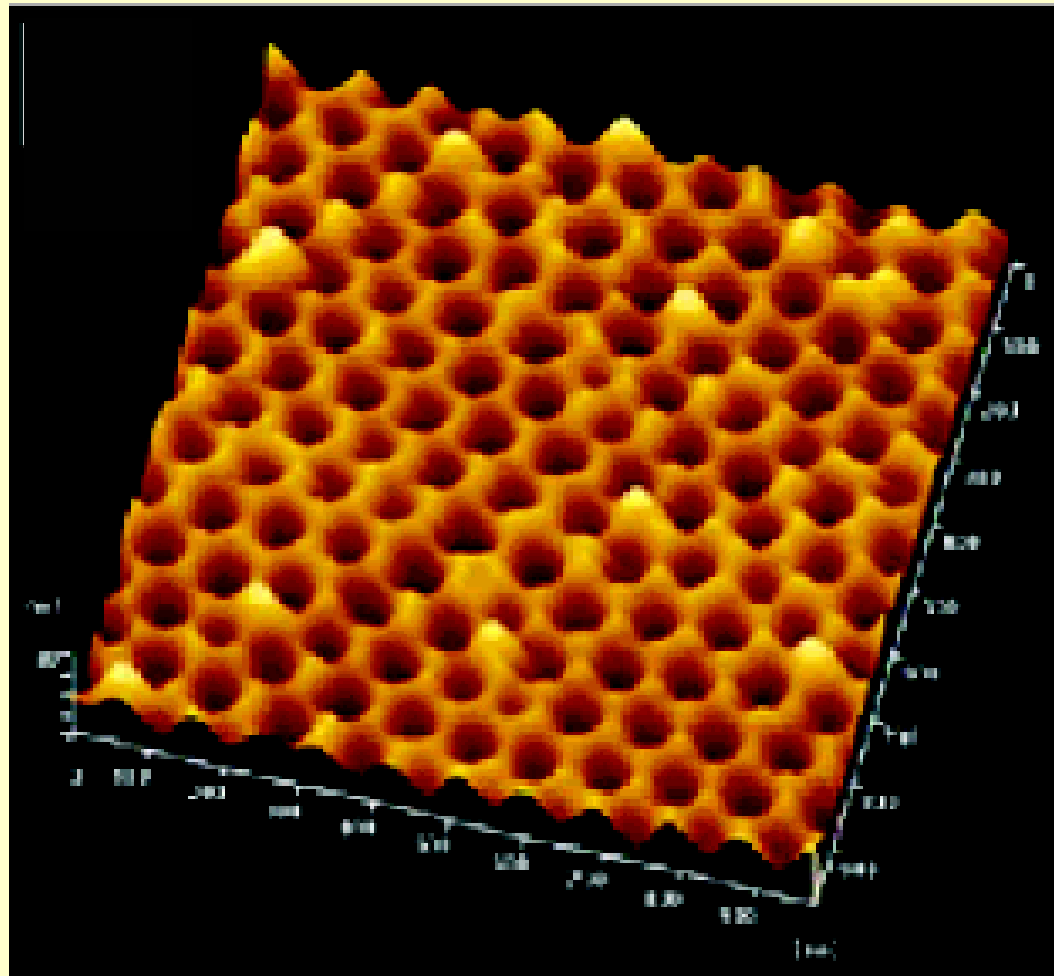
SYNTHESIS OF THIN FILMS

☛ **THERMAL OXIDATION**

Oxides, metal exposed to a glow discharge

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

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

Nitrides, exceptionally hard, high temperature protective coating

$Ti + NH_3 \rightarrow TiN$

$Al + NH_3 \rightarrow AlN$
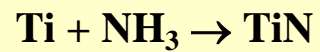
SYNTHESIS OF THIN FILMS

☛ **CHEMICAL VAPOR DEPOSITION**

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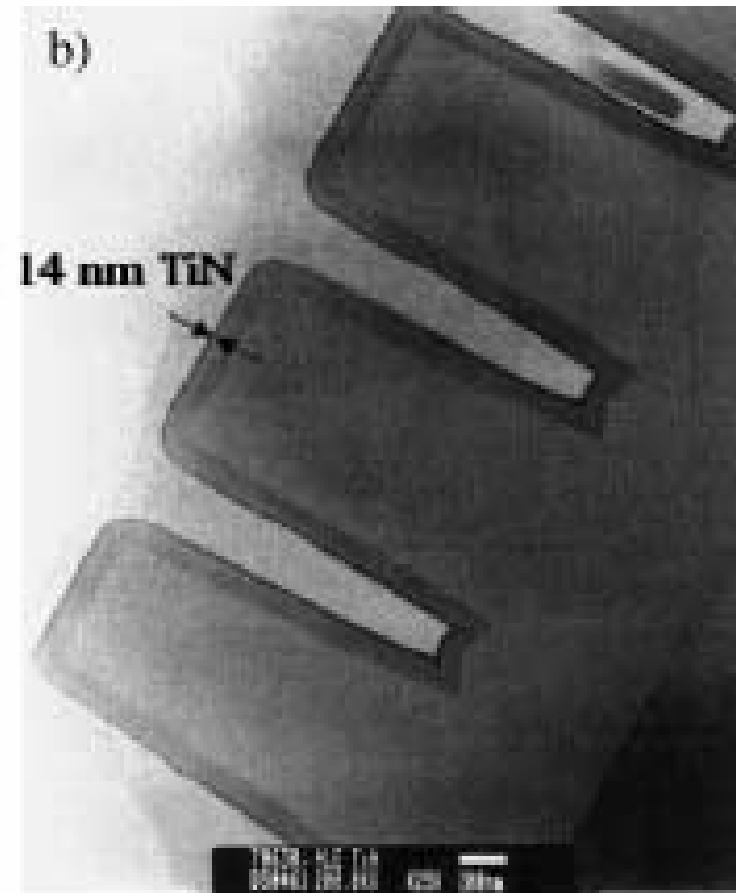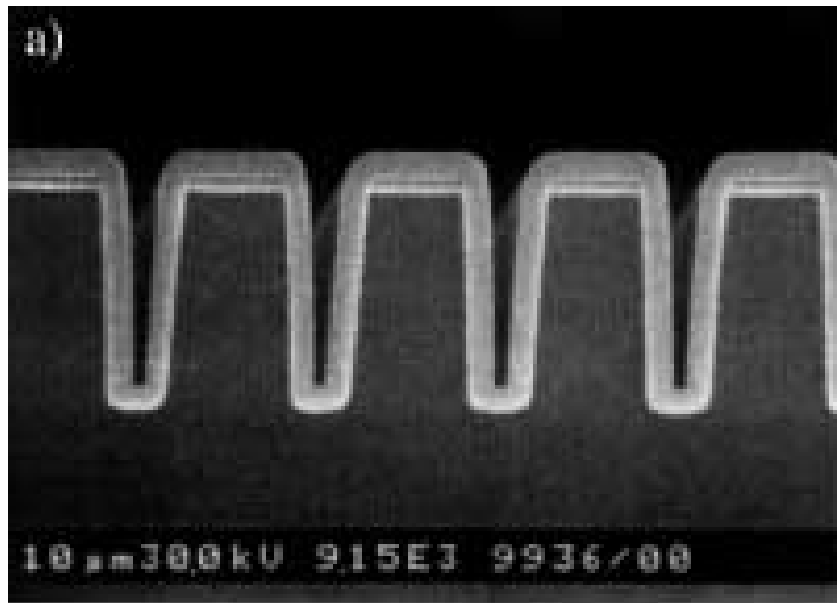**Epitaxial films, correct matching to substrate lattice**

EXAMPLES OF CVD

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

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**

a)

10 µm 30.0 kV 9.15E3 9936/00

b)

14 nm TiN

SYNTHESIS OF THIN FILMS

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

Me_3Ga (laser photolysis, heating) $\rightarrow$ Ga

$Me_3Ga + AsH_3 + H_2 \rightarrow GaAs + CH_4$

Si (laser evaporation, supersonic jet) Si_n^+ (size selected cluster deposition) $\rightarrow$ 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

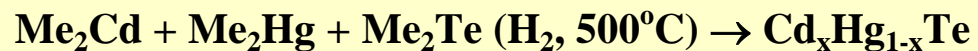**MOCVD PRECURSORS, SINGLE SOURCE MATERIALS**

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

Specially designed MOCVD reactors
Controlled flow of precursors to single crystal heated substrate
Most reactions occur in range 400-1300°C
Complications of diffusion at interfaces, disruption of atomically flat
epitaxial surfaces/interfaces occurs during deposition
Photolytic processes (photoepitaxy) help to bring the deposition
temperatures to more reasonable temperatures

REQUIREMENTS OF MOCVD PRECURSORS

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

HOMO : HETERO rates ~ 1 : 1000

SYNTHESIS OF THIN FILMS

Heterogeneous reaction on substrate
Greater than on other hot surfaces in reactor
Not on supports, vessel etc
Ready chemisorption of precursor on substrate
Detailed surface and gas phase studies of structure of adsorbed species, reactive intermediates, kineticss, vital for quantifying film nucleation and growth processes
Electronic and optical films synthesized in this way
Semiconductors, metals, silicides, nitrides, oxides, mixed oxides (e.g., high T_c superconductors)

CRITICAL PARAMETERS IN MATERIALS PREPARATION
FOR SYNTHESIS OF THIN FILMS

Composition control
Variety of materials to be deposited
Good film uniformity over large areas to be covered, > 100 cm^2
Precise reproducibility
Growth rate, thickness control, 2-2000 nm layer thickness
Precise control of film thickness = accurate control of deposition,
film growth rate
Crystal quality, epitaxy
High degree of film perfection
Defects degrade device performance
Purity of precursors: usually less than 10^{-9} impurity levels
Stringent demands on starting material purity
Challenge for chemistry, purifying and analyzing at the ppb level
Demands exceptionally clean growth system otherwise defeats the
object of controlled doping of films for device applications
Interface widths
Abrupt changes of composition and dopant concentration required,
quantum confined structures
30-40 sequential layers often needed
Alternating composition and graded composition films
0.5-50 nm thickness required with atomic level precision
All of the above has been more-or-less perfected in the electronics
and optics industries

Thin Films

SYNTHESIS OF THIN FILMS

TECHNIQUES USED TO GROW SEMICONDUCTOR FILMS AND MULTILAYERED FILMS

MOCVD

Liquid phase epitaxy

Chemical vapor transport

Molecular beam epitaxy

Laser ablation

PHYSICAL METHODS FOR PREPARING THIN FILMS

✿ **CATHODE SPUTTERING**
Bell jar equipment
10^{-1} **to** 10^{-2} **torr of Ar, Kr, Xe**
Glow discharge created
Positively charged rare gas ions
Accelerated in a high voltage 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**
Heating e-beam, resistive, laser
Gaseous material deposited on substrate
Thin films nucleate and grow
Containers must be chemically inert:
W, Ta, Nb, Pt, BN, Al_2O_3, ZrO_2, Graphite
Substrates include insulators, metals, glass, alkali halides, silicon
Sources include metals, alloys, semiconductors, insulators, inorganic salts

SYNTHESIS OF THIN FILMS

☛ **MOLECULAR BEAM EPITAXY**

Million dollar thin film machine, ideal for preparing high quality artificial semiconductor quantum superlattices, ferroelectrics, superconductors

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

High energy electron diffraction for surface structure analysis

Mass spectrometer for control and detection of vapor species

e-gun for heating the substrate

SYNTHESIS OF THIN FILMS
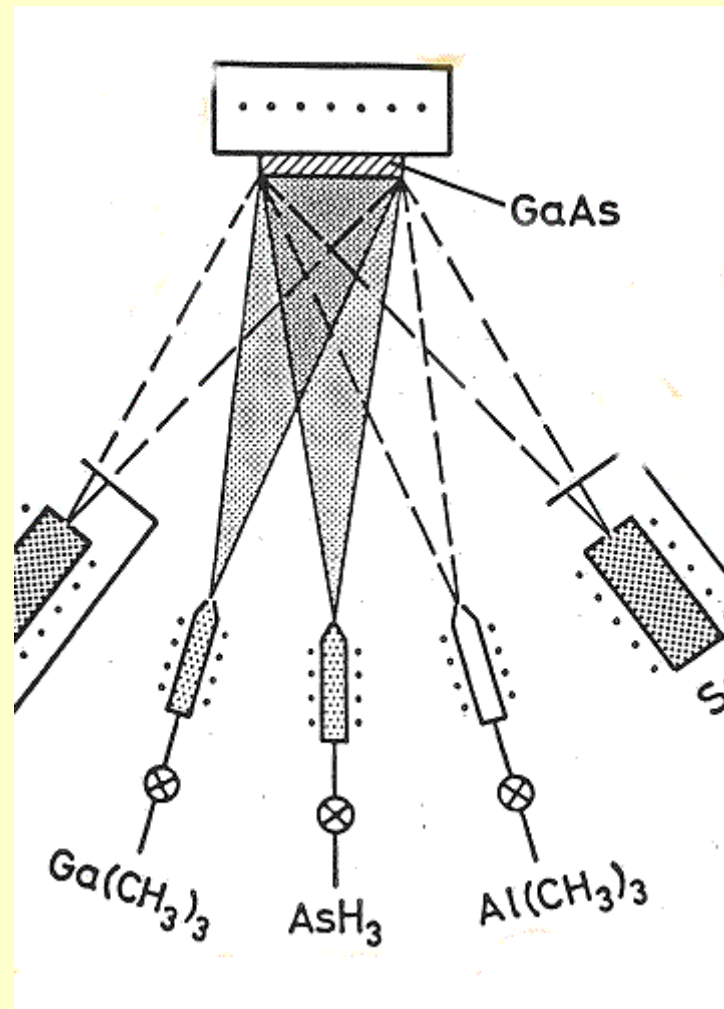
SYNTHESIS OF THIN FILMS

☛ **PHOTOEPITAXY**

Making atomically perfect thin films under milder and more controlled conditions, Mullin and Tunnicliffe 1984

$$Et_2Te + Hg \text{ (pool)} + H_2 \text{ (h}\nu\text{ , 200 }^oC) \rightarrow HgTe + 2C_2H_6$$
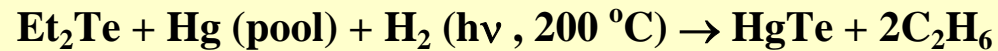
MOCVD preparation requires 500 ^oC using $Me_2Te + Me_2Hg$

Advantages of photoepitaxy

Lower temperature operation
Multilayer formation
Less damage of layers
Lower interlayer diffusion
Easy to fabricate abrupt boundaries
Less defects, strain, irregularities at interfaces

CdTe can be deposited onto GaAs at 200-250 ^oC even with a 14% lattice mismatch
GaAs is susceptible to damage under MOCVD conditions 650-750 ^oC

EXTENSIONS OF PHOTOLYTIC METHODS - LASER WRITING AND LASER ETCHING

☞ **Laser writing:**

Substrate GaAs

Me_3Al or Me_2Zn adsorbed layer or gas phase

Focussed UV laser on film

Photodissociation of organometallic precursor:

$$Me_3Al \rightarrow Al + C_2H_6$$
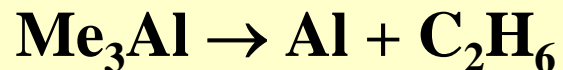
Creates sub-micron lines of Al or Zn

SYNTHESIS OF THIN FILMS

☛**Laser photoetching:**
GaAs substrate
Gaseous or adsorbed layer of CH_3Br
Focussed UV laser
Creates reactive Br atoms

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

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

$GaAs...Br_n(ad) \rightarrow GaBr_n(g) + AsBr_n(g)$
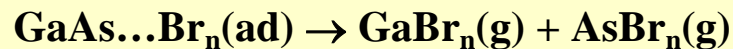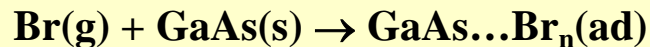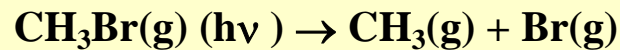
Adsorbed reactive surface Br atoms erode surface regions irradiated with laser
Vaporization of volatile gallium and arsenic bromides from surface creates sub-micron etched line

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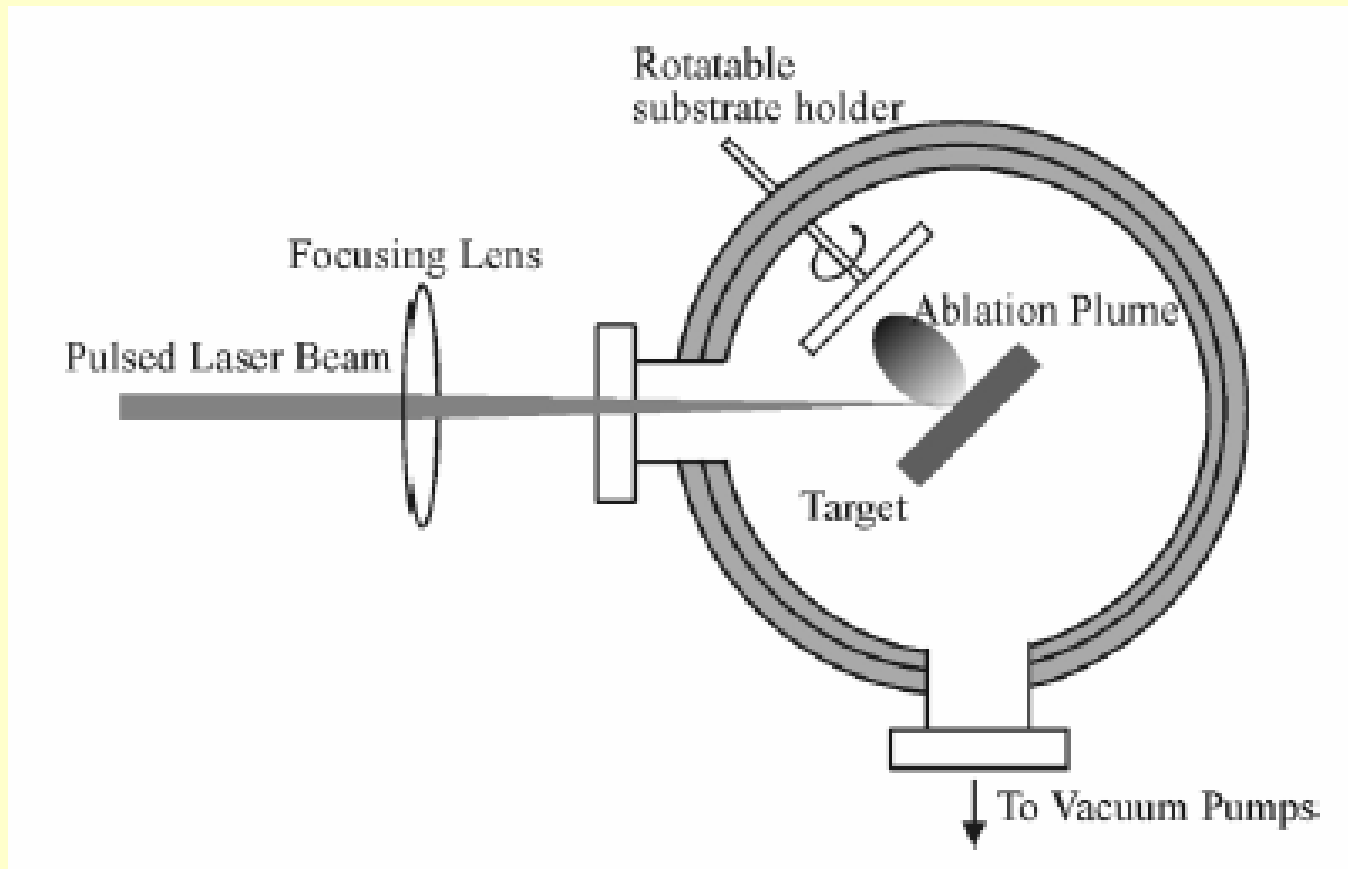
Pulsed Laser Ablation
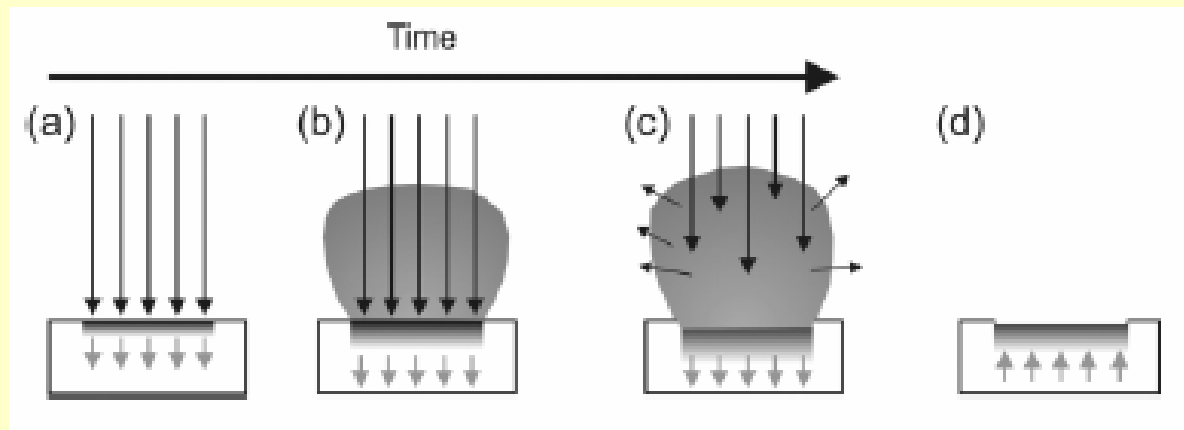
(a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid–liquid interface)

(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.

Porous Si
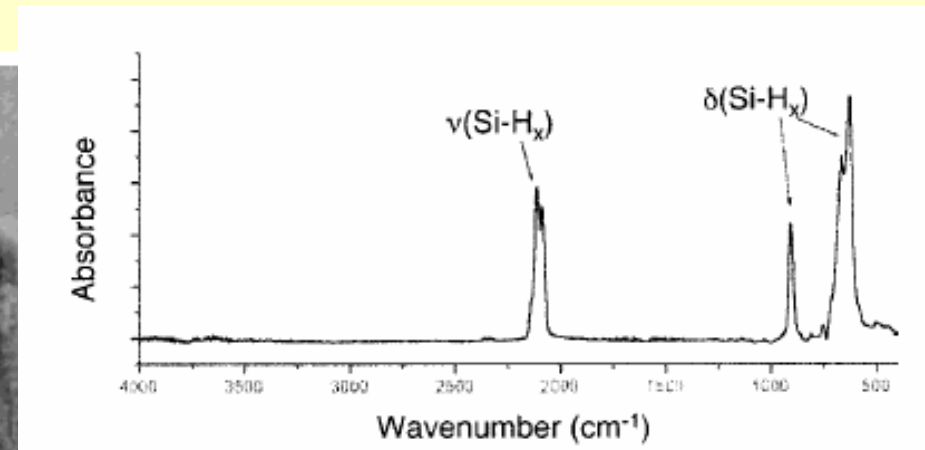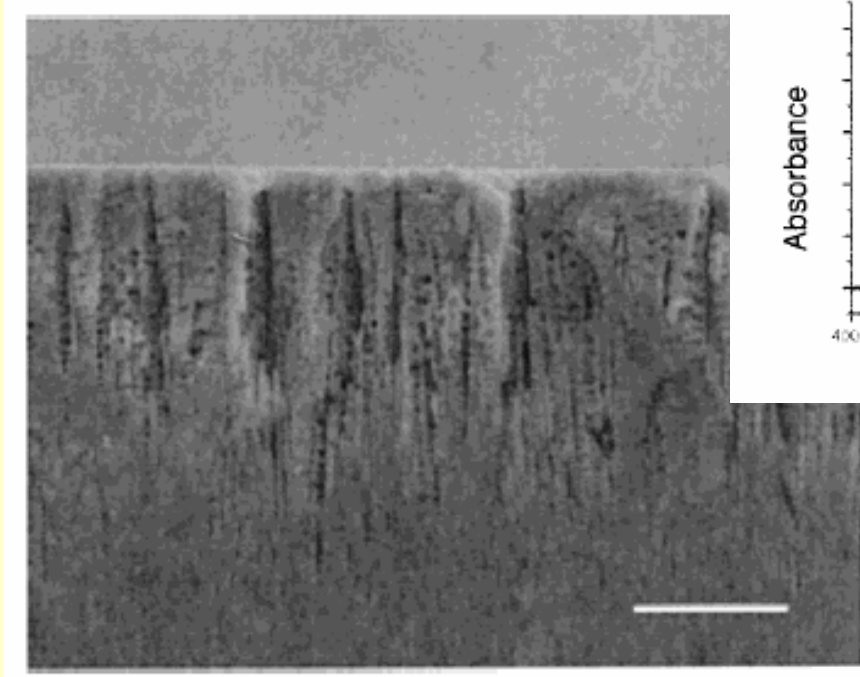
SEM of a porous silicon, the pores extending from the surface of the Si(100) wafer down into the bulk, etched from n-type Si(100) (P-doped, 0.75-0.95 ø,cm) at 77.2 mA cm^{-2} for 1 min with a 1:1 solution of 49% HF(aq)/ EtOH. Scale bar is 10 μm.
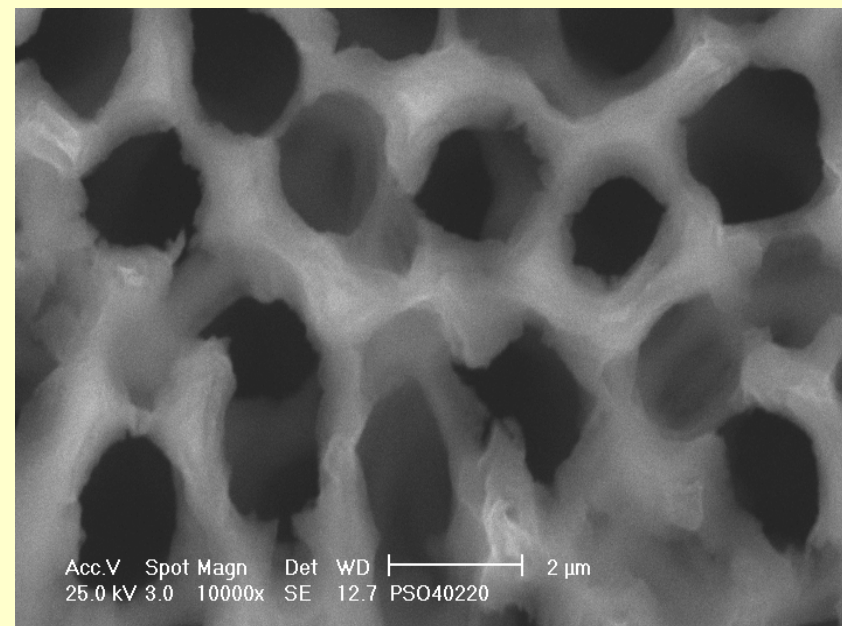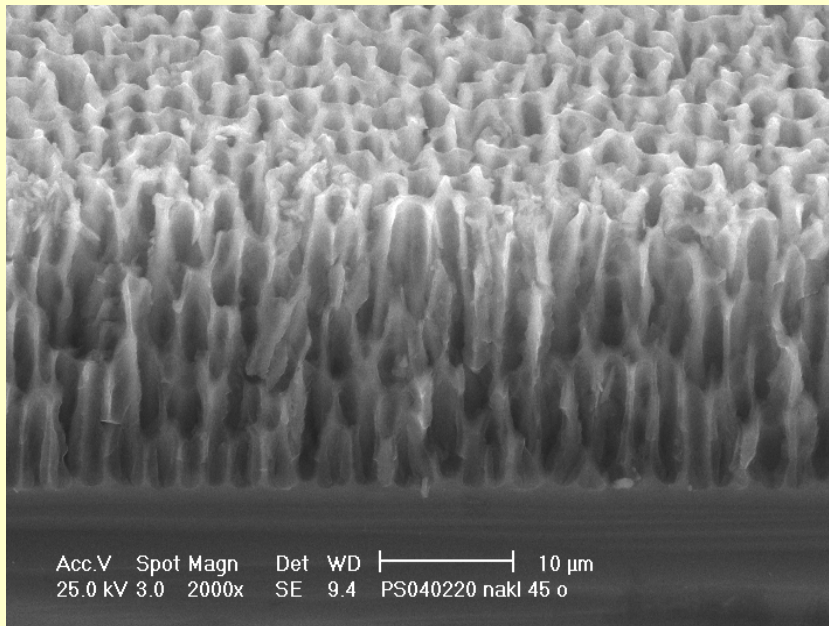
Porous Si

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

Chemistry on Si Surface

native oxide capped Si(100) → 1-2% HF (aq) → dihydride terminated flat Si(100)

native oxide capped Si(111) → 40% NH₄F (aq) → monohydride terminated flat Si (111)

native oxide capped Si(100) → HF (aq) electrochemical, chemical or photochemical etch → Si-Hₓ terminated porous silicon
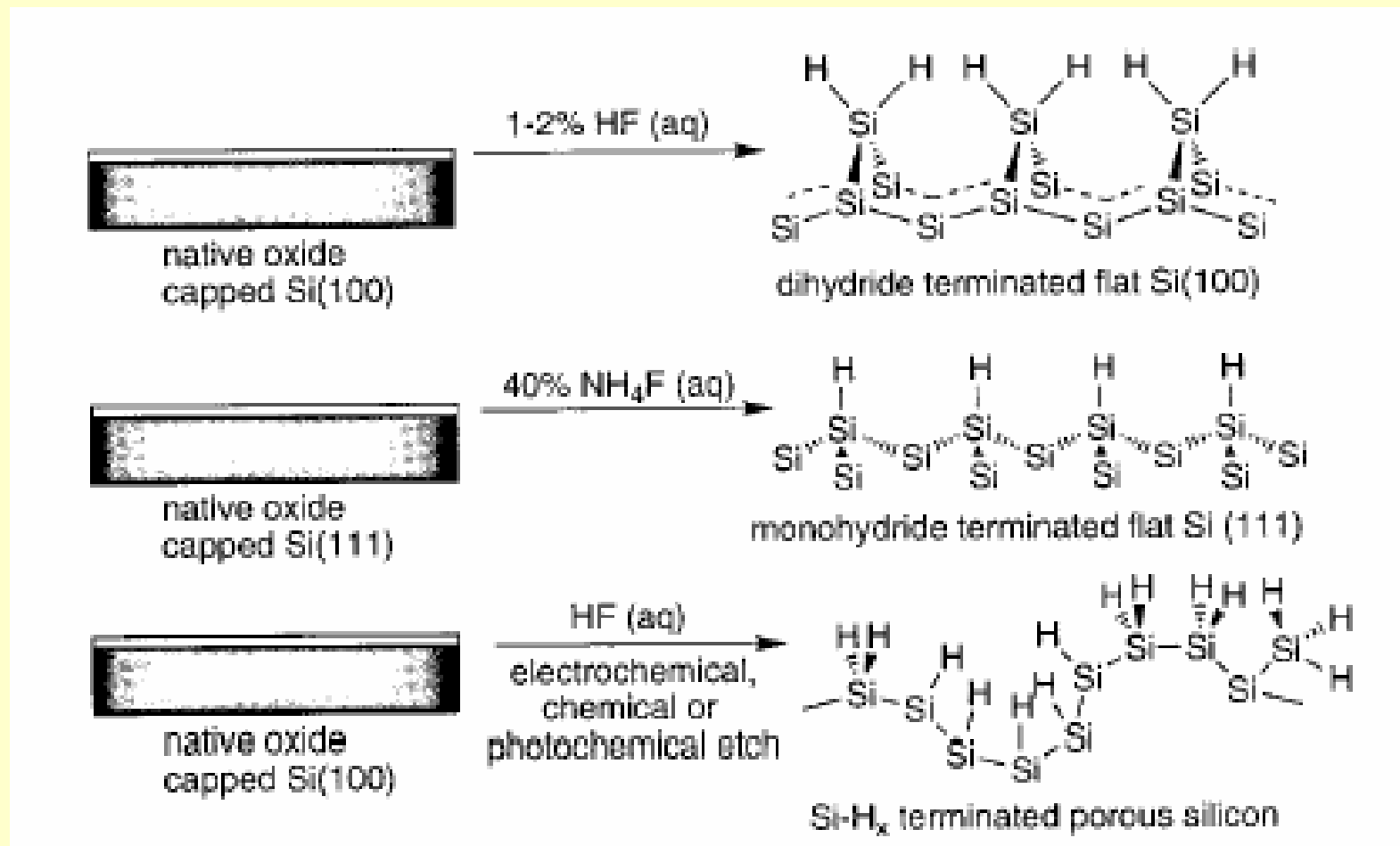
Porous Si

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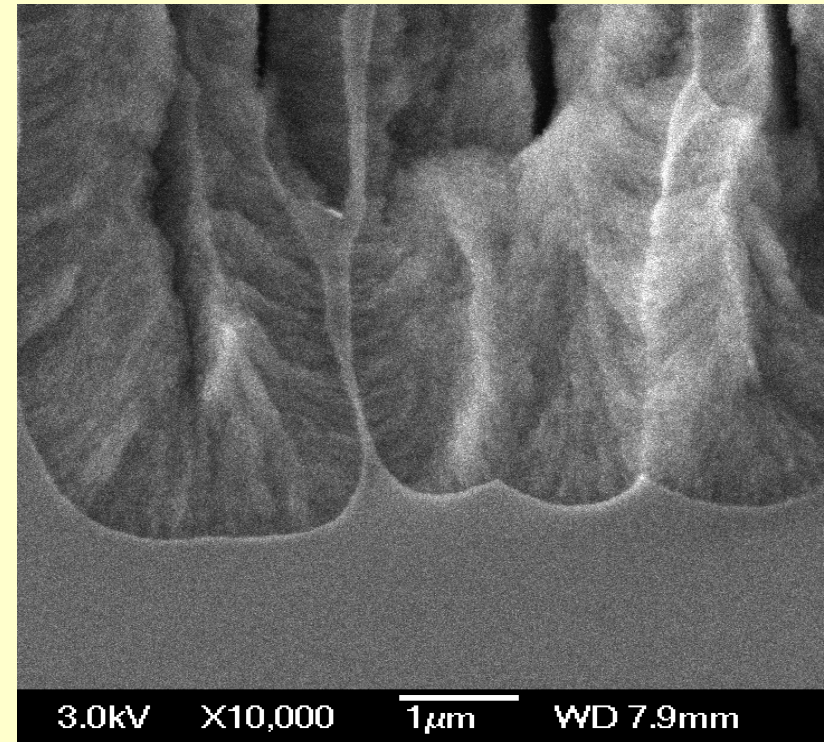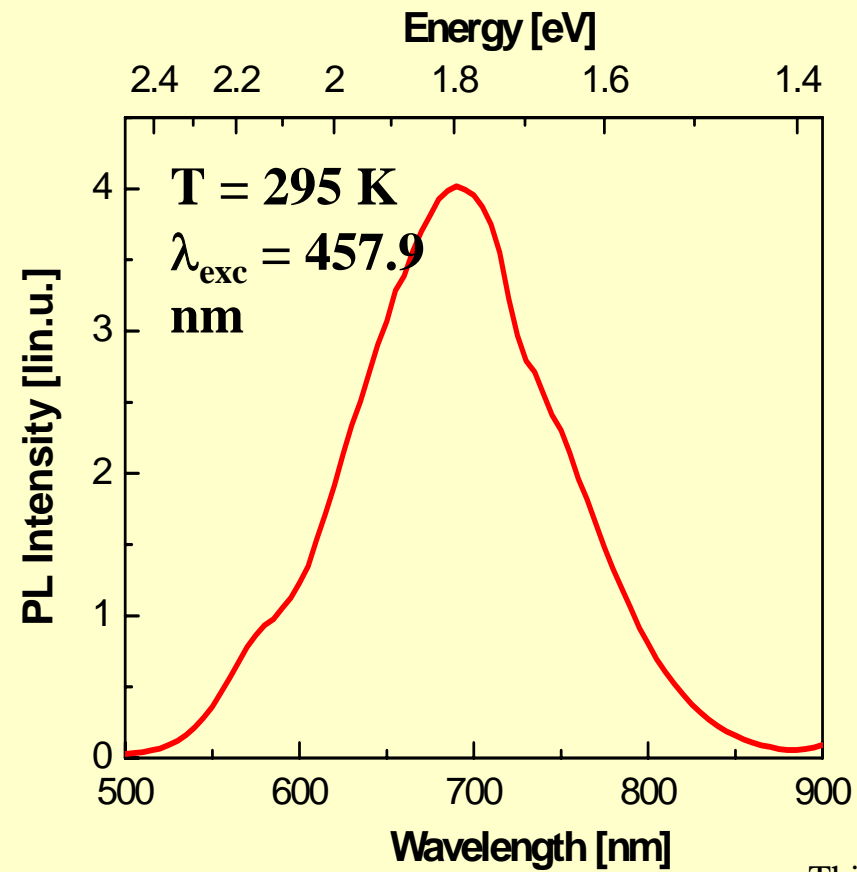
Table 1. Typical Bond Energies for Various Groups Related to Group(IV) Elements (kJ mol^{-1})

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)							

Chemistry on Si Surface

Hydrosilylation

a) $[RC(O)O]_2 \longrightarrow 2\,RC(O)\cdot \longrightarrow R\cdot + CO_2$
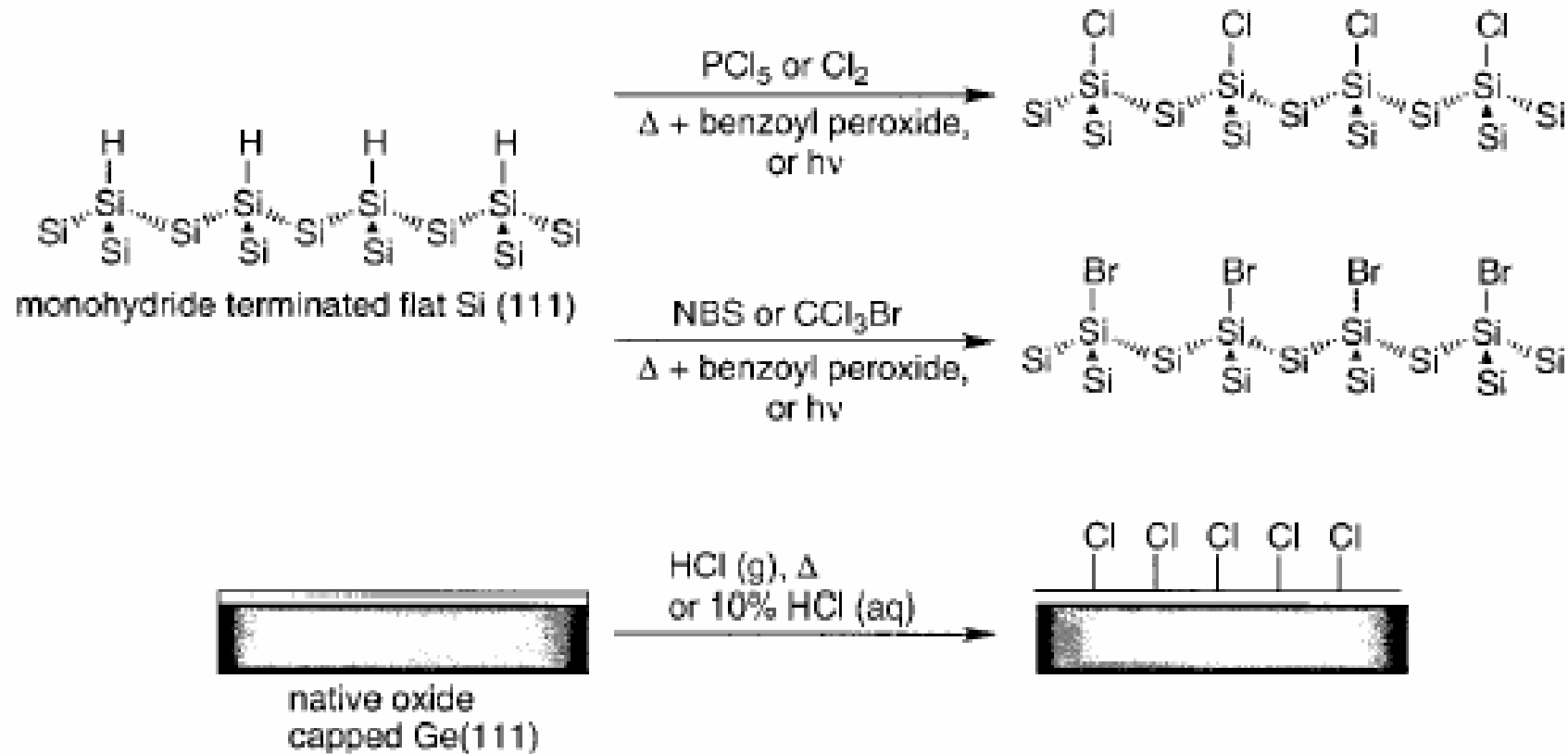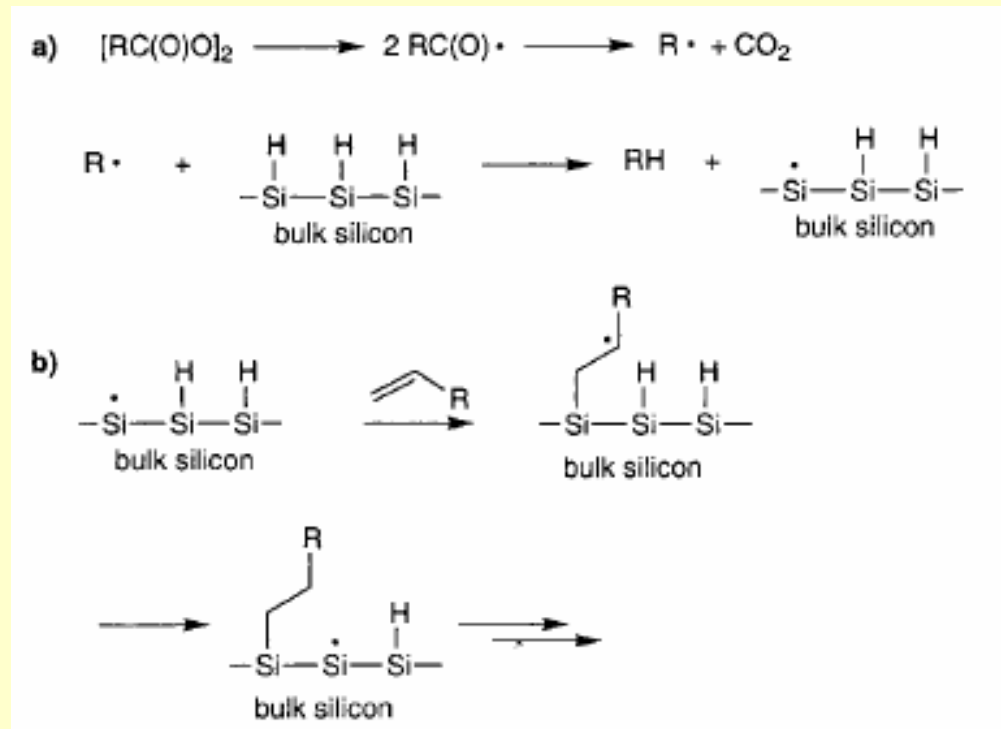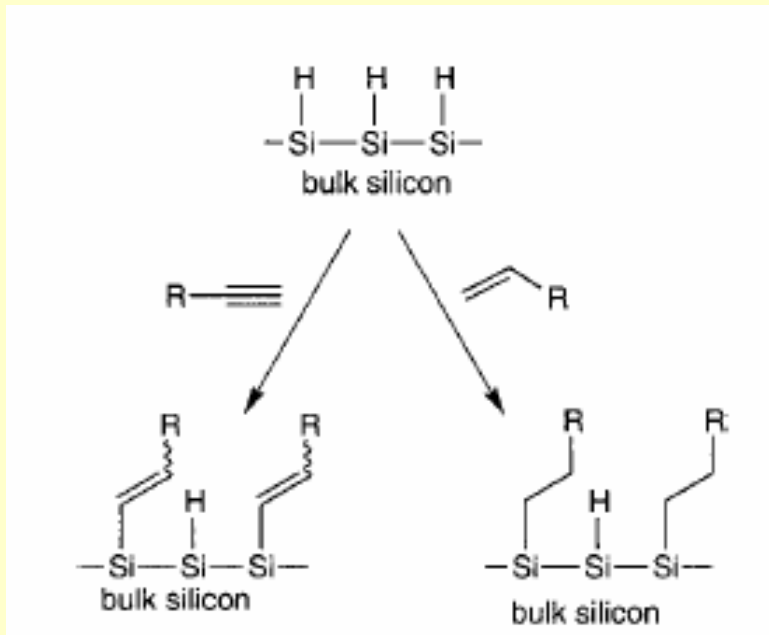
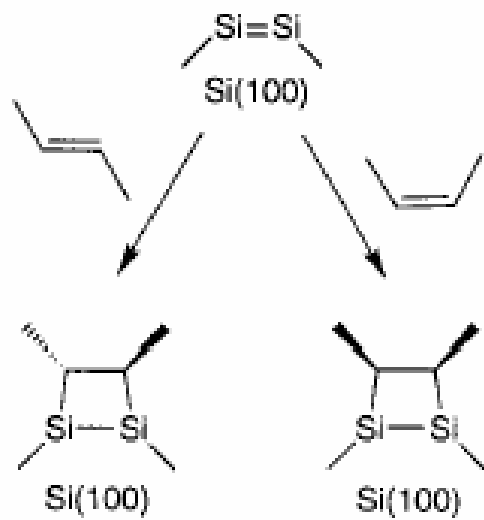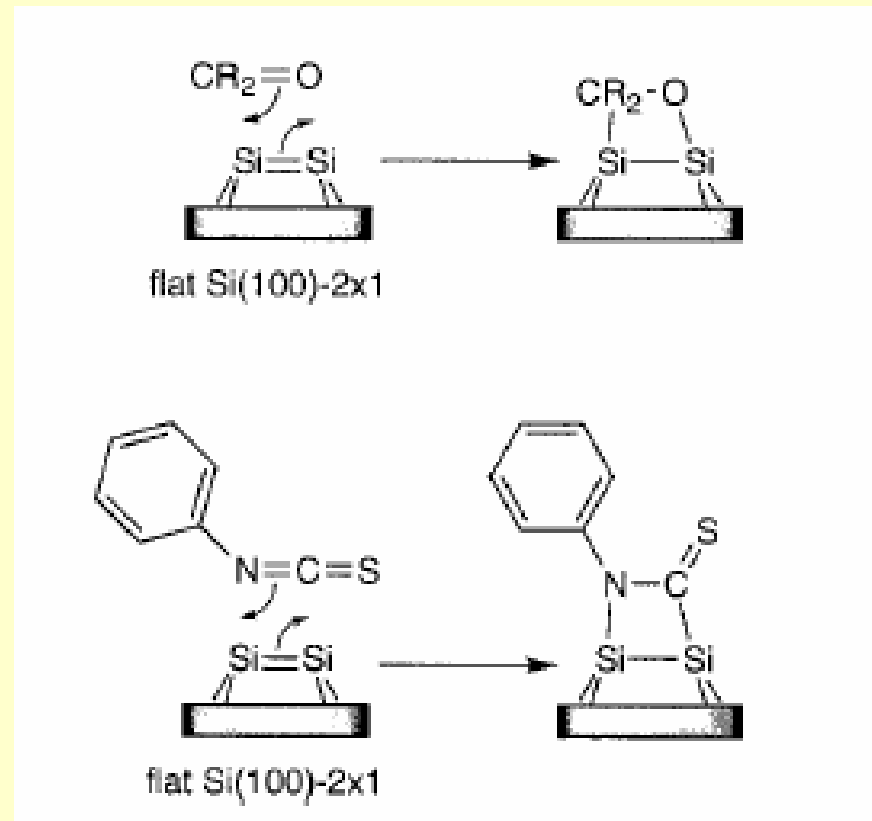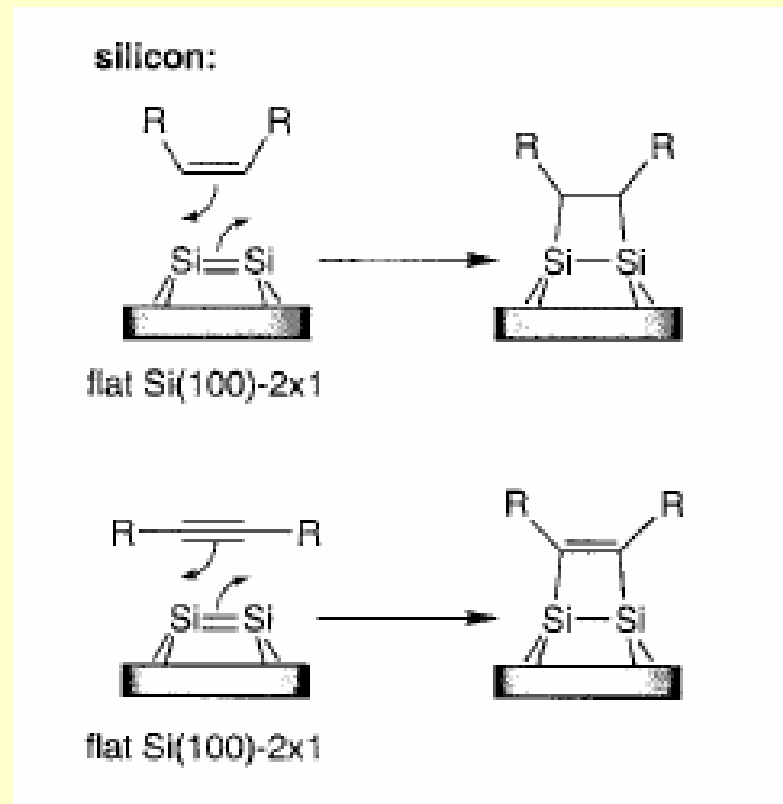# Chemistry on Si Surface
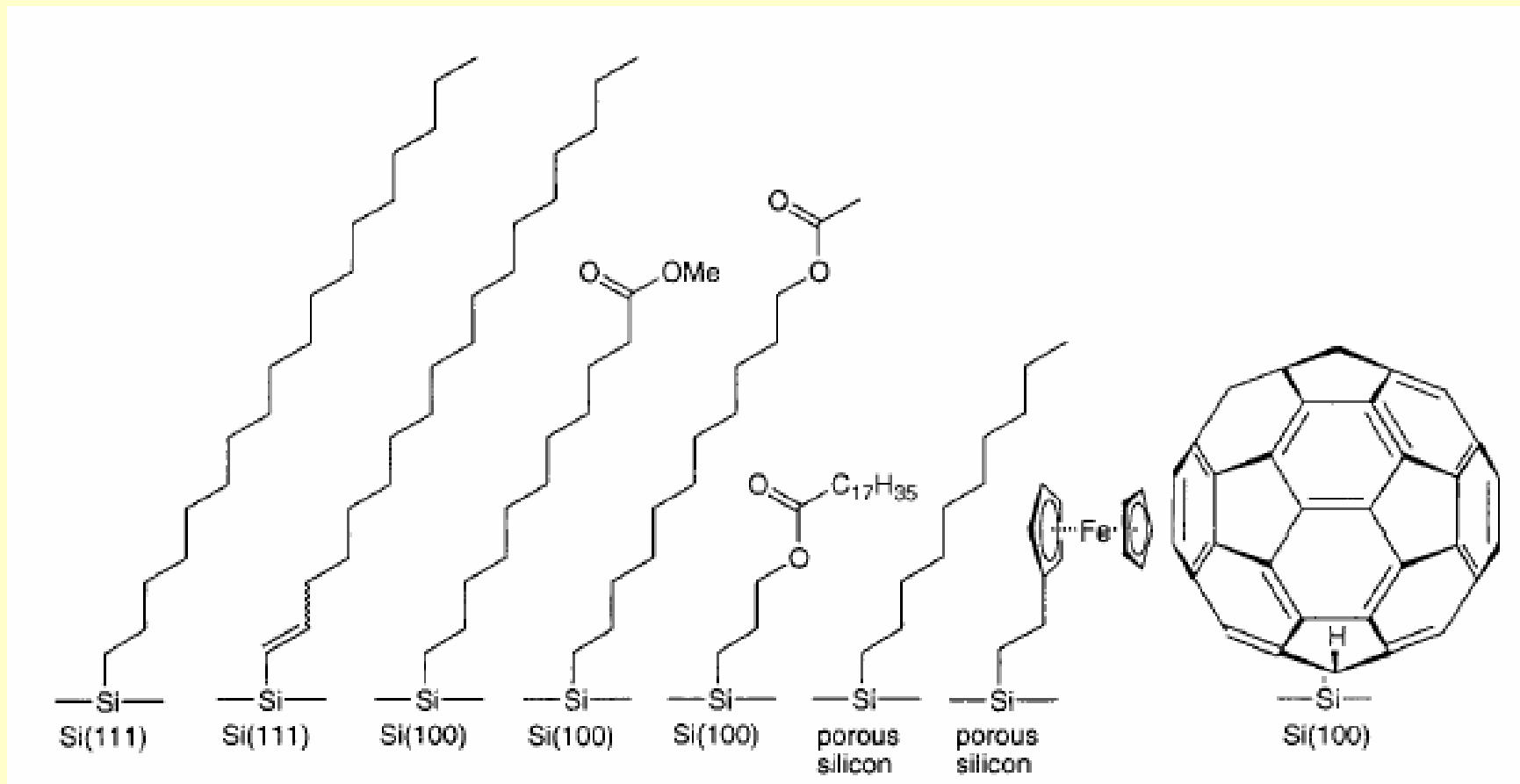
Carbaanion LiR, RMgX
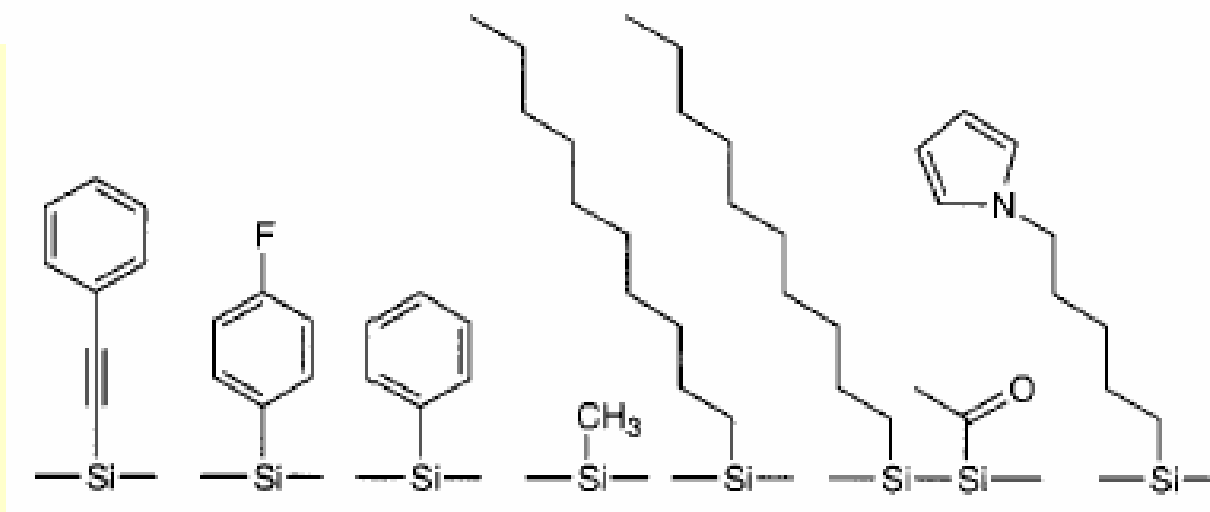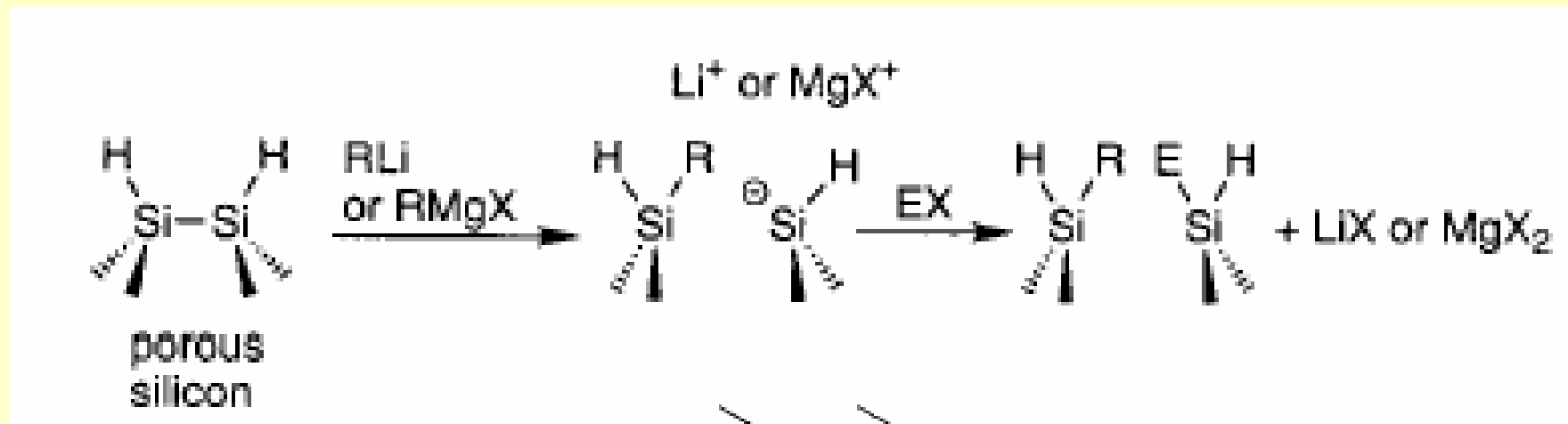
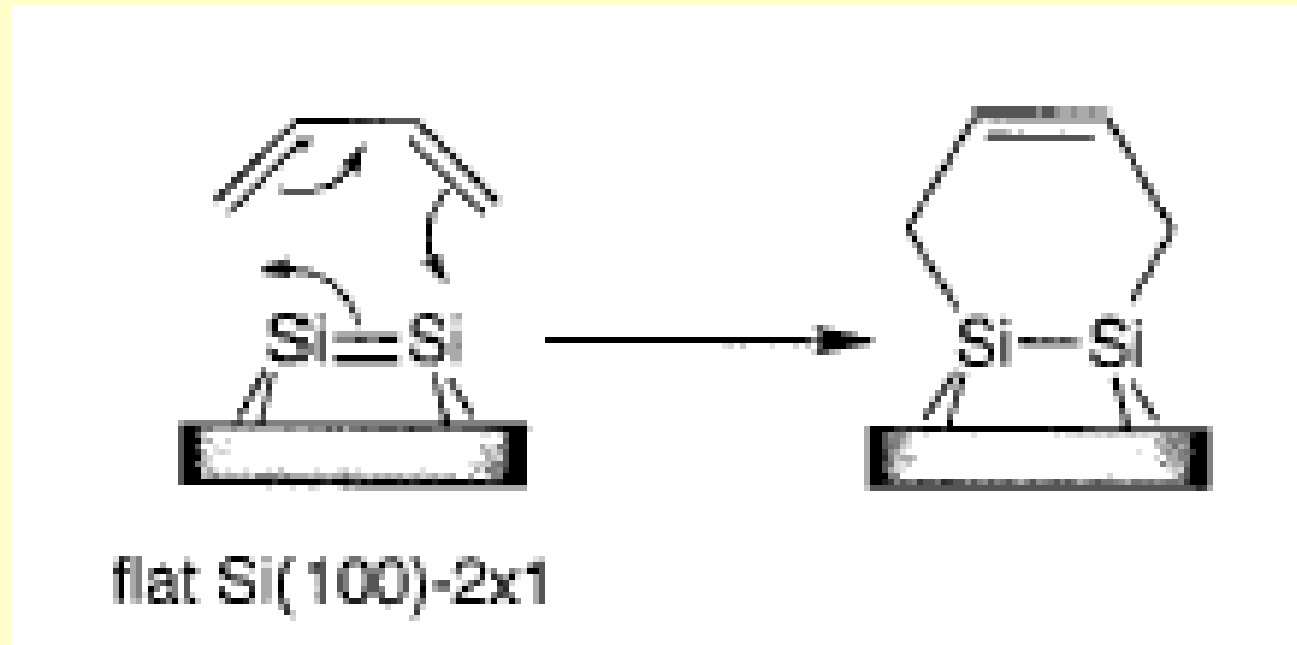a) Cathodic Electrografting (CEG)
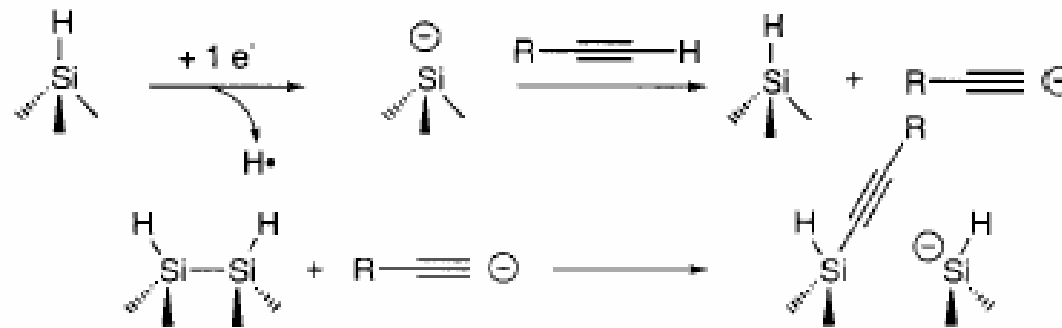
b) Anodic Electrografting (AEG)

Thin Films

2+2 Cycloaddition

Si=Si
Si(100)

Si—Si
Si(100)

Si=Si
Si(100)

A)   B)   C)

2+2 Cycloaddition

silicon:

flat Si(100)-2x1

flat Si(100)-2x1

$CR_2{=}O$

flat Si(100)-2x1

$N{=}C{=}S$

flat Si(100)-2x1

DA 4+2

flat Si(100)-2x1
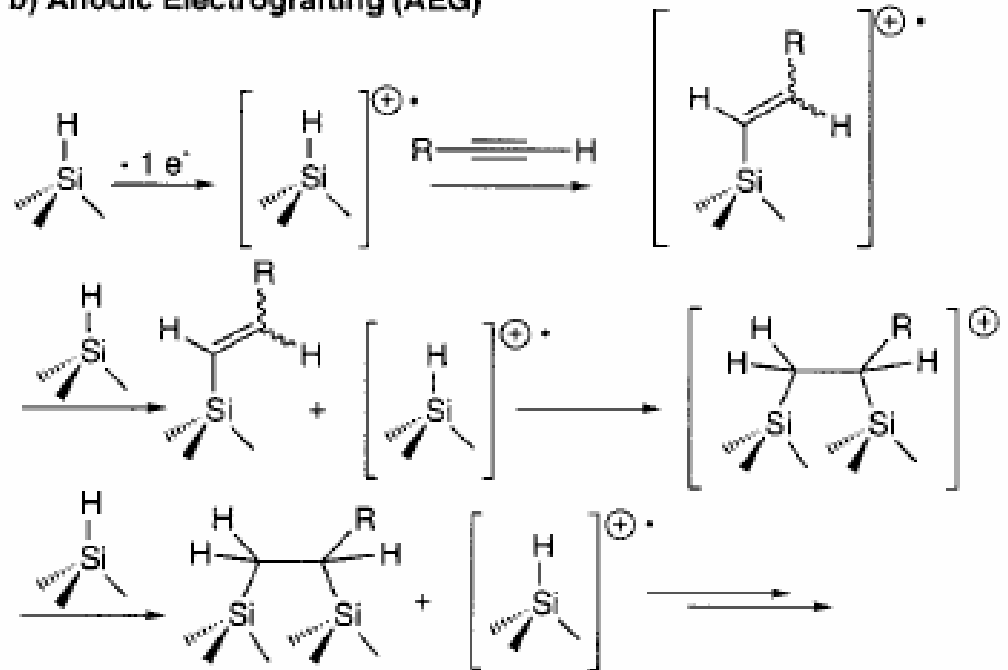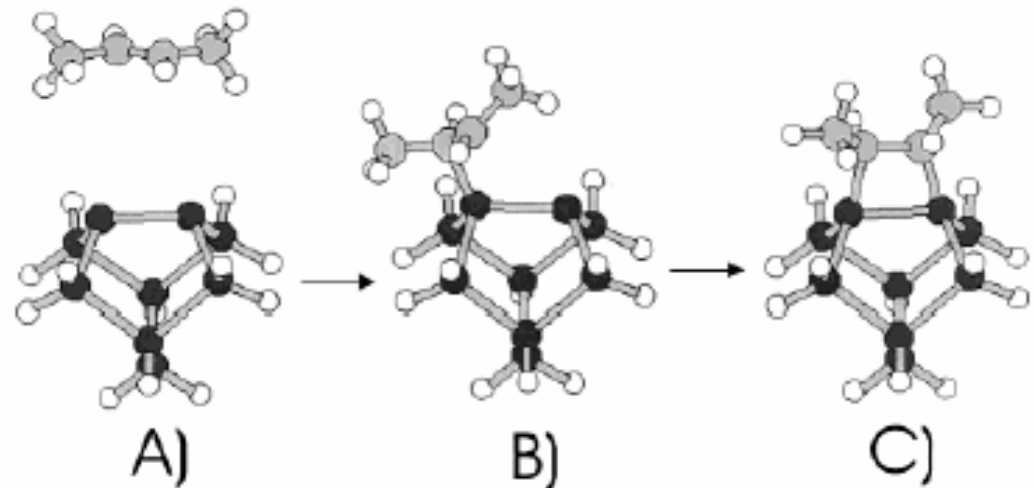
Secondary Chemistry

A+B. C-H bond activation, followed by amide and sulfonamide formation

H$_2$NR, where R = DNA, dendrimer, aliphatic groups
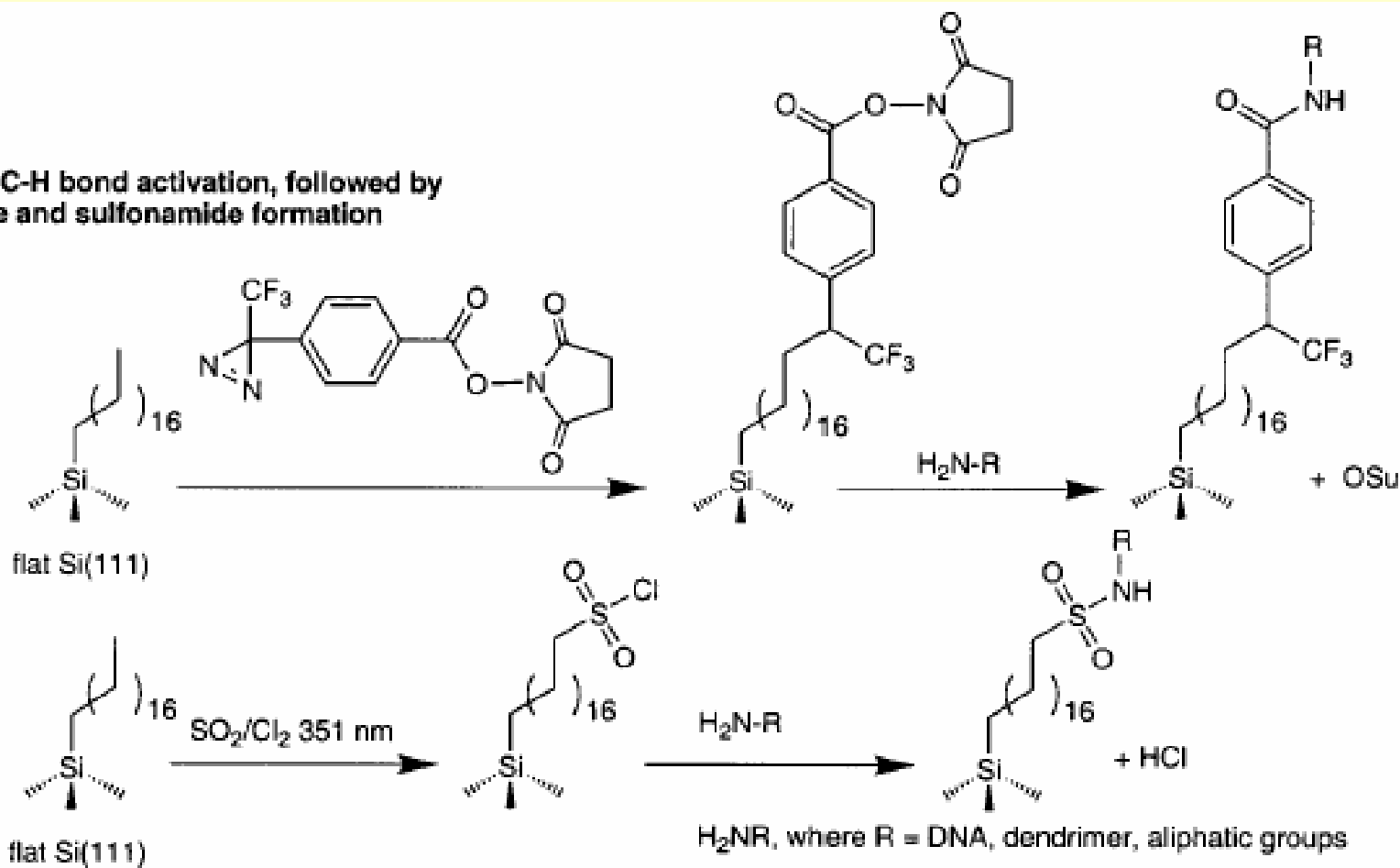
Secondary Chemistry

C. Ester hydrolysis

flat Si(100)

boiling, acidic H$_2$O

+ MeOH
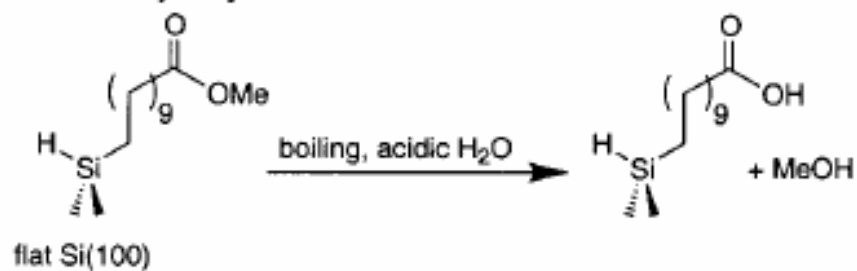
D. Ester reduction and cleavage

flat Si(100)

hydride source
(LiAlH$_4$ or NaBH$_4$)

flat Si(111)

2 CH$_3$(CH$_2$)$_9$MgX

+ 2 MgX(OEt)

porous silicon

TFA
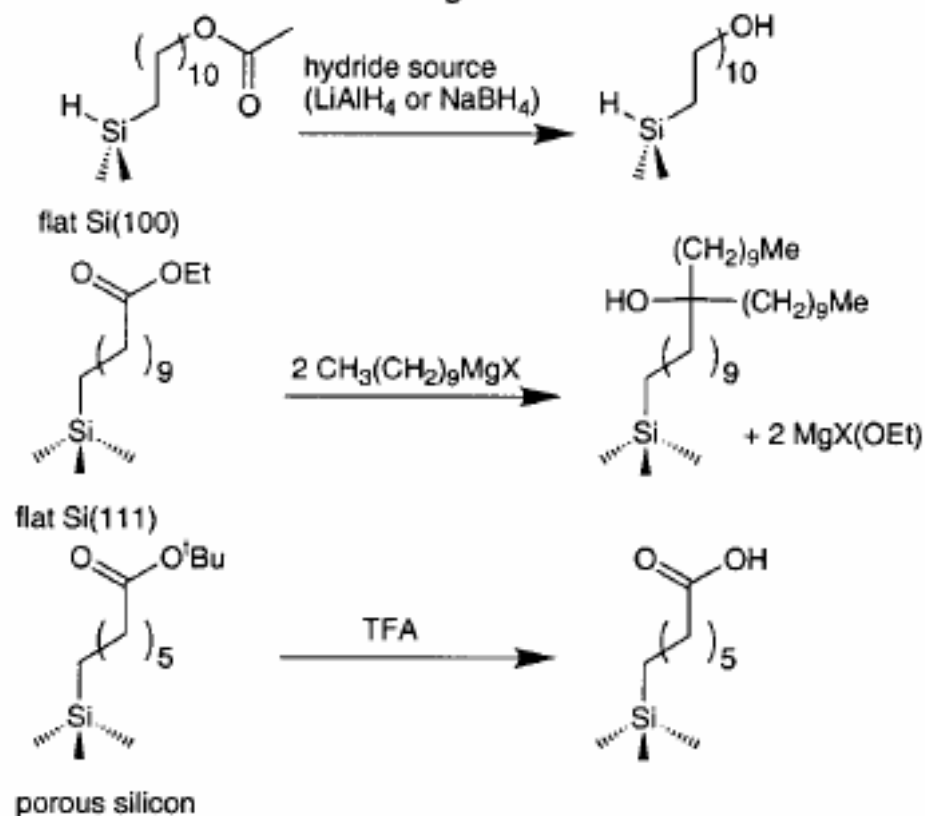
Secondary Chemistry

E. Ester Formation

flat Si(100)

flat Si(111)
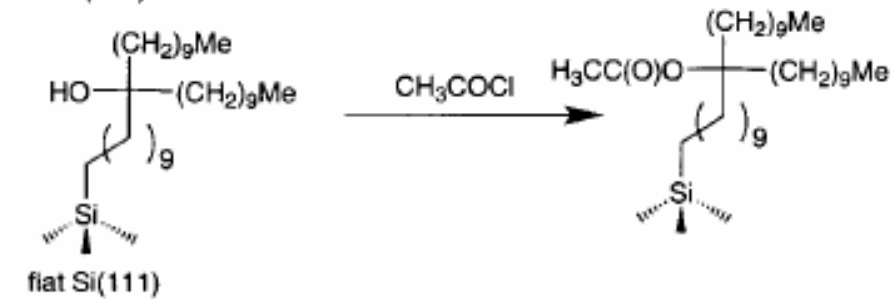
F. Hydroboration of olefins

porous silicon

porous silicon
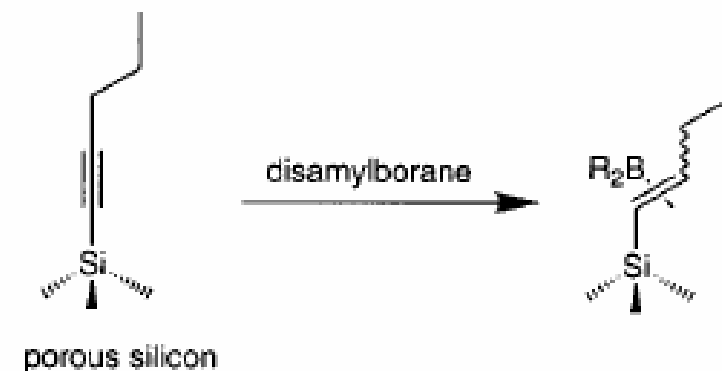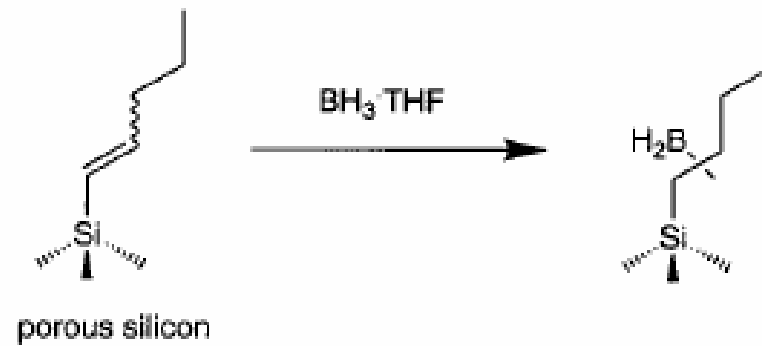
Secondary Chemistry

G. Polymerization

flat Si(111)

porous silicon

applied potential

P = polypyrrole

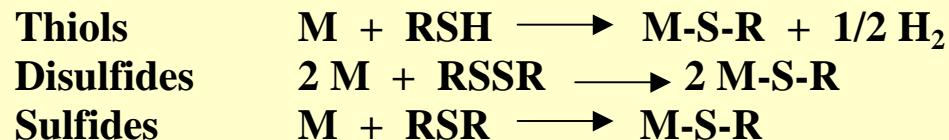57
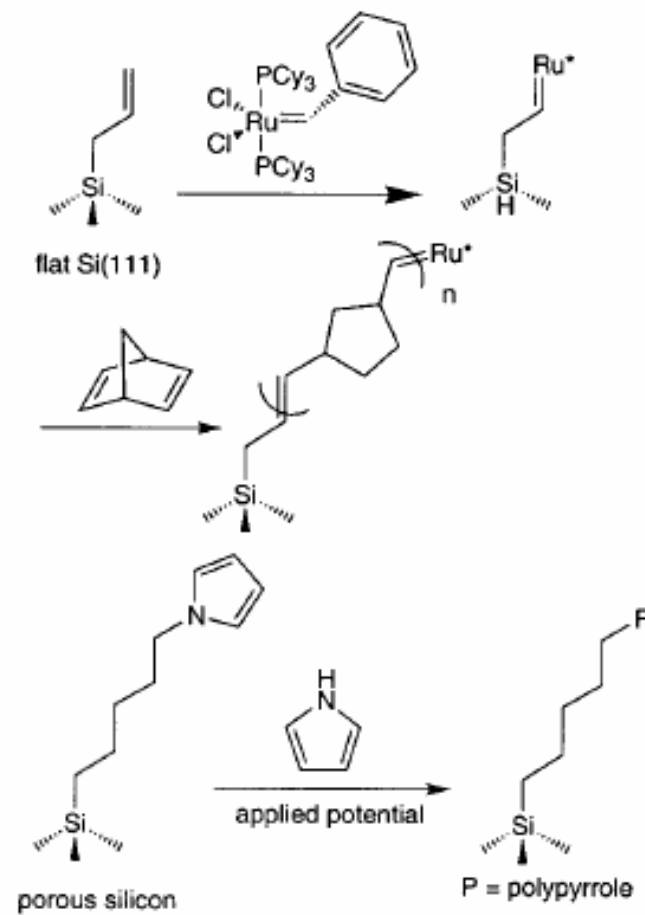
SELF-ASSEMBLED MONOLAYERS

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**

Thiols	$M + RSH \longrightarrow M\text{-}S\text{-}R + 1/2\ H_2$
Disulfides	$2\ M + RSSR \longrightarrow 2\ M\text{-}S\text{-}R$
Sulfides	$M + RSR \longrightarrow M\text{-}S\text{-}R$

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
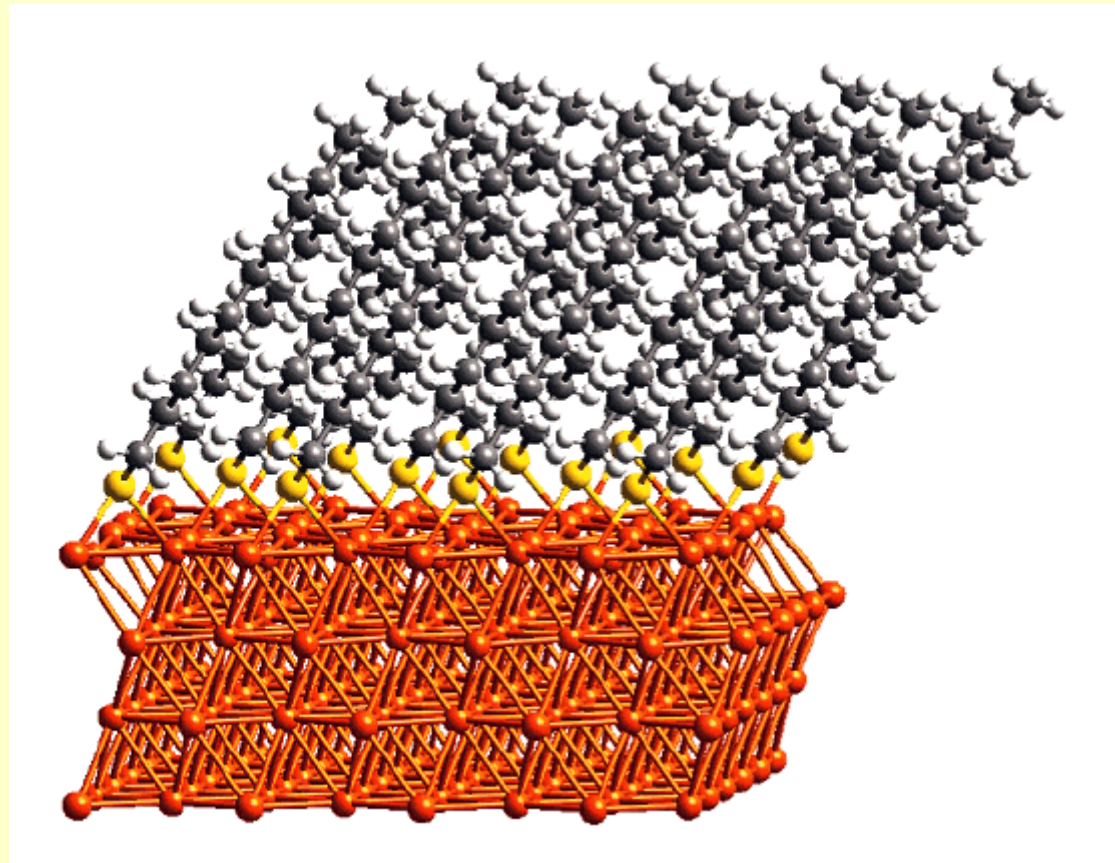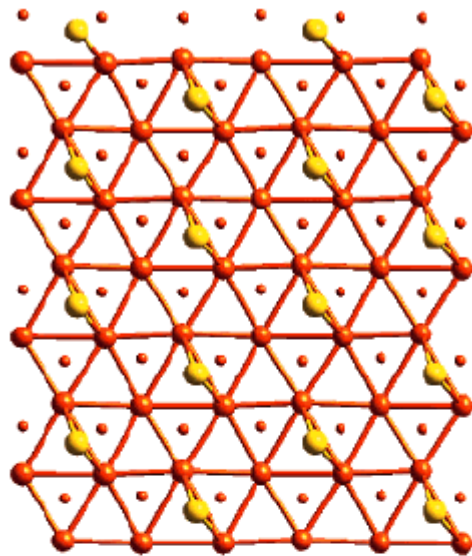**on Si(SiO$_2$), glass, mica.**

Thickness 5-300 nm, sputtering, evaporation

Atomically flat

R R R R R R R R R R R R R

S S S S S S S S S S S S

Metal Surface

Tilt

Twist

Precession
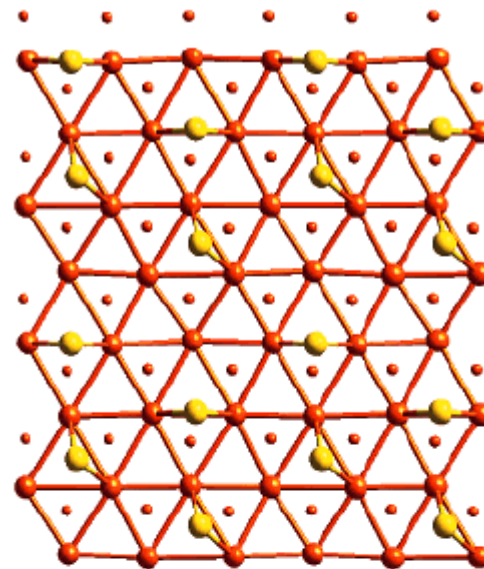
A   **A^{I}**
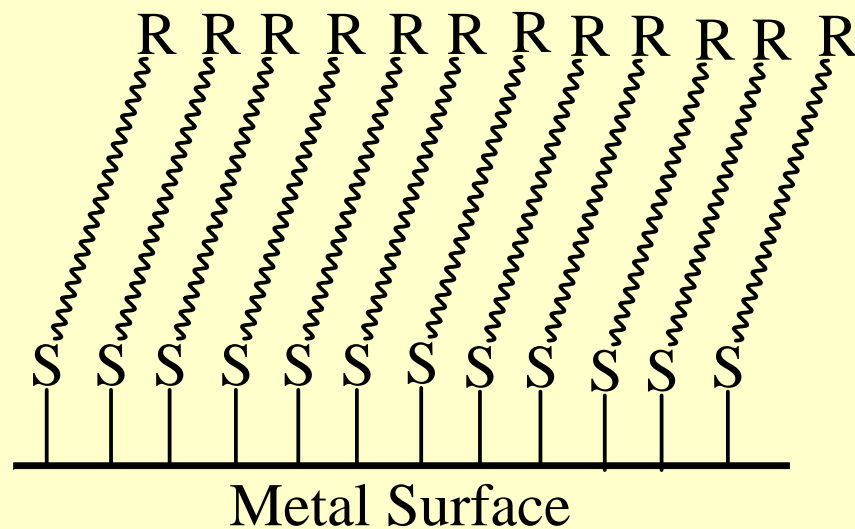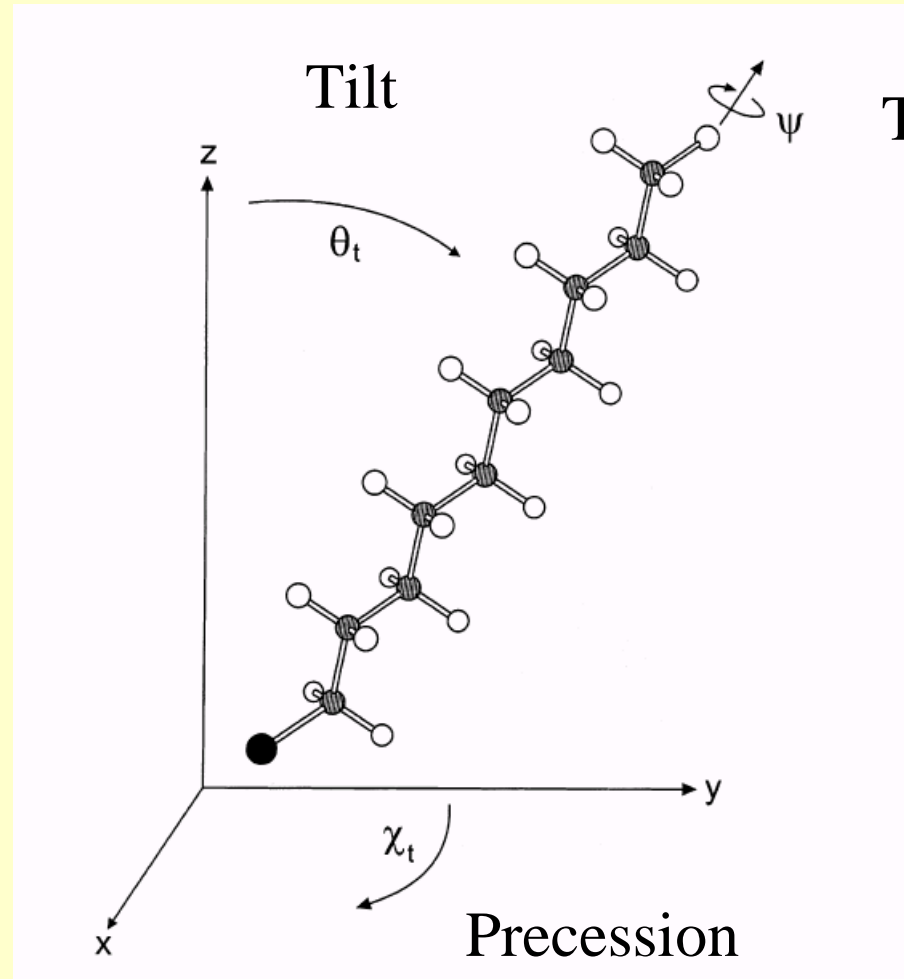
SELF-ASSEMBLED MONOLAYERS

�֎ **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-C$_{18}$SH competition reaction, the linear alkyl thiol binds 300 – 700 times better.

Surface coverage 10^{14} molecules per cm^2
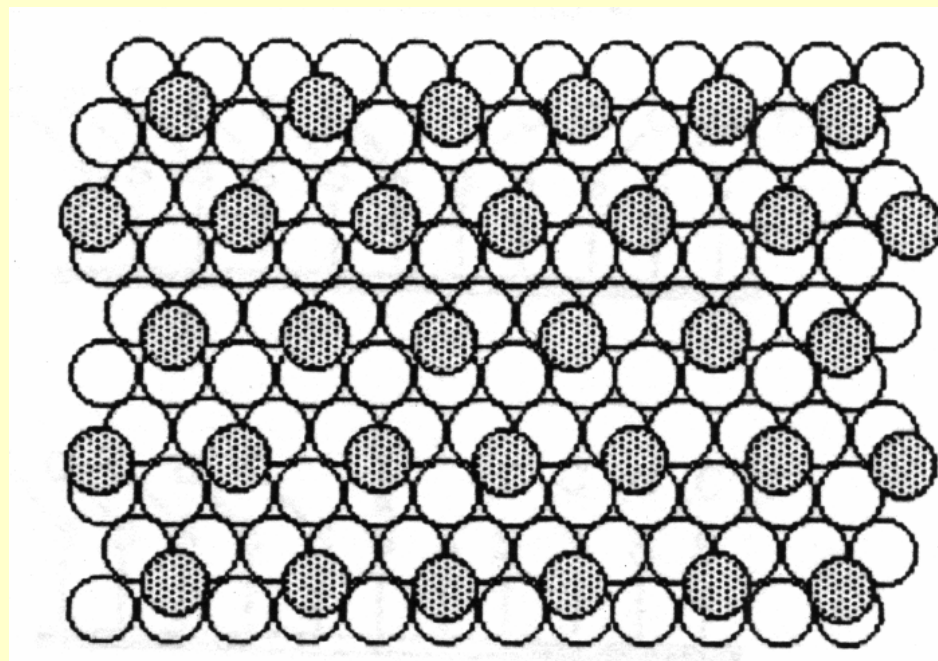**C$_{16}$ chain length ~2.2 nm, 32-40° tilted, all-trans**

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}

SELF-ASSEMBLED MONOLAYERS

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

SiO$_2$ Surfaces

> **native oxide on Si**
> **silicagel**

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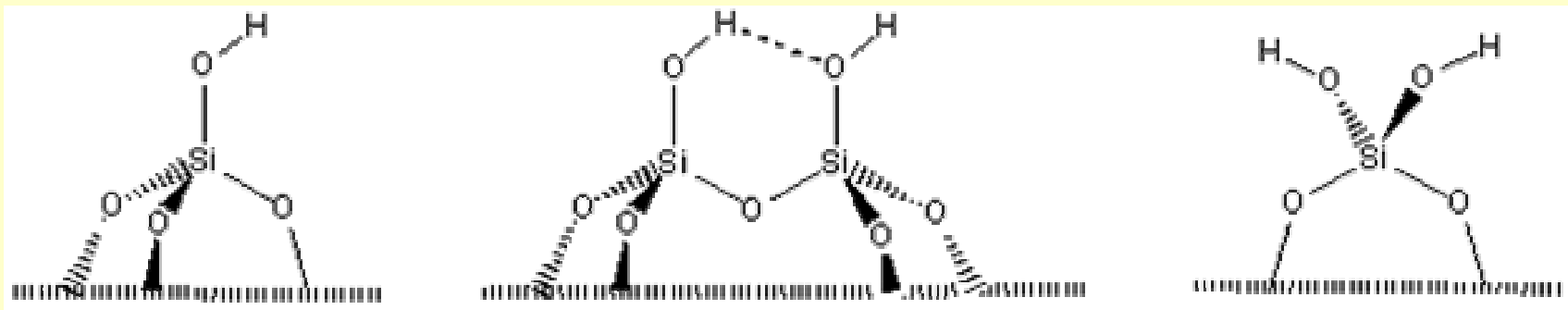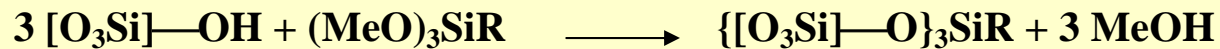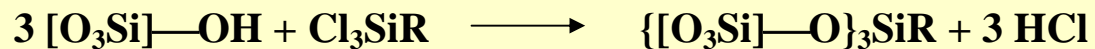

isolated   vicinal   geminal

SiO$_2$ Surfaces

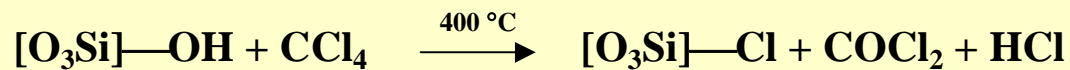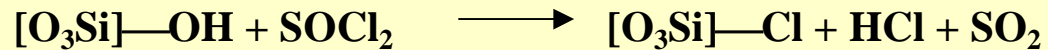[O$_3$Si]—OH stands for the siliceous surface

1. Grafting
Reactions with trifunctional reagents, such as alkyltrichlorosilanes and trialkoxyalkylsilanes, lead to the three-fold attachment of the SiR groups.
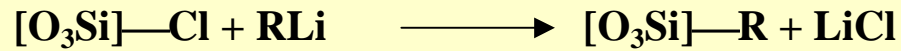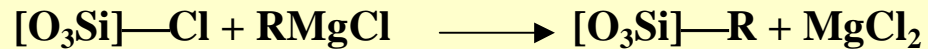
3 [O$_3$Si]—OH + Cl$_3$SiR $\longrightarrow$ {[O$_3$Si]—O}$_3$SiR + 3 HCl

3 [O$_3$Si]—OH + (MeO)$_3$SiR $\longrightarrow$ {[O$_3$Si]—O}$_3$SiR + 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.

$$[O_3Si]\!\!-\!\!OH + SOCl_2 \longrightarrow [O_3Si]\!\!-\!\!Cl + HCl + SO_2$$

$$[O_3Si]\!\!-\!\!OH + CCl_4 \xrightarrow{400\ °C} [O_3Si]\!\!-\!\!Cl + COCl_2 + HCl$$

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

$$[O_3Si]\!\!-\!\!Cl + RMgCl \longrightarrow [O_3Si]\!\!-\!\!R + MgCl_2$$

$$[O_3Si]\!\!-\!\!Cl + RLi \longrightarrow [O_3Si]\!\!-\!\!R + LiCl$$

SiO$_2$ Surfaces

3. Post Modification Method
The organic groups (R) covalently anchored to the siliceous surface by the two previous methods can be subsequently chemically modified. The most extensively developed is chemistry of 3-aminopropyl(trimethoxy)silane. A large number of chemical transformations of the amino moiety to other functional groups are known.
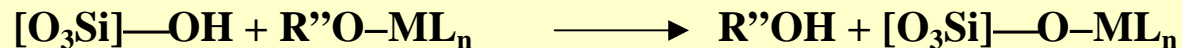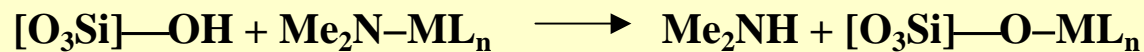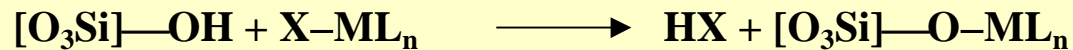
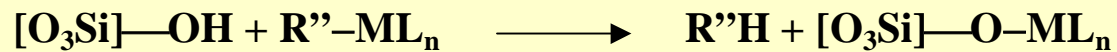**4. Hybrid sol-gel method (co-condensation)**
A thin layer of a hybrid (organically modified) silica gel can be deposited on the silica surface from a solution of TEOS and (MeO)$_3$SiR by controlled hydrolysis and condensation.

(MeO)$_3$SiR + (MeO)$_4$Si + 7 H$_2$O $\longrightarrow$ [O$_3$Si]—R + 7 MeOH
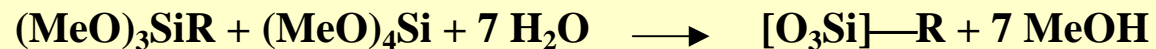
SiO$_2$ Surfaces

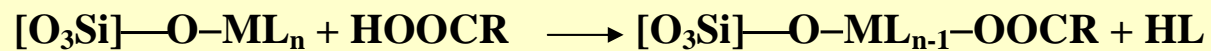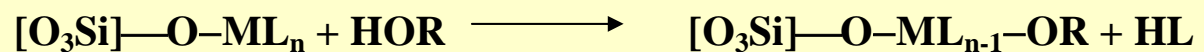**5. Organometallic modification method**
Organometallic reagents, such as metal alkyls, halides, amides, and alkoxides can be used to deposit a monolayer of metal complexes on the surface (ML$_n$ stands for an organometallic group, M for a metal, L for a ligand, R" for a short alkyl chain, X for halogen).

$$[O_3Si]\!-\!OH + R''\!-\!ML_n \longrightarrow R''H + [O_3Si]\!-\!O\!-\!ML_n$$

$$[O_3Si]\!-\!OH + X\!-\!ML_n \longrightarrow HX + [O_3Si]\!-\!O\!-\!ML_n$$

$$[O_3Si]\!-\!OH + Me_2N\!-\!ML_n \longrightarrow Me_2NH + [O_3Si]\!-\!O\!-\!ML_n$$

$$[O_3Si]\!-\!OH + R''O\!-\!ML_n \longrightarrow R''OH + [O_3Si]\!-\!O\!-\!ML_n$$
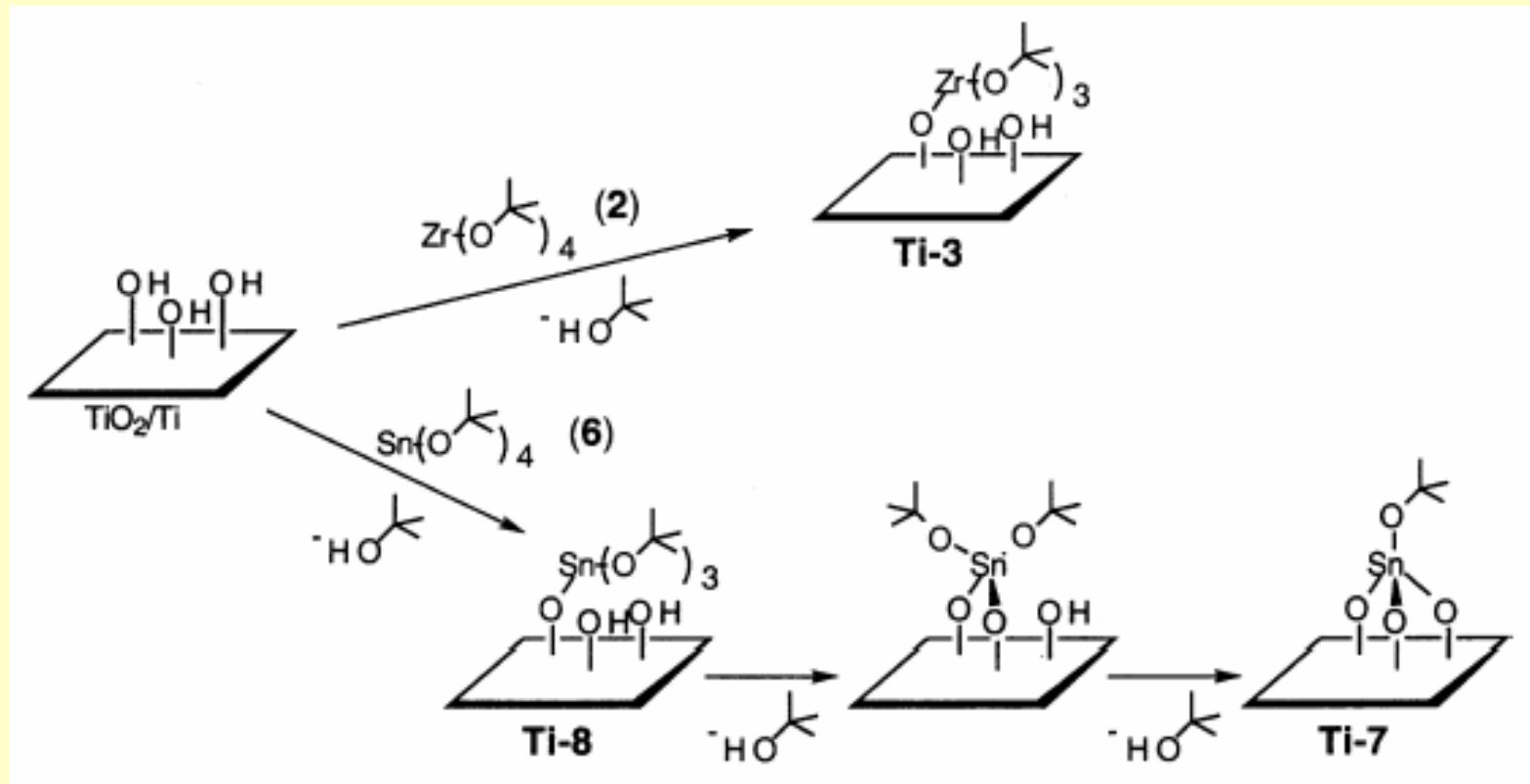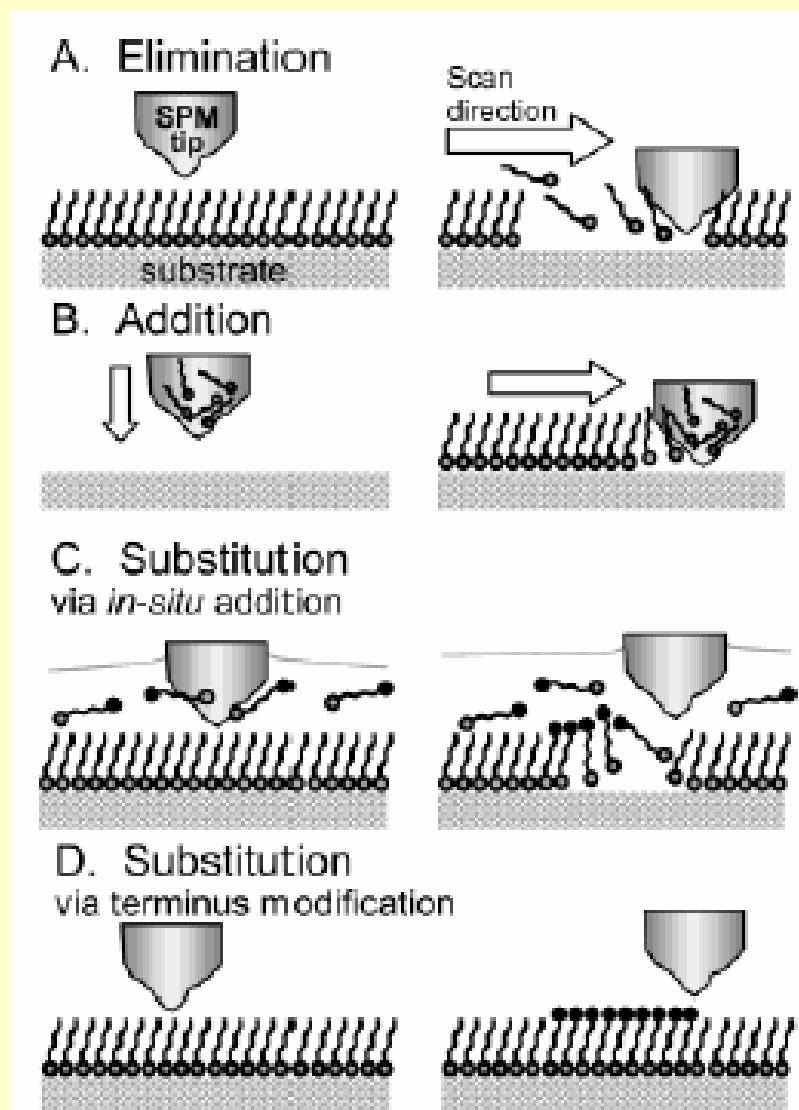
SiO$_2$ Surfaces

These organometallic moieties can serve as attachment points for further modification with long chain alcohols, thiols, carboxylic acids, phosphates, and diketonates.
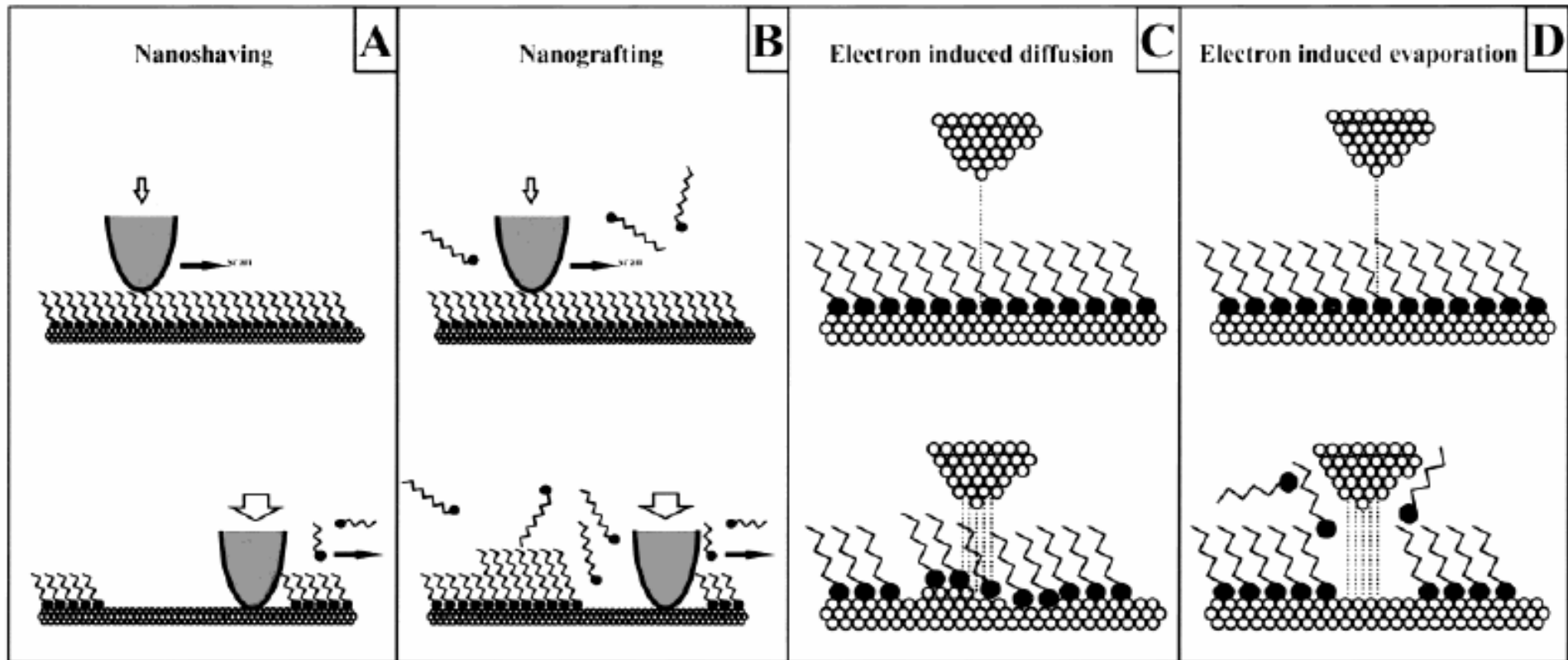
$$[O_3Si]\!\!-\!\!-O\!-\!ML_n + HOR \longrightarrow [O_3Si]\!\!-\!\!-O\!-\!ML_{n-1}\!-\!OR + HL$$

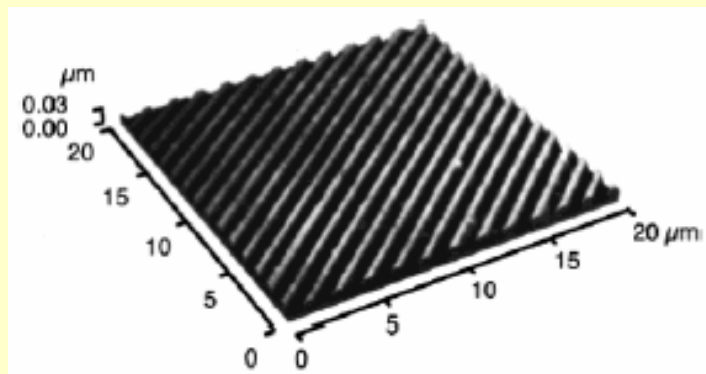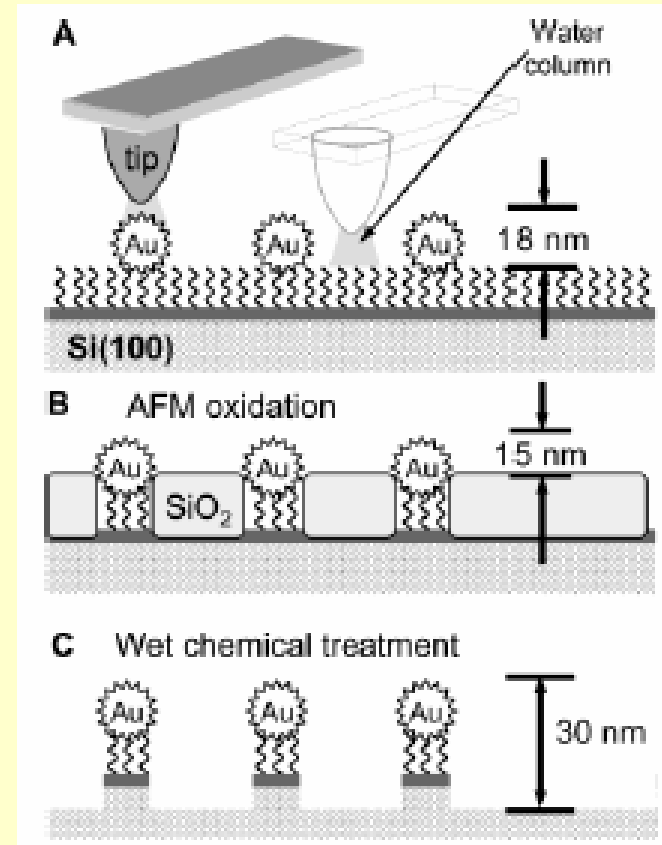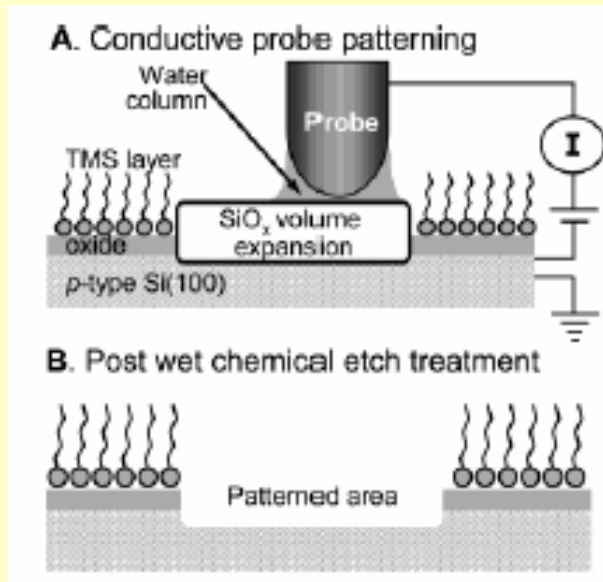$$[O_3Si]\!\!-\!\!-O\!-\!ML_n + HOOCR \longrightarrow [O_3Si]\!\!-\!\!-O\!-\!ML_{n-1}\!-\!OOCR + HL$$

Manipulations with SAM
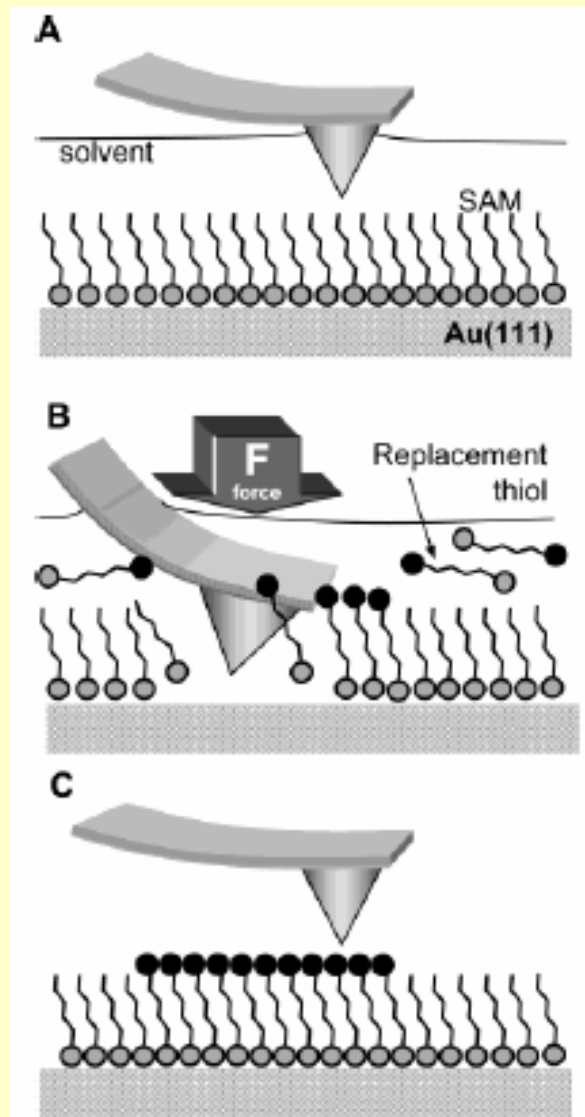
Manipulations with SAM

Manipulations with SAM
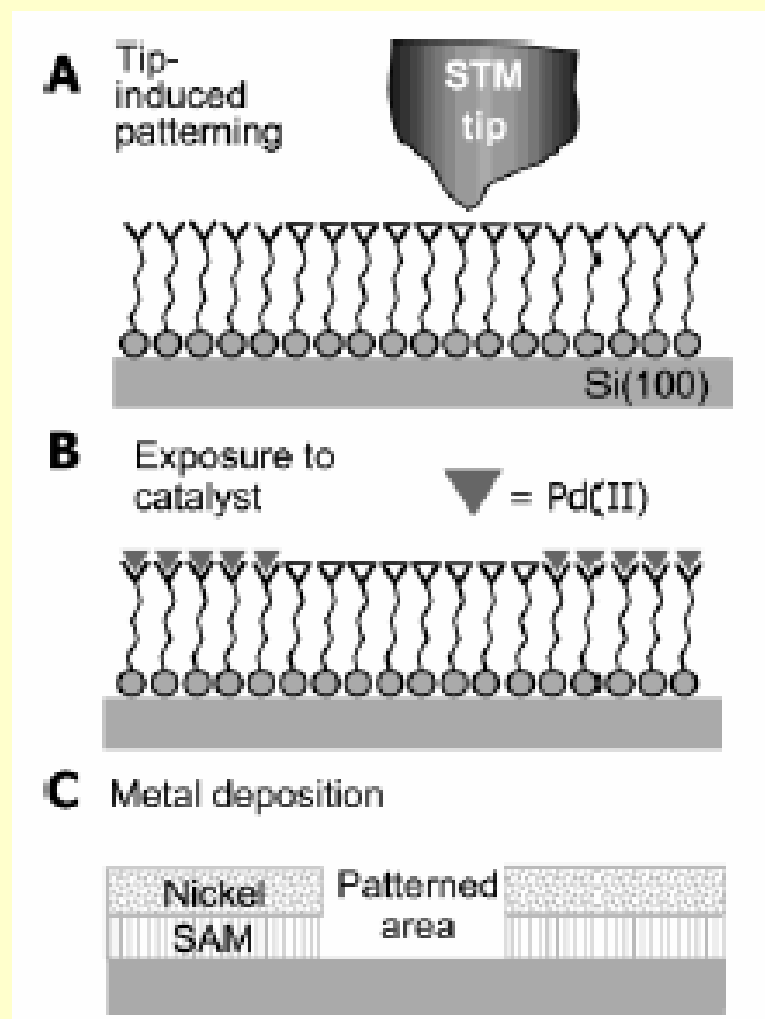
Manipulations with SAM

Manipulations with SAM