

Synthesis of Thin Films

THIN FILMS ARE VITAL IN MODERN TECHNOLOGY:

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

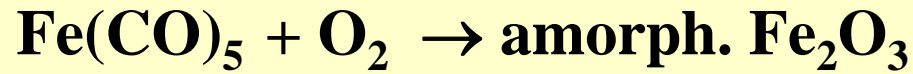
Catalyst surfaces

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



Prepared 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, hydrophilicity (Si-OH vs. Si-H)

Composition

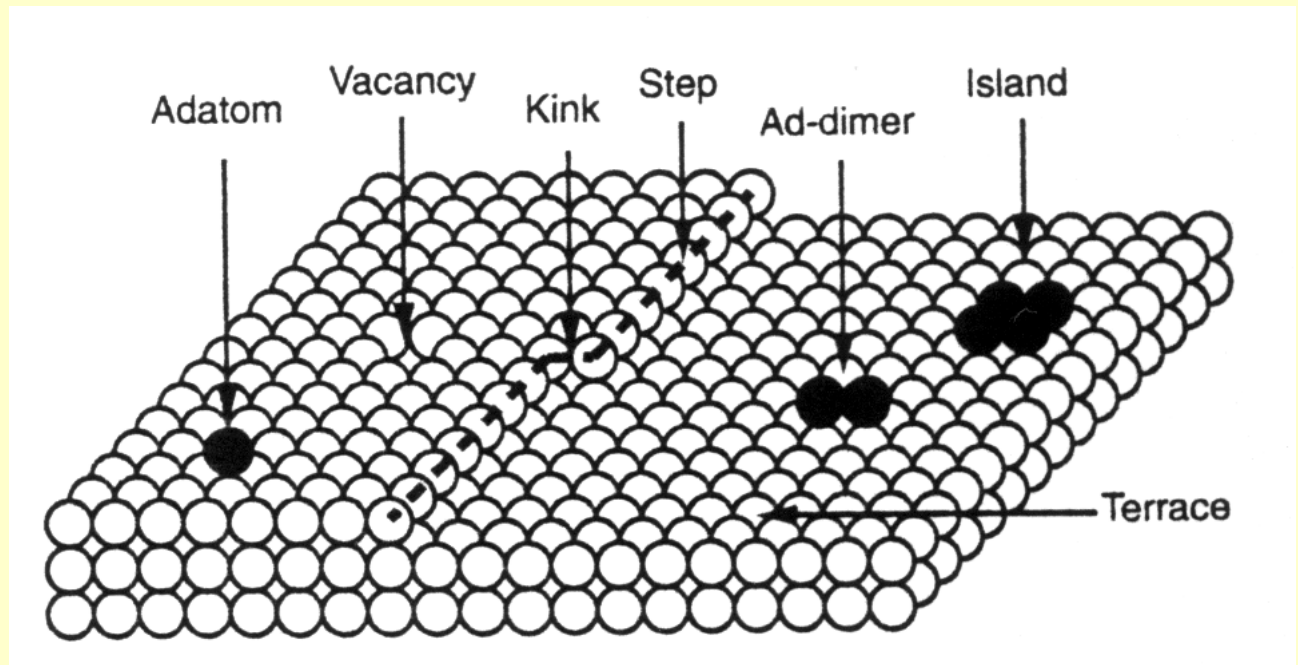
Texture: single crystal, microcrystalline, domains, orientation

Form: supported or unsupported, nature of substrate

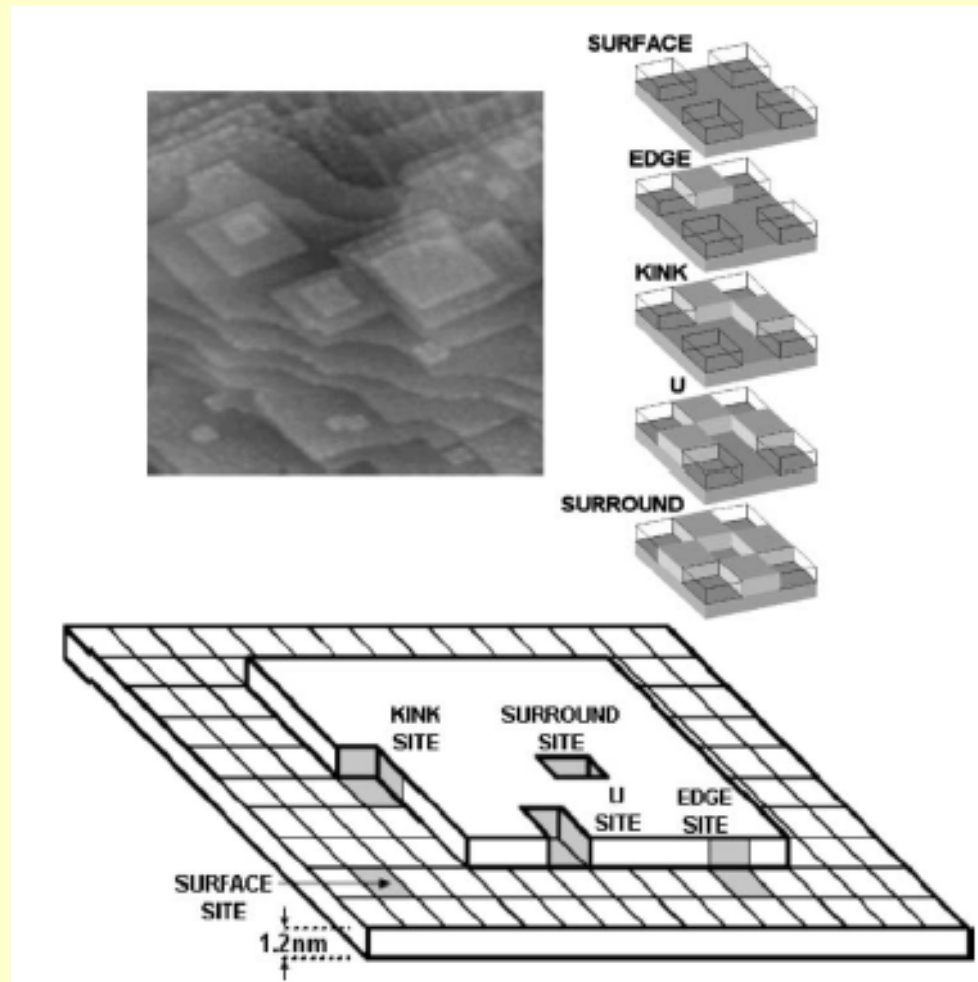
Synthesis of Thin Films

The TSK Model of a Surface

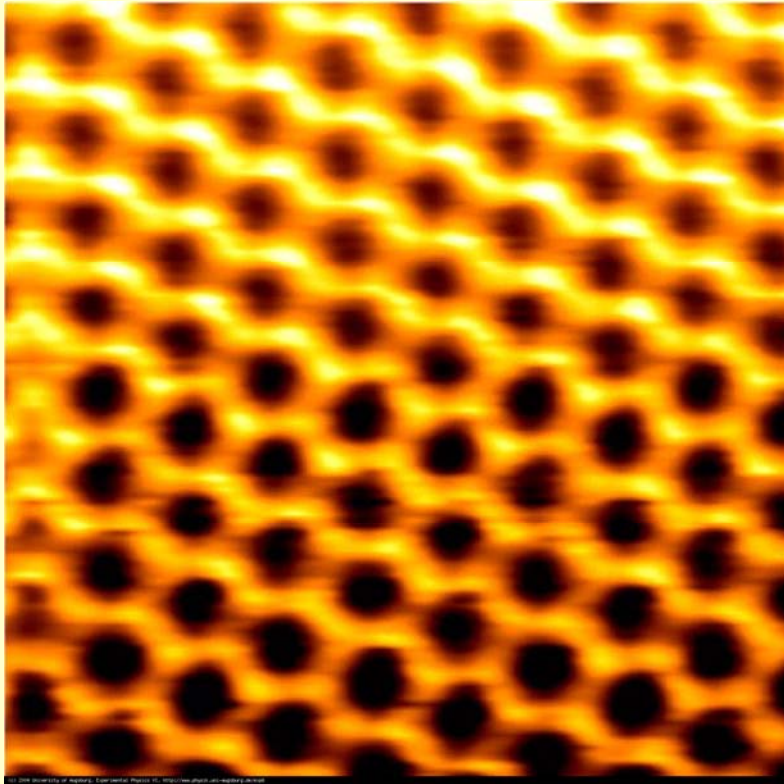
- Terrace
- Step
- Kink
- Vacancy
- Adatom
- Island



Synthesis of Thin Films



Thin Films



AFM showing C atoms
within the hexagonal
graphite unit cells.
Image size $2 \times 2 \text{ nm}^2$.

Synthesis of Thin Films

Surface diffusion coefficient D

$D = a^2 k_s$ a ... effective hopping distance between sites

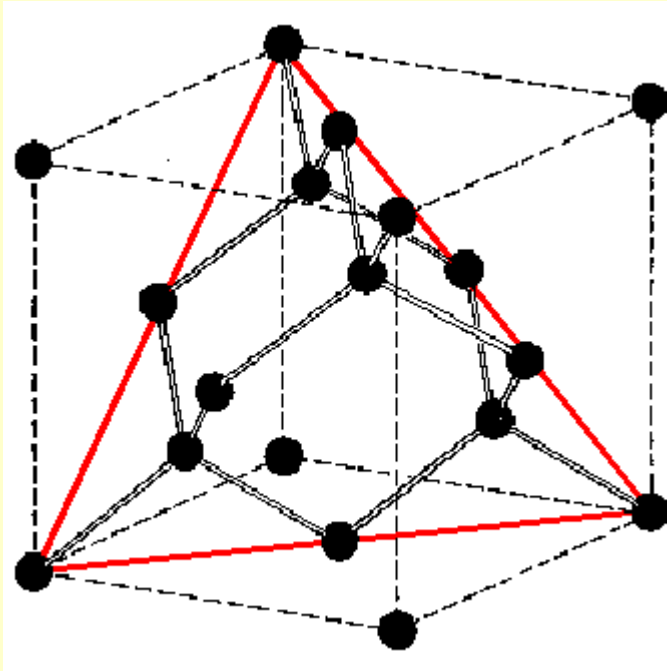
k_s ... site-to-site hopping rate of an adatom

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

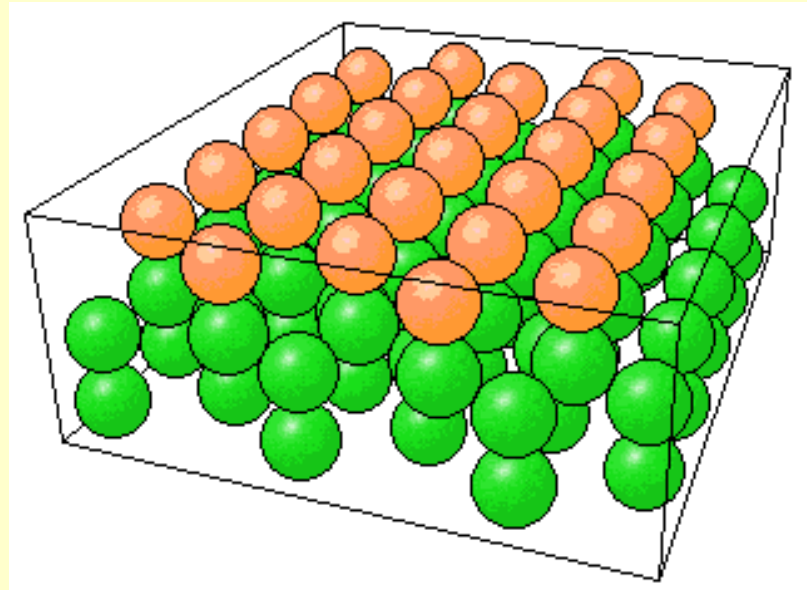
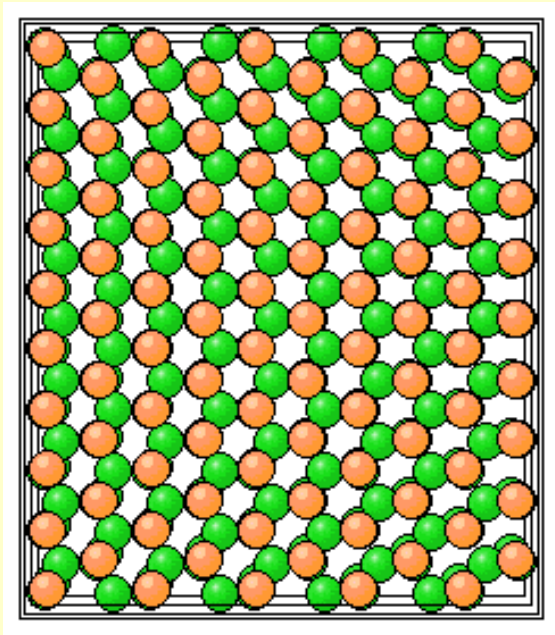
$$a = 5.463 \text{ \AA}$$

Si(111) = a set of atomic planes

One plane outlined with red

Si(111) Surface

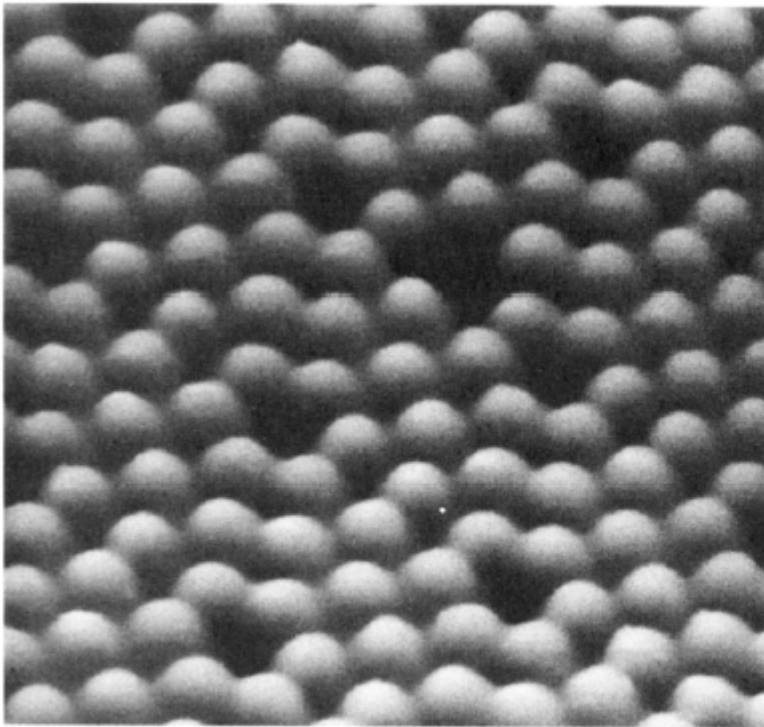
A top view of the atomic arrangement for the (111) plane



orange = the top layer
green = deeper layers

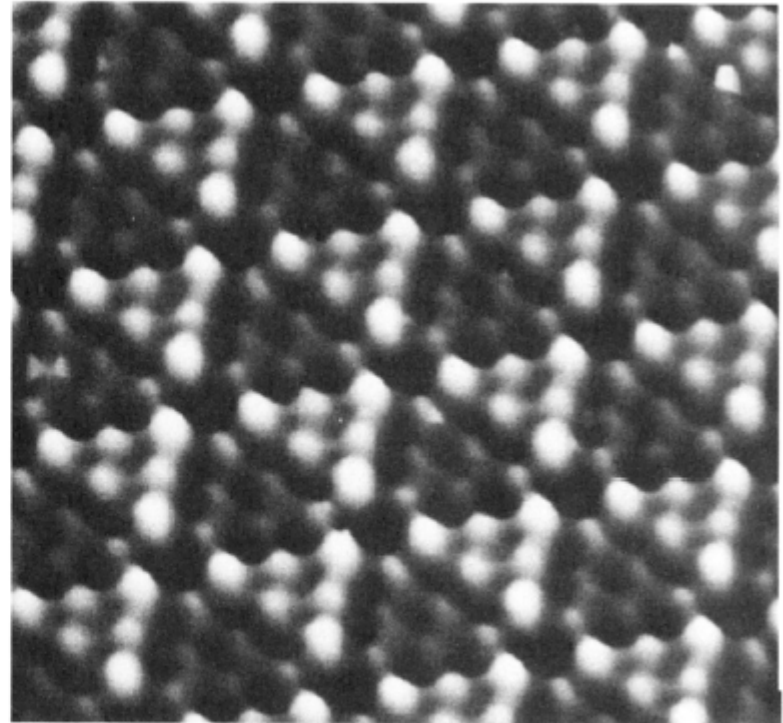
Si(111) Surface

a) Unoccupied states



20 Å

b) Occupied states

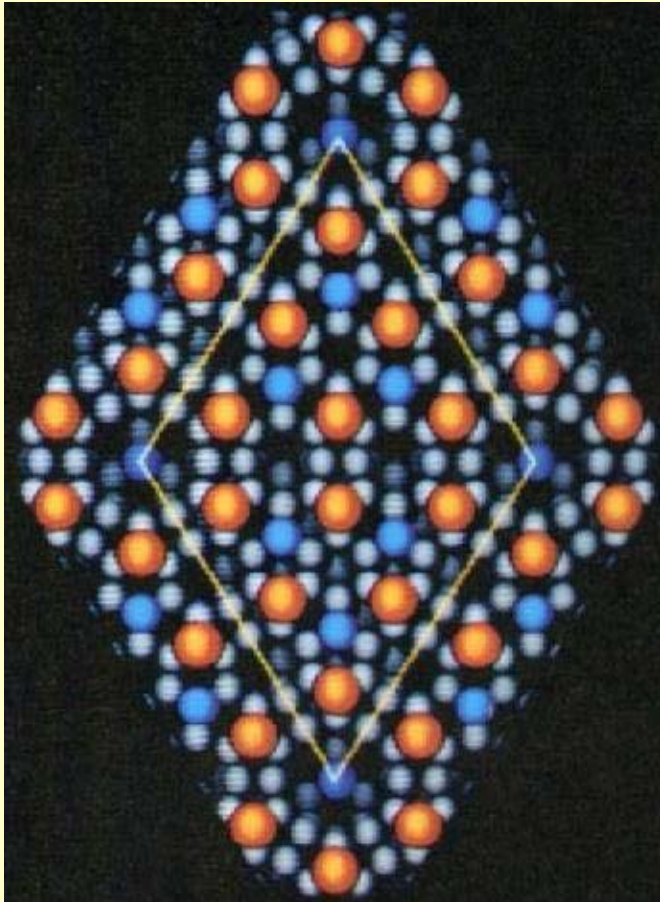


20 Å

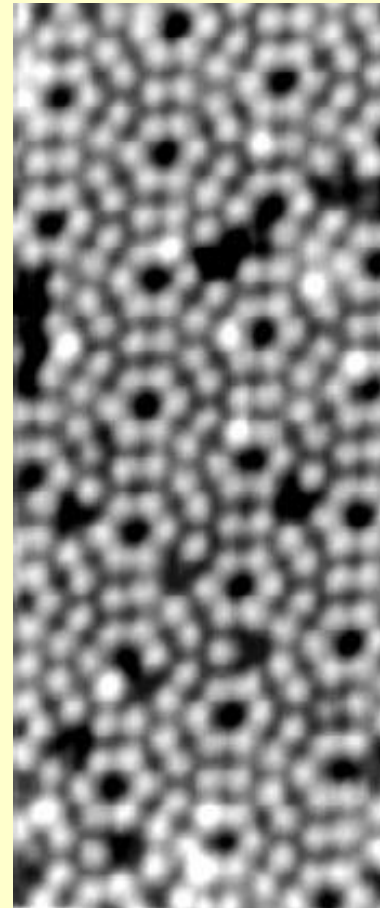
Figure 7. STM topographs of the clean Si(111)-(7 \times 7) surface: (a) unoccupied states imaged at +2.0 V crystal bias, (b) occupied states imaged at -2.0 V crystal bias. The 12 adatoms are clearly visible in both images, and in the occupied state image the stacking fault and differences between corner 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.

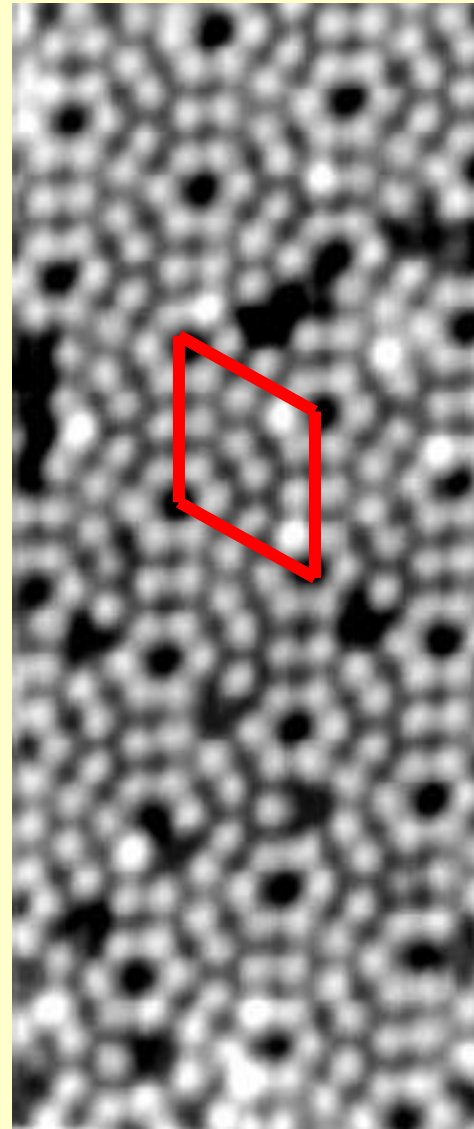
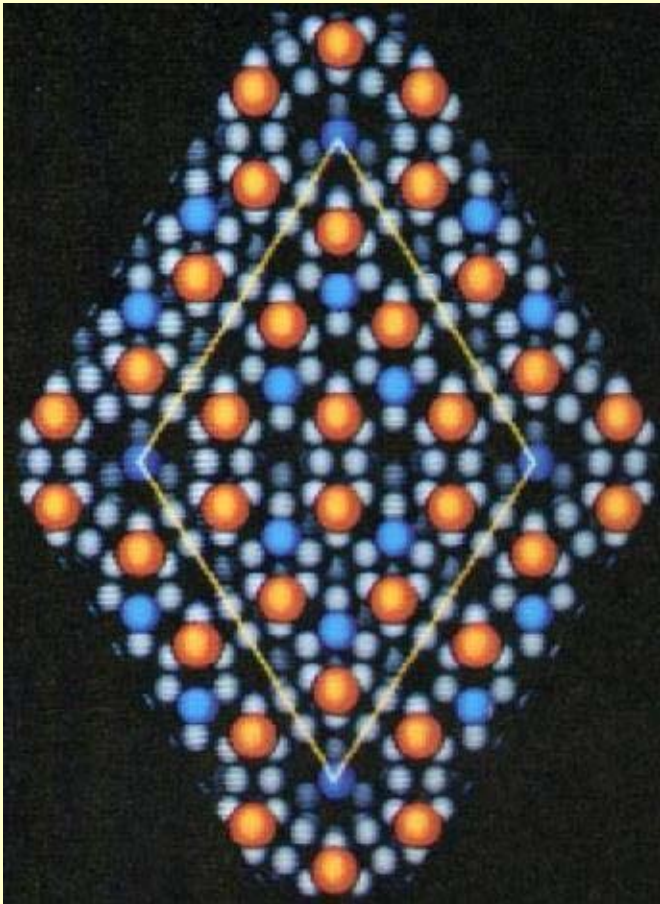


Thin Films



STM image of
Si(111) surface

7x7 Reconstruction

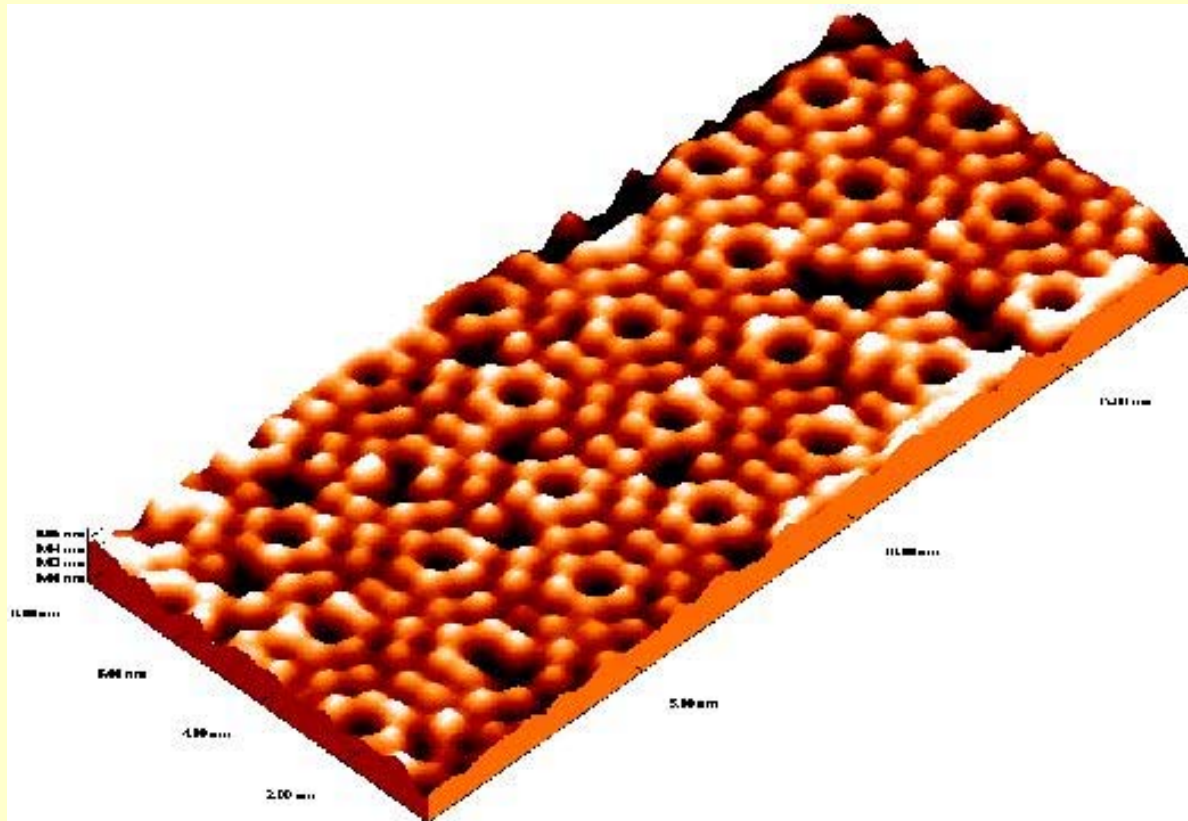


Thin Films

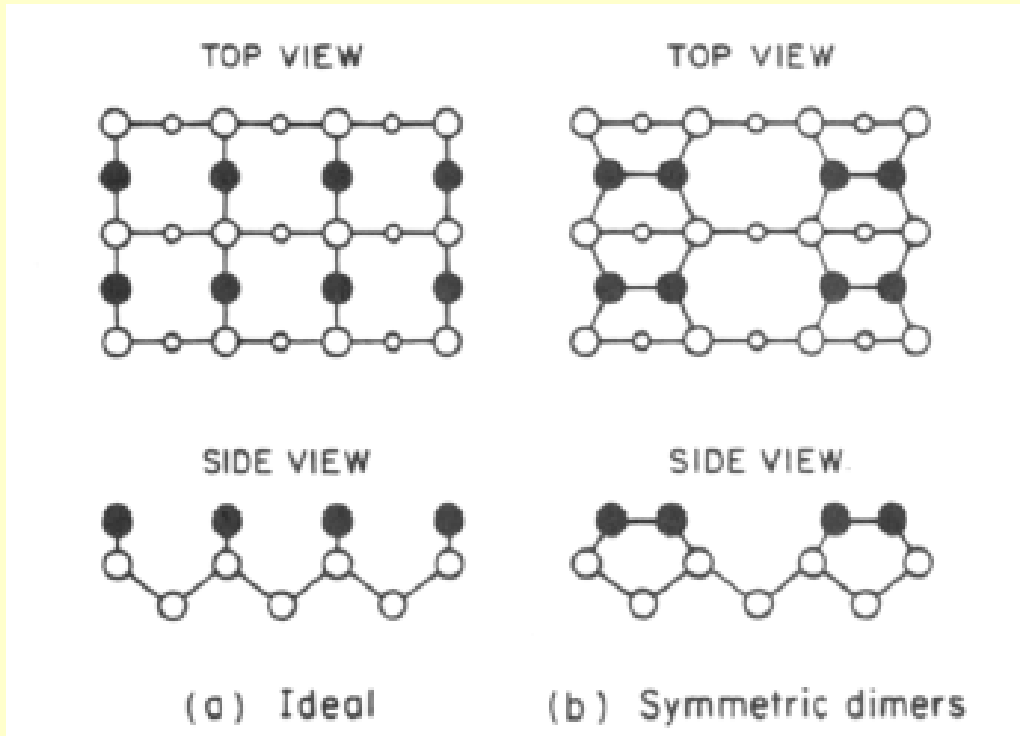
7x7 Reconstruction

3D representation of the 7x7 STM image

The image area is $18 \times 8 \text{ nm}^2$, the height of the "bumps" is only about 0.04 nm

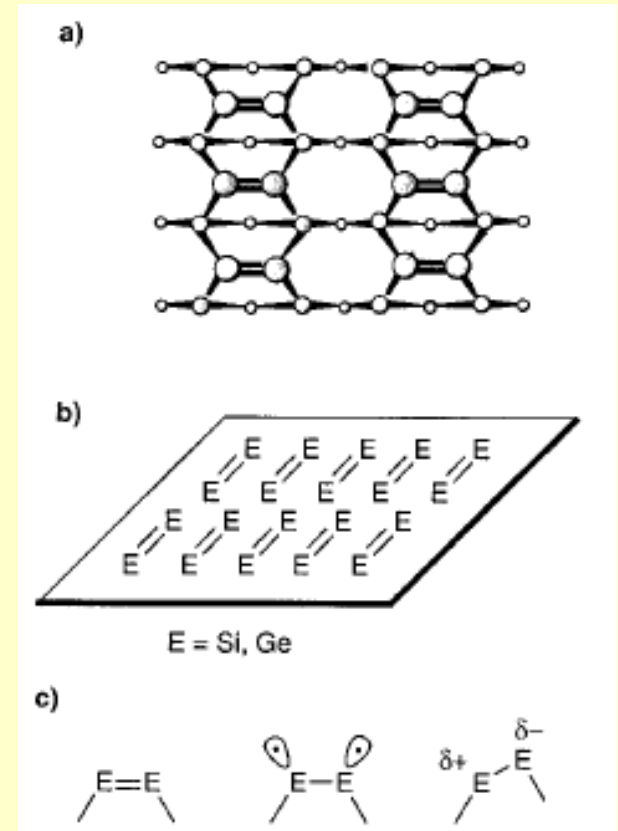


Si(100) Surface



ideal

reconstructed



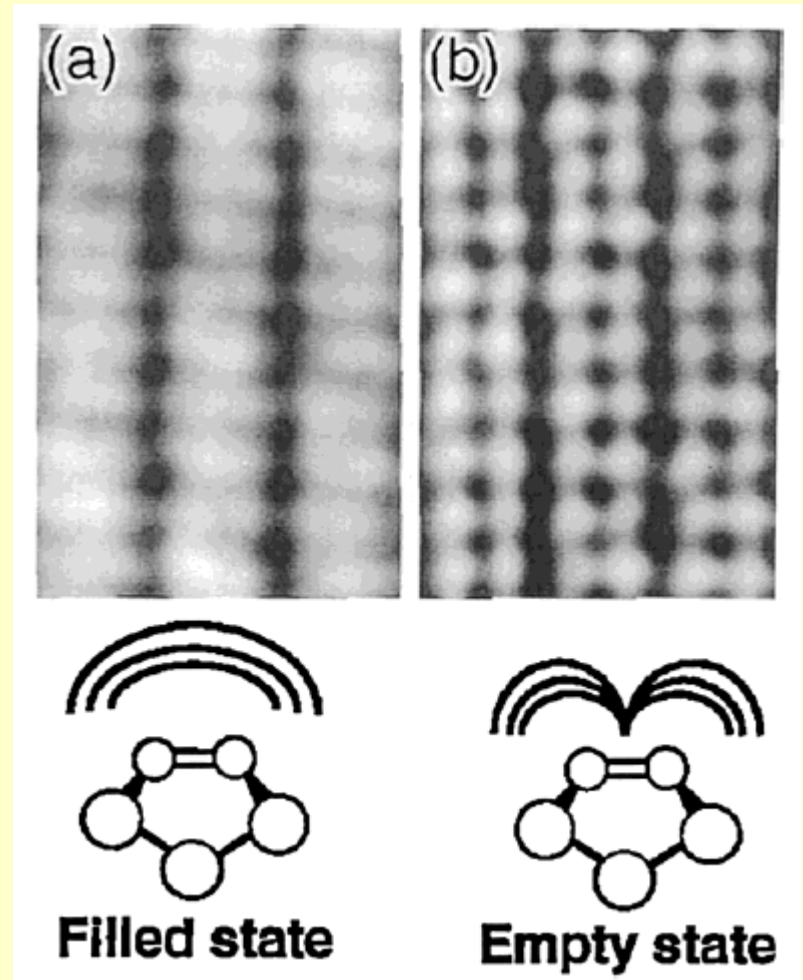
STM images of the silicon-silicon dimers imaged with

(a) $V_{\text{sample}} = -2.0 \text{ V}$

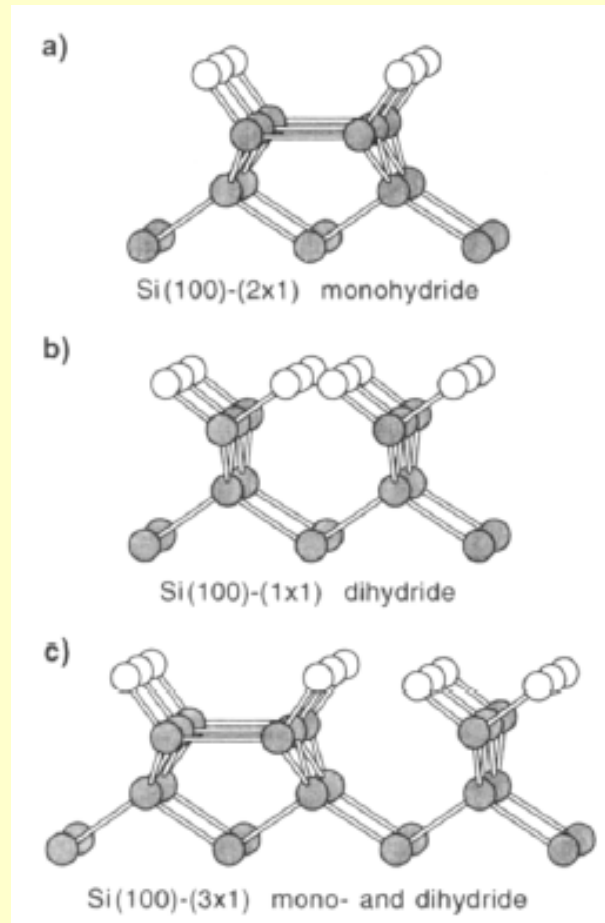
(b) $V_{\text{sample}} = 2.3 \text{ V}$

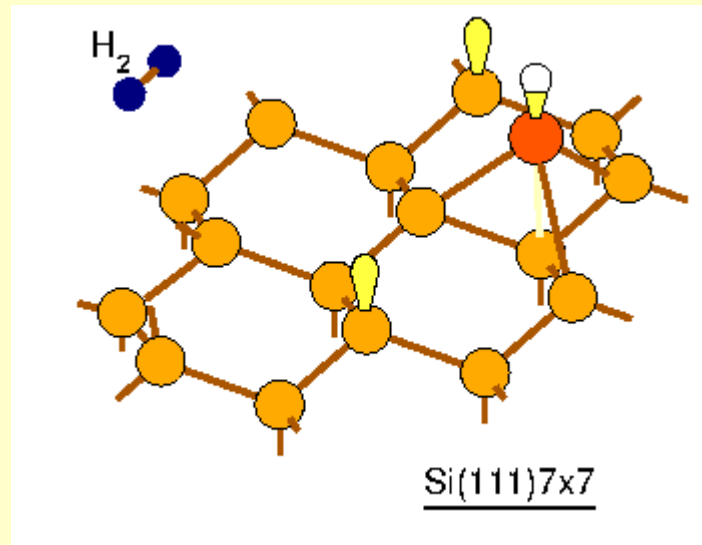
The filled and empty states of these highly ordered dimers can be probed by biasing the surface in the opposite directions

The dimensions of the figure are 2.3 nm x 7.7nm.



H-terminated Si(100) Surface





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

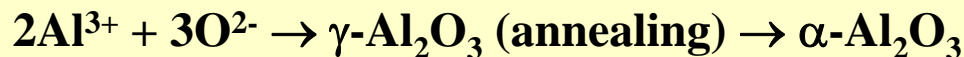
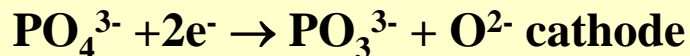
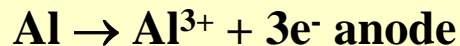
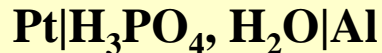
☛ ANODIC DEPOSITION

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

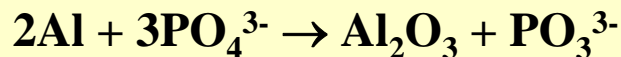
Porous Alumina Films

Example:

Anodic oxidation of aluminum in oxalic or phosphoric acid



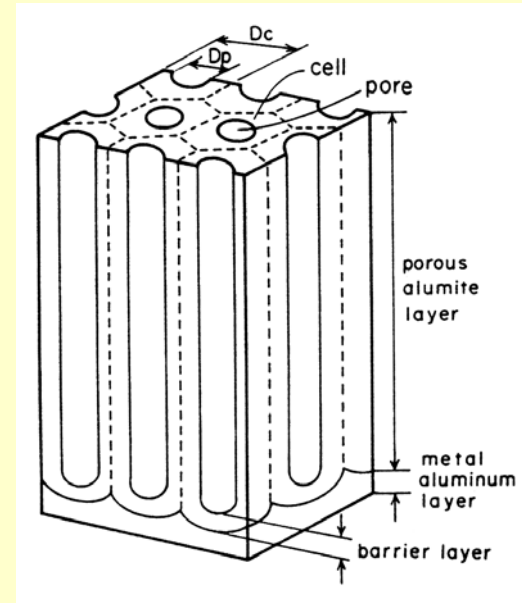
overall electrochemistry:



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

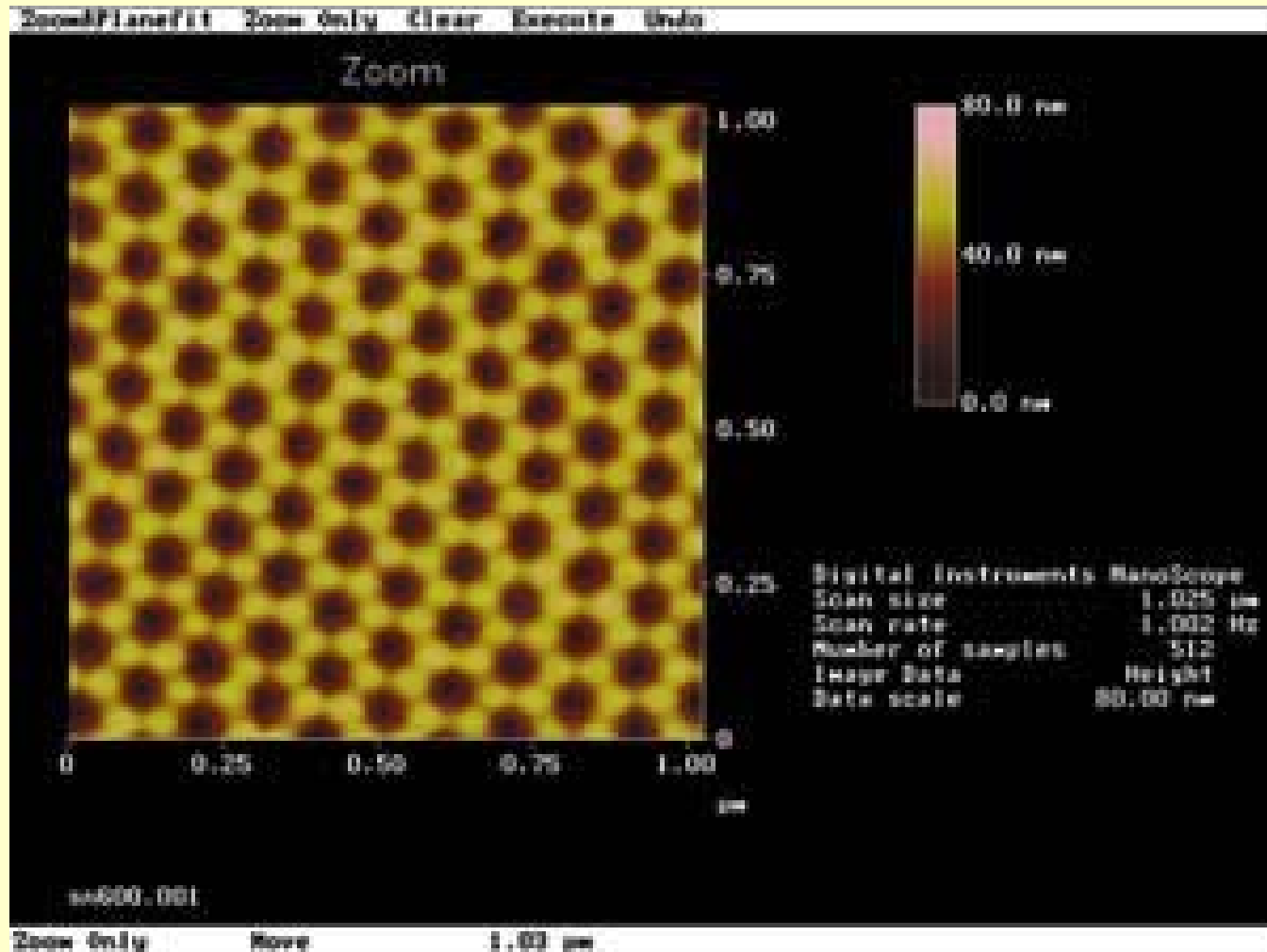
Porous Alumina Films

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

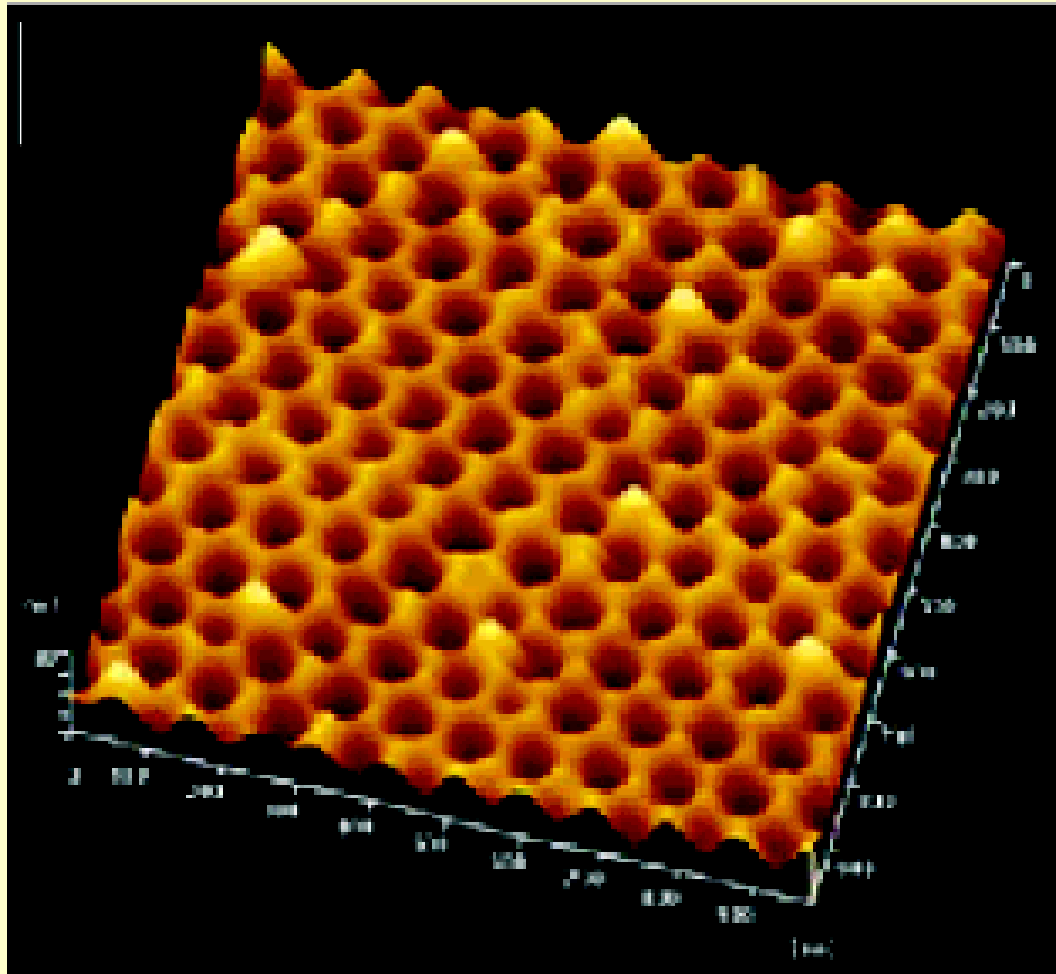


Exceptionally useful process for creating controlled porosity membranes, photonic gap materials, template for synthesizing semiconductor nanostructures, host for synthesizing and organizing aligned carbon nanotubes for high intensity electron emission displays, and last but not least, fuel cell electrode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

AFM picture of porous alumina film

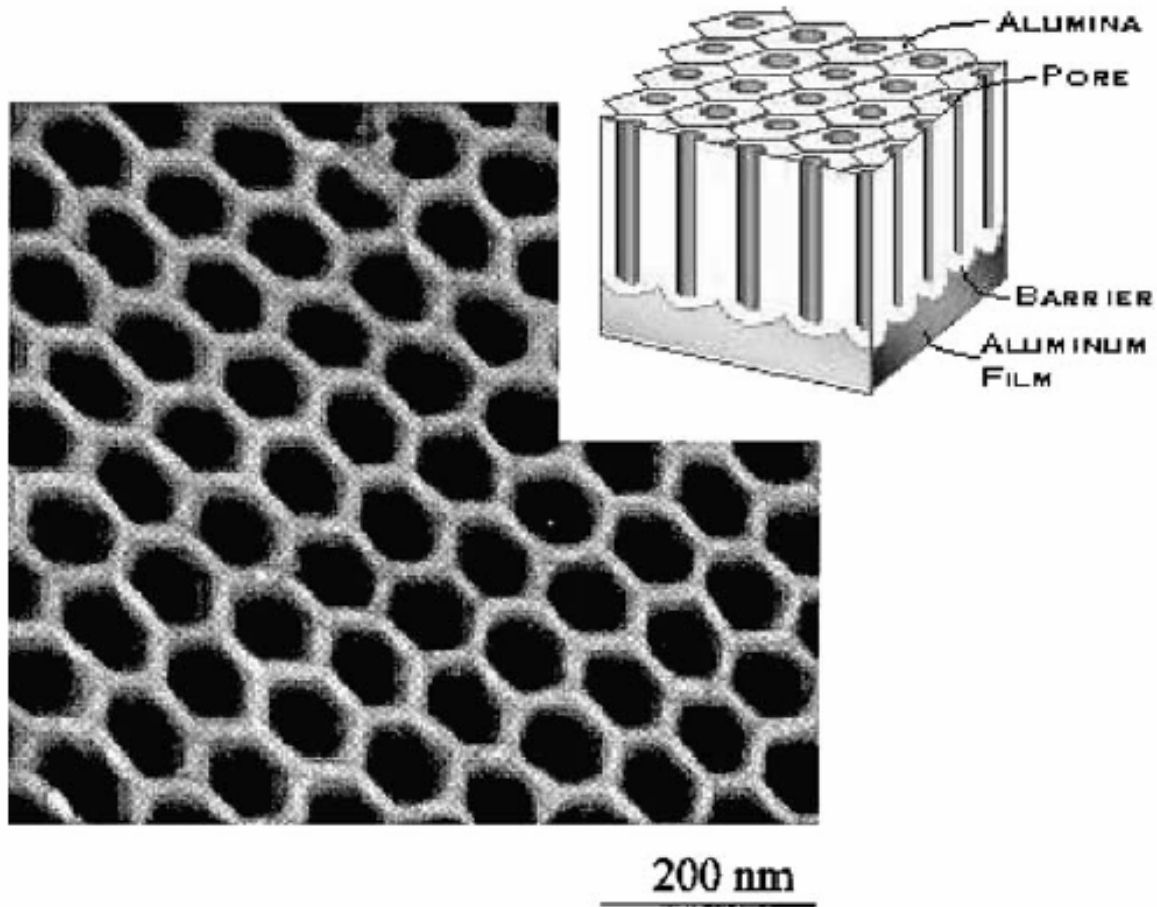


AFM picture of porous alumina film



Thin Films

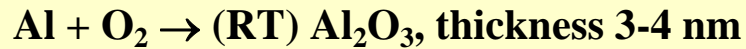
Porous Alumina Films



SYNTHESIS OF THIN FILMS

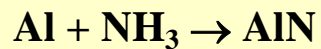
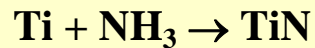
☛ THERMAL OXIDATION

Oxides, metal exposed to a glow discharge



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

Nitrides, exceptionally hard, high temperature protective coating



Synthesis of Thin Films

☛ CHEMICAL VAPOR DEPOSITION

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

EXAMPLES OF CVD

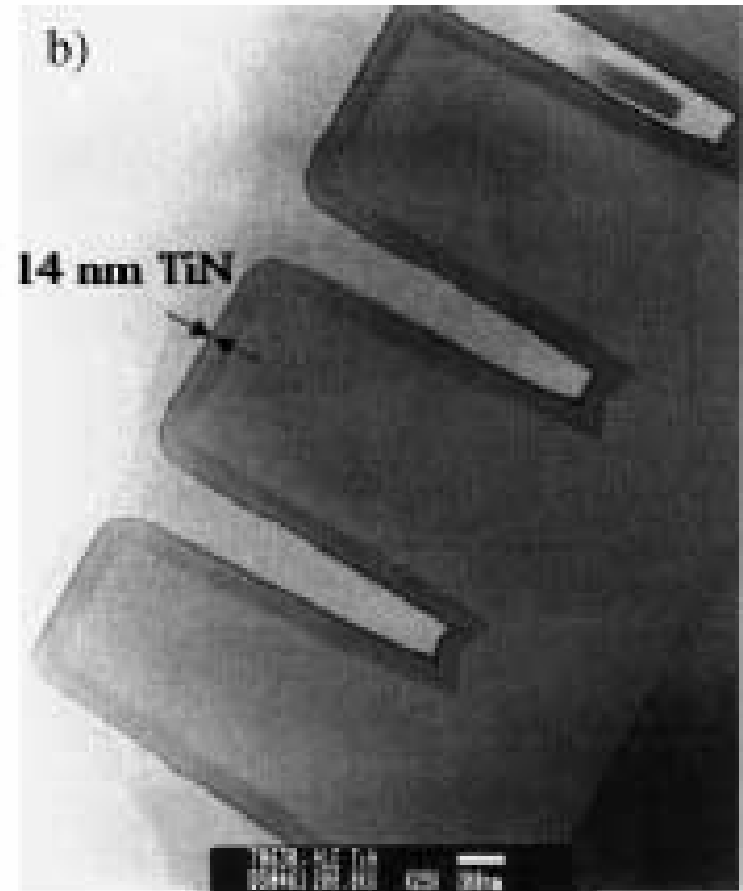
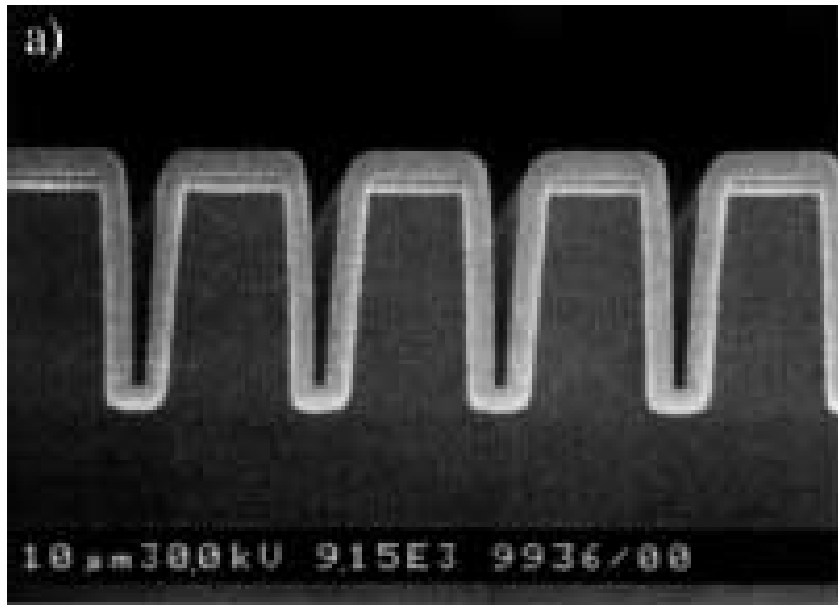
$\text{CH}_4 + \text{H}_2$ (RF, MW) \rightarrow C, diamond films

Et_4Si (thermal, air) \rightarrow SiO_2

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

$\text{SiH}_4 + \text{PH}_3$ (RF) \rightarrow n-Si

$\text{Si}_2\text{H}_6 + \text{B}_2\text{H}_6$ (RF) \rightarrow p-Si



SYNTHESIS OF THIN FILMS

SiH₃SiH₂SiH₂PH₂ (RF) → n-Si

Me₃Ga (laser photolysis, heating) → Ga

Me₃Ga + AsH₃ + H₂ → GaAs + CH₄

Si (laser evaporation, supersonic jet) Si_n⁺ (size selected cluster deposition) → 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

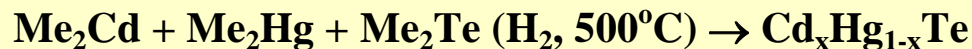
NH_3 , PH_3 , AsH_3

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:



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 $T < 100^\circ\text{C}$

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, kinetics, 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 cm²

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**

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

MBE

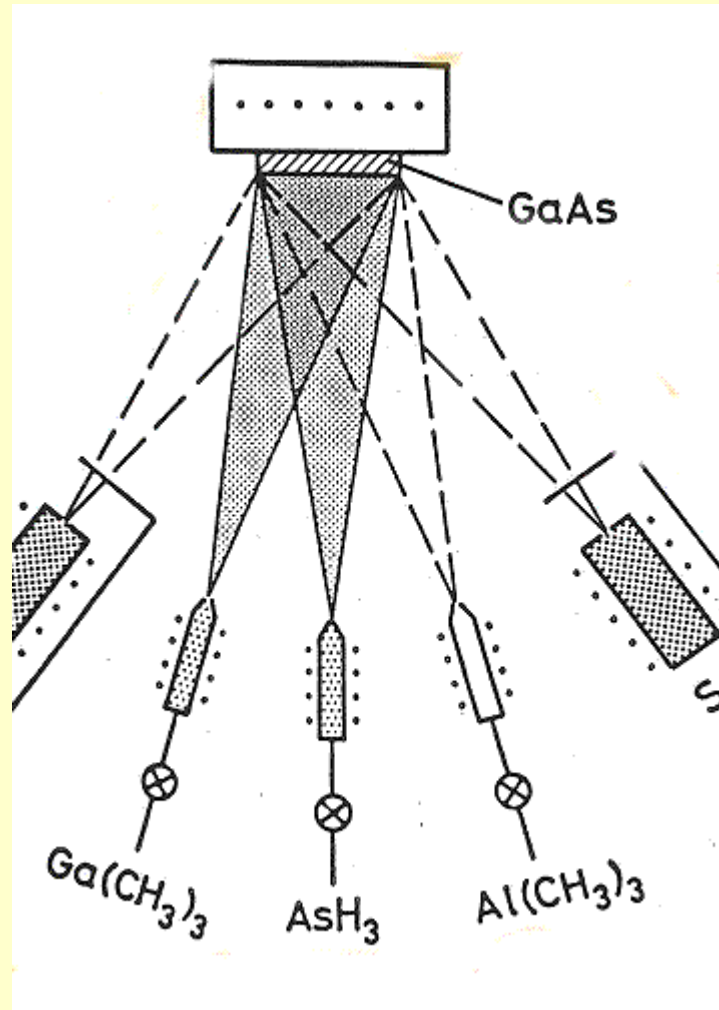
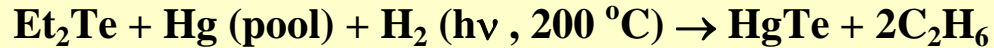


FIGURE 1.1.1.1.1.1

SYNTHESIS OF THIN FILMS

☛ PHOTOEPITAXY

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



MOCVD preparation requires 500 °C using Me₂Te + Me₂Hg

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 °C even with a 14% lattice mismatch

GaAs is susceptible to damage under MOCVD conditions 650-750 °C

SYNTHESIS OF THIN FILMS

EXTENSIONS OF PHOTOLYTIC METHODS - LASER WRITING AND LASER ETCHING

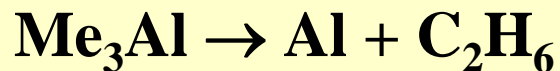
☛ **Laser writing:**

Substrate GaAs

Me₃Al or Me₂Zn adsorbed layer or gas phase

Focussed UV laser on film

Photodissociation of organometallic precursor:



Creates sub-micron lines of Al or Zn

SYNTHESIS OF THIN FILMS

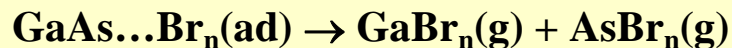
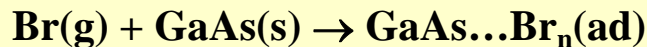
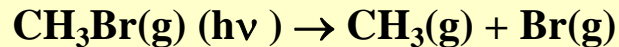
☛ **Laser photoetching:**

GaAs substrate

Gaseous or adsorbed layer of CH₃Br

Focussed UV laser

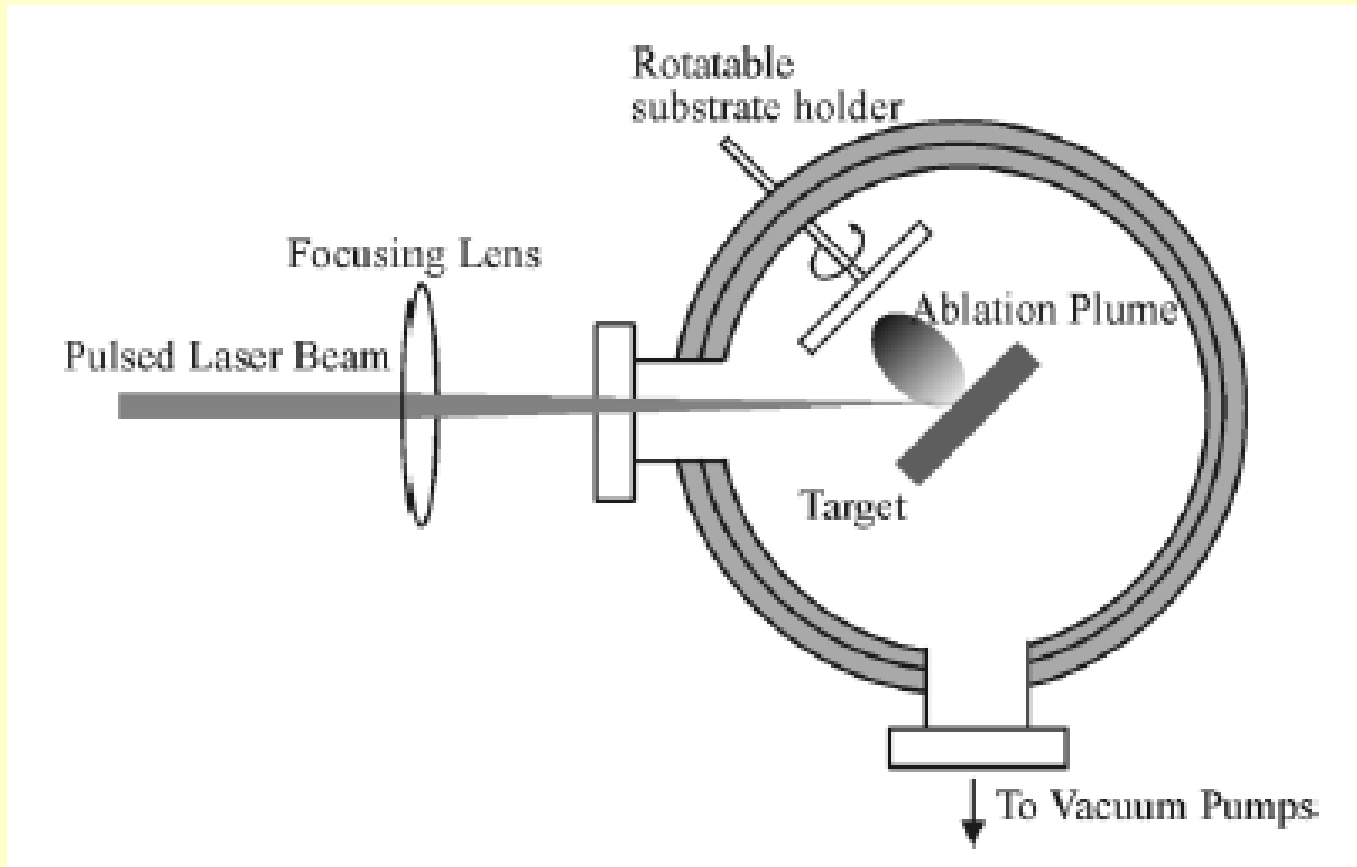
Creates reactive Br atoms



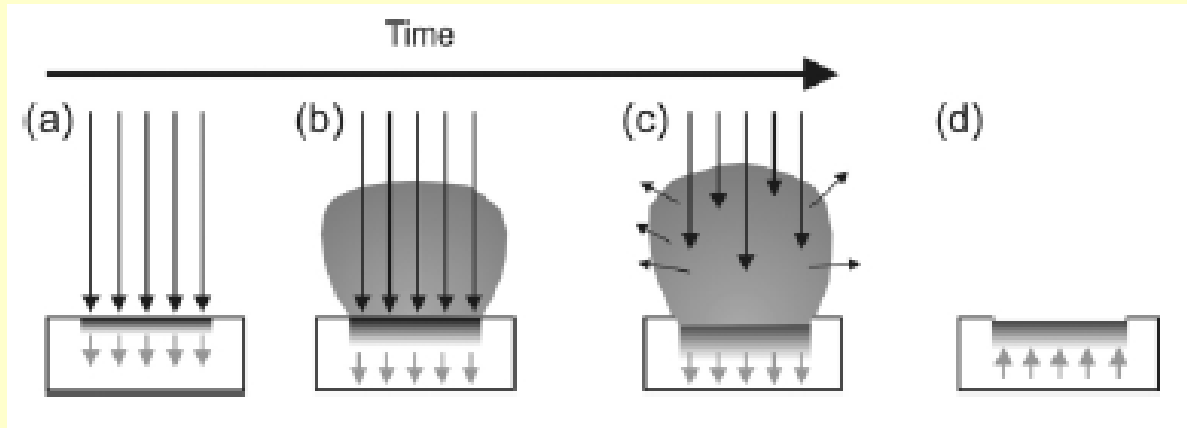
Adsorbed reactive surface Br atoms erode surface regions irradiated with laser

Vaporization of volatile gallium and arsenic bromides from surface creates sub-micron etched line

Pulsed Laser Ablation



Pulsed Laser Ablation



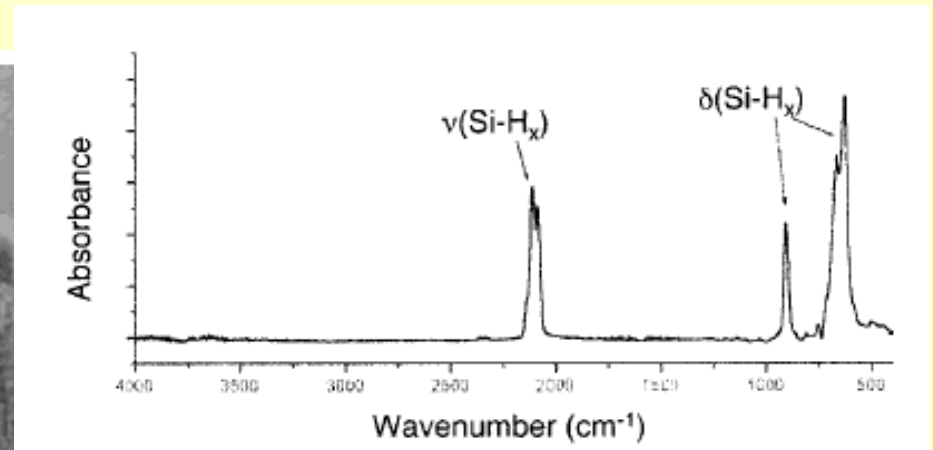
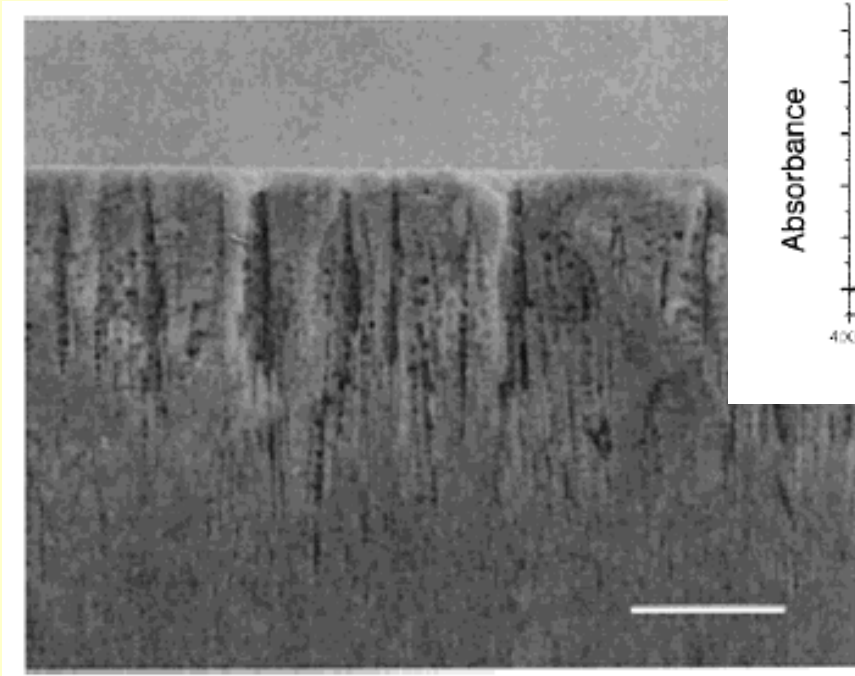
(a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid-liquid interface)

(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

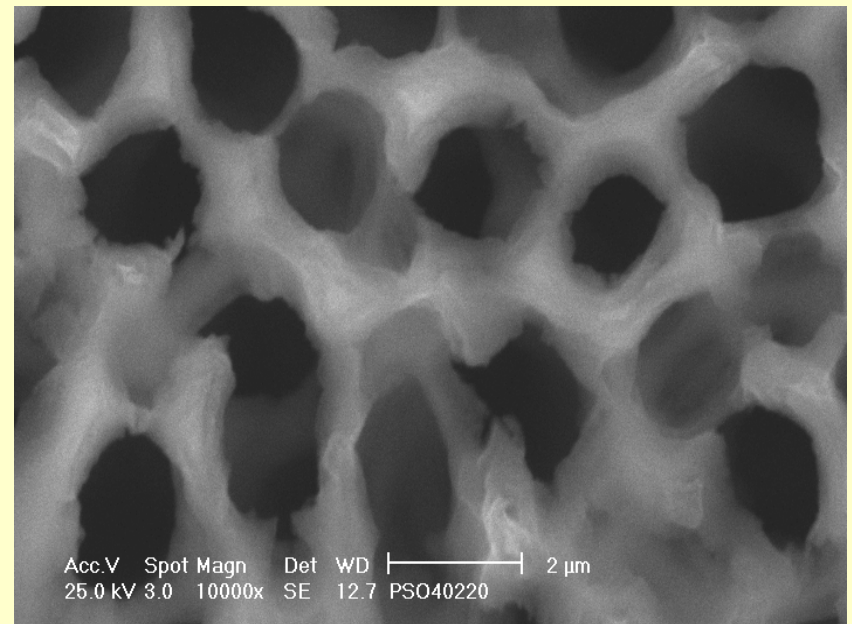
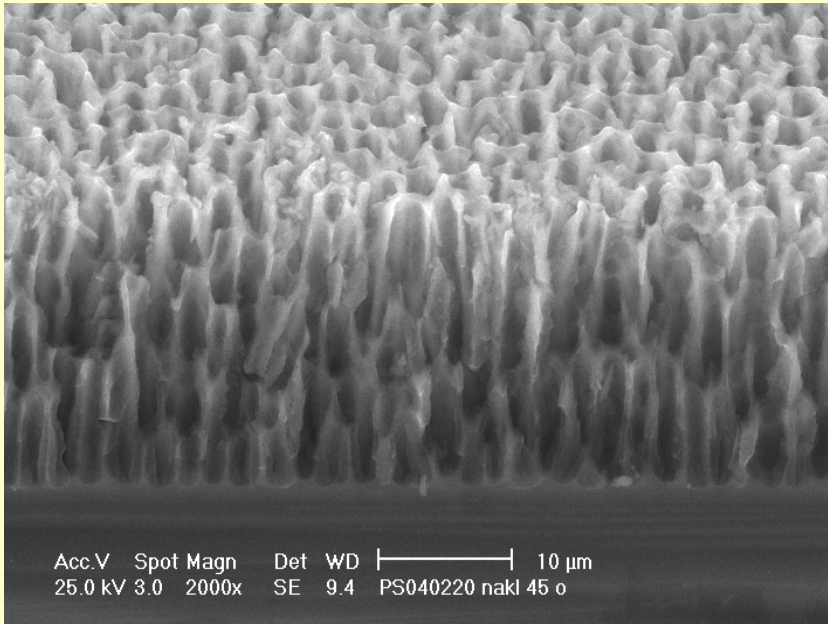
(d) Melt front recedes leading to eventual re-solidification.

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 ϕ ,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

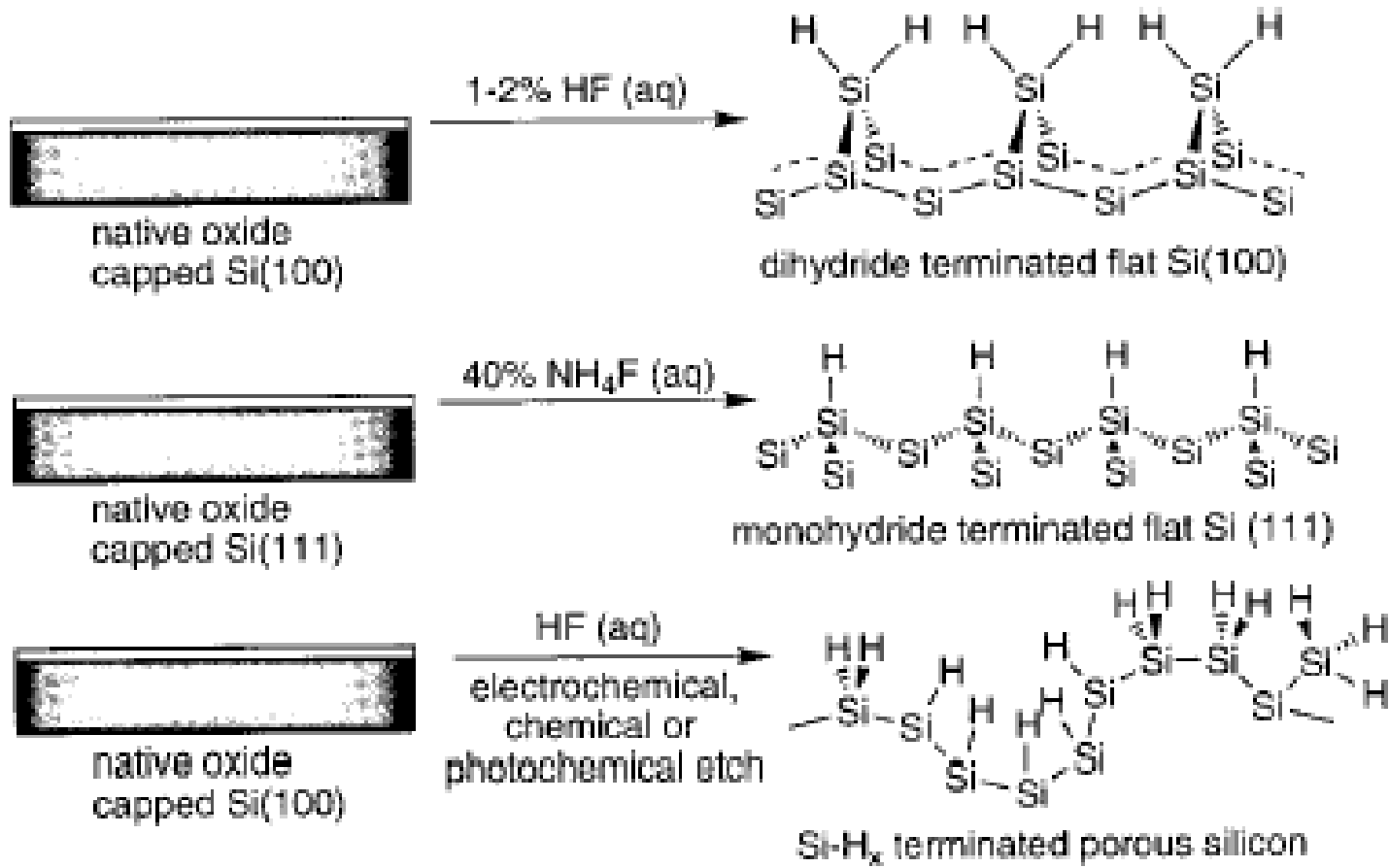


HF:EtOH = 1:2.5

$j = 10 \text{ mA/cm}^2$

$t = 30 \text{ min}$

Chemistry on Si Surface



Porous Si

Luminiscence of p-Si

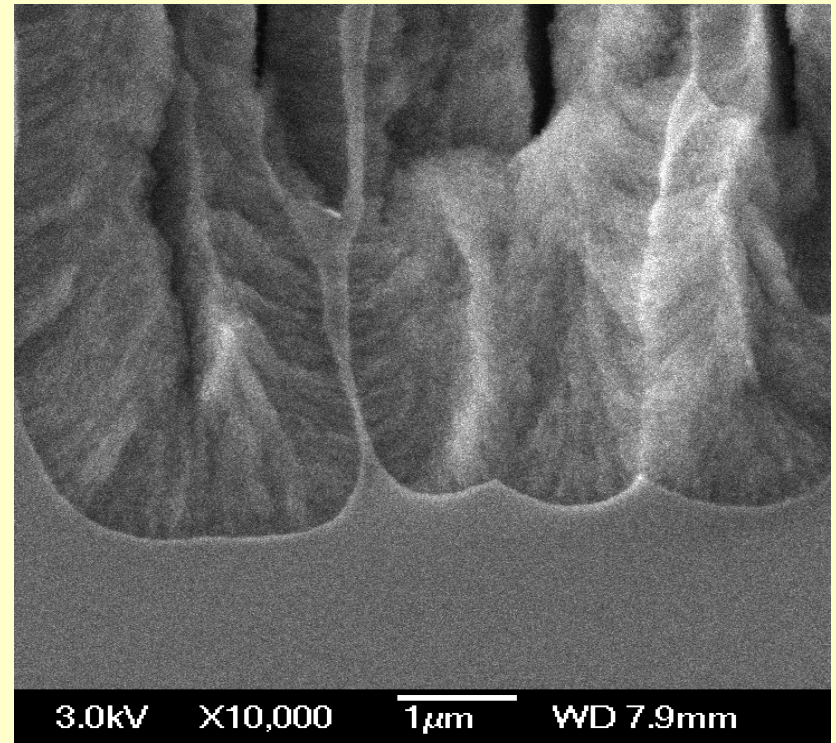
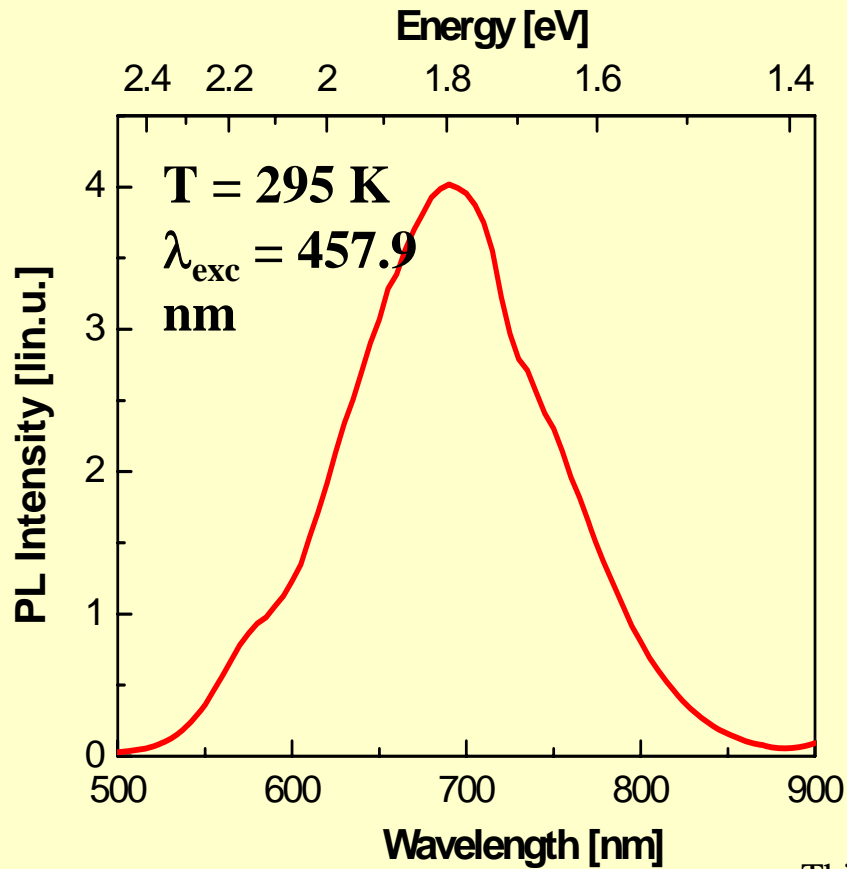
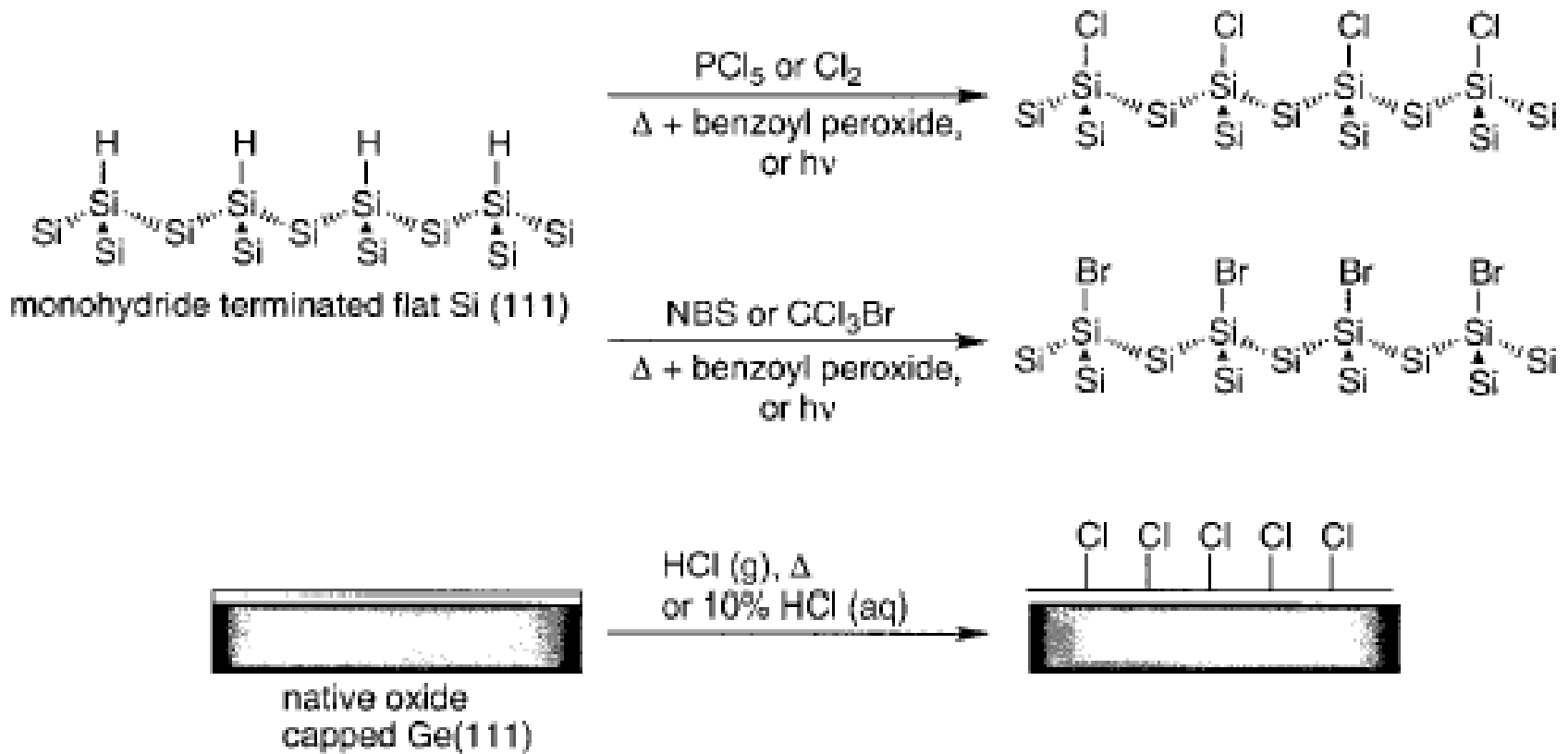


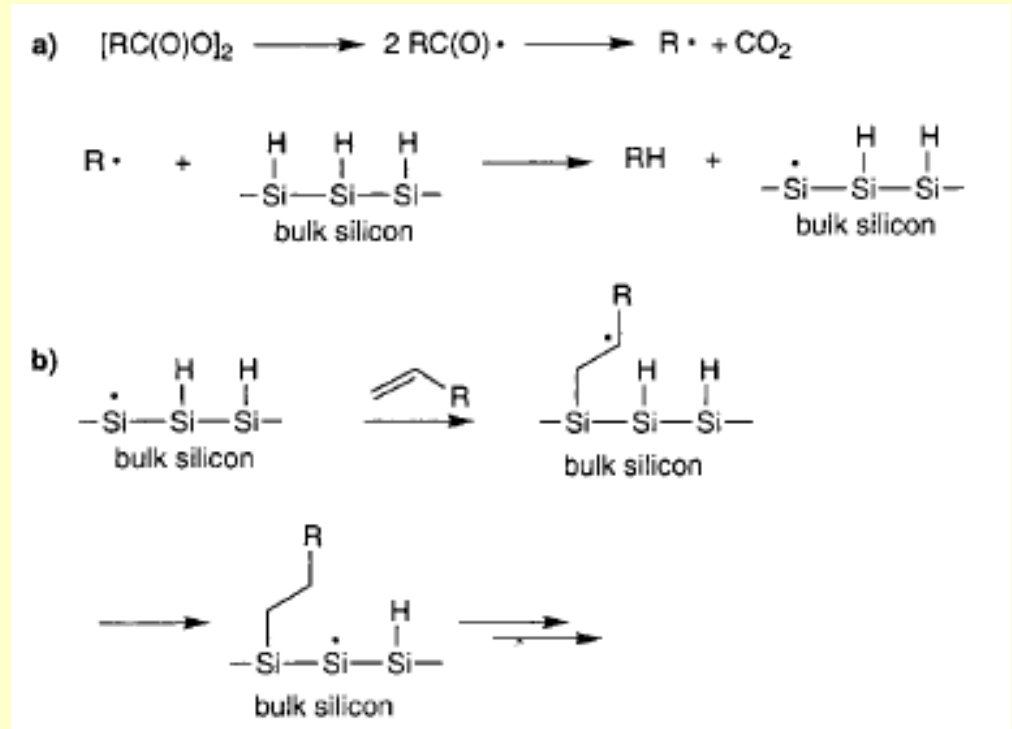
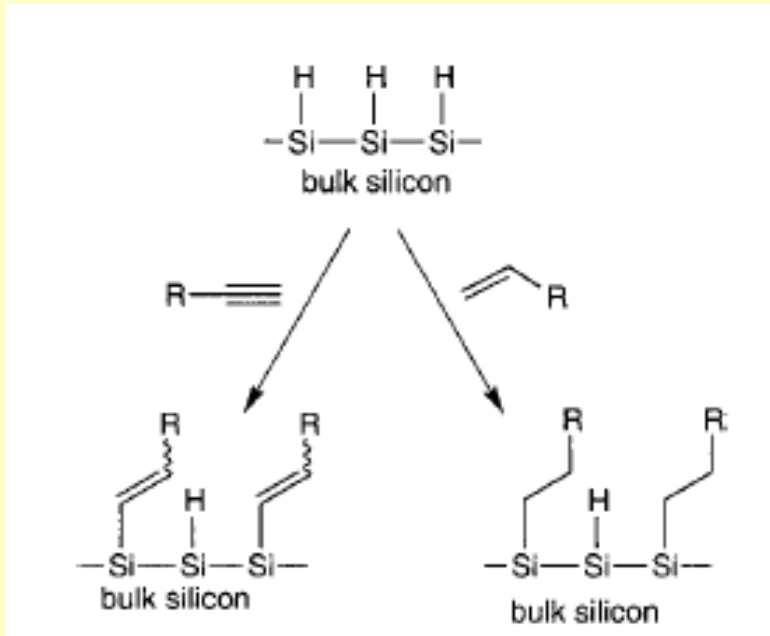
Table 1. Typical Bond Energies for Various Groups Related to Group(IV) Elements (kJ mol⁻¹)

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

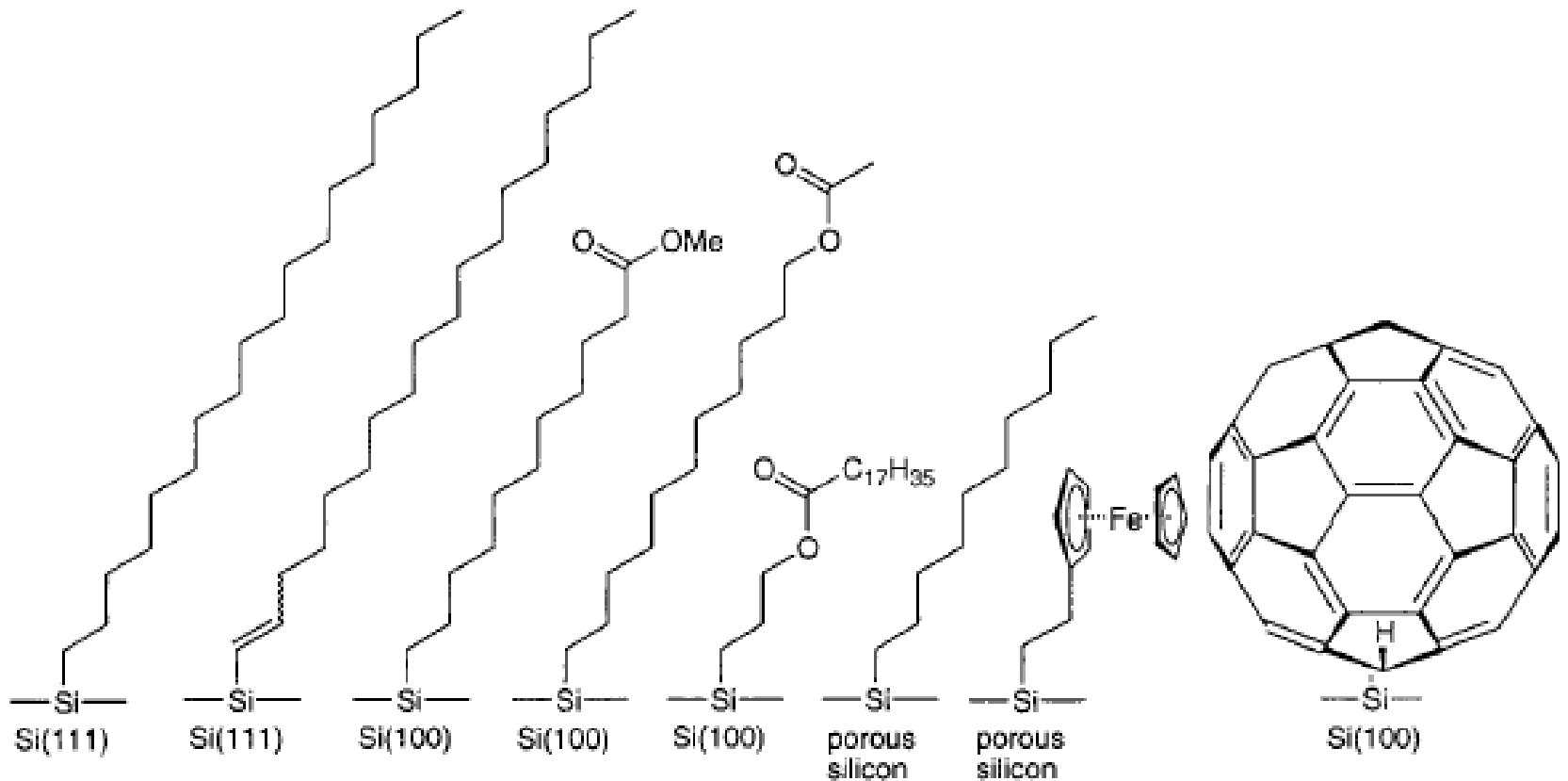
Chemistry on Si Surface



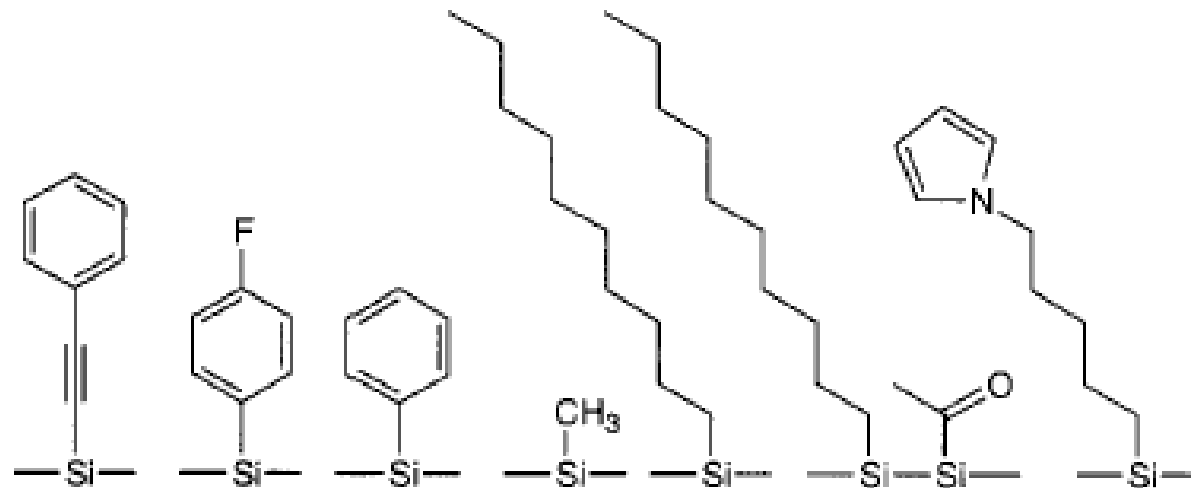
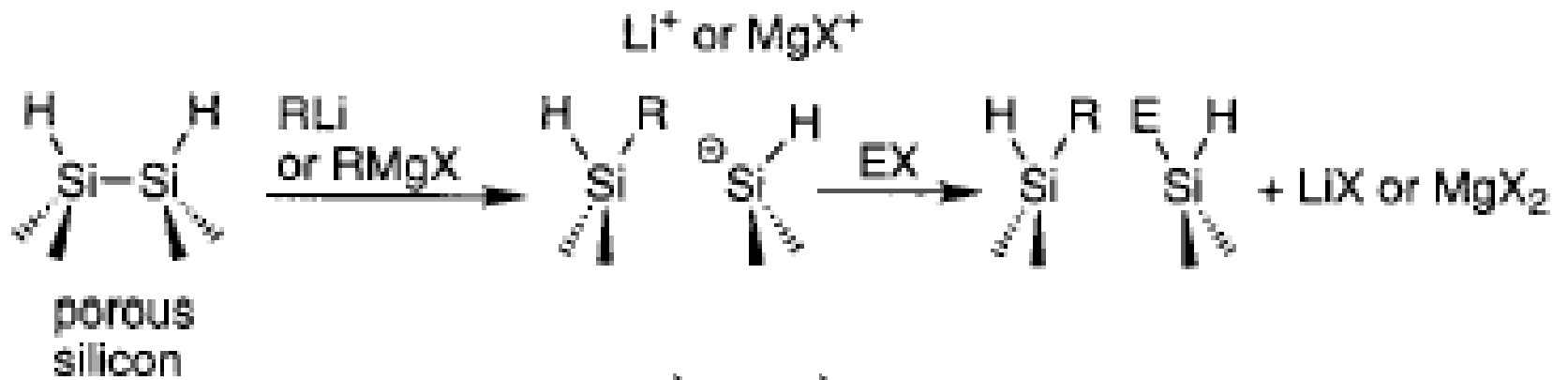
Hydrosilylation



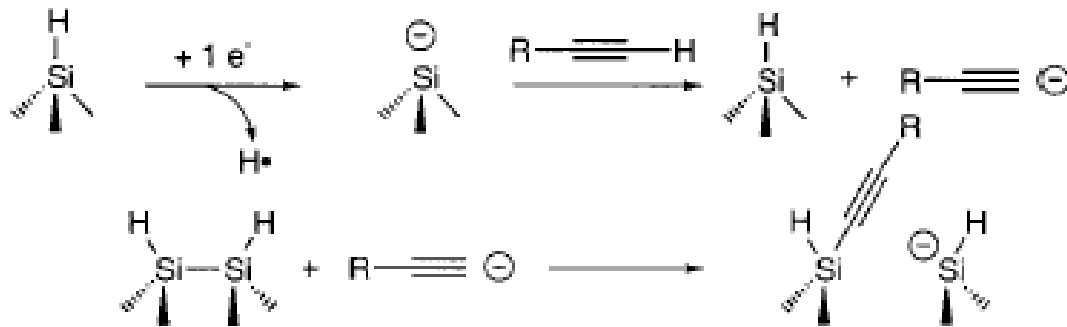
Chemistry on Si Surface



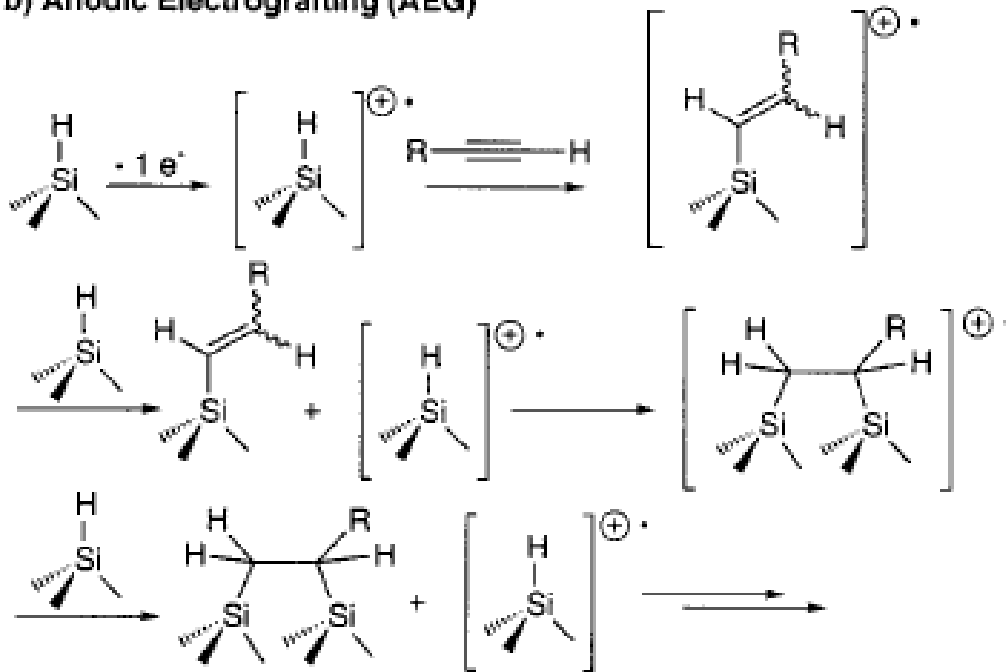
Carbaanion LiR, RMgX



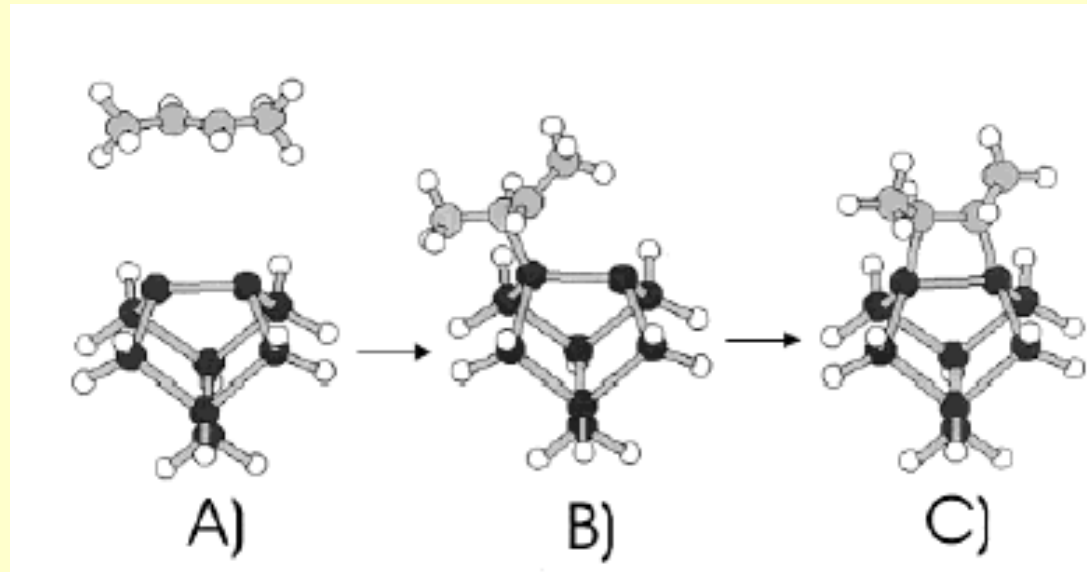
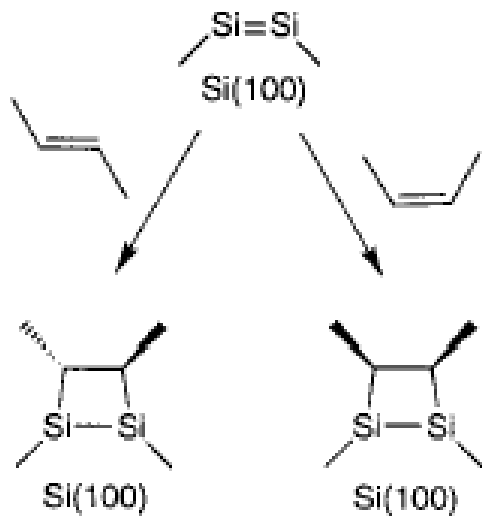
a) Cathodic Electrografting (CEG)



b) Anodic Electrografting (AEG)

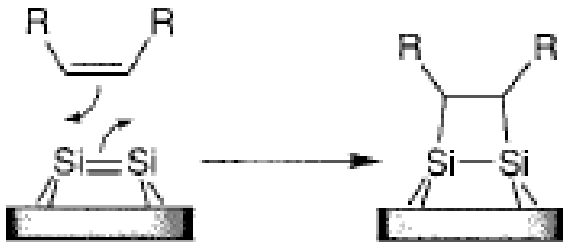


2+2 Cycloaddition

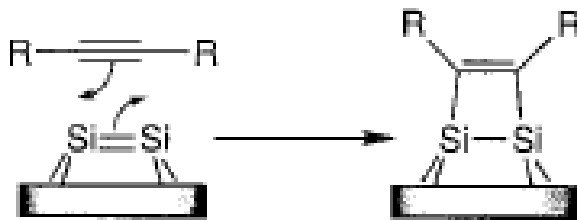


2+2 Cycloaddition

silicon:



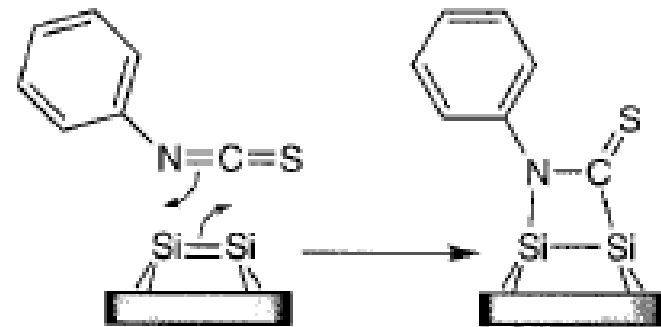
flat Si(100)-2x1



flat Si(100)-2x1

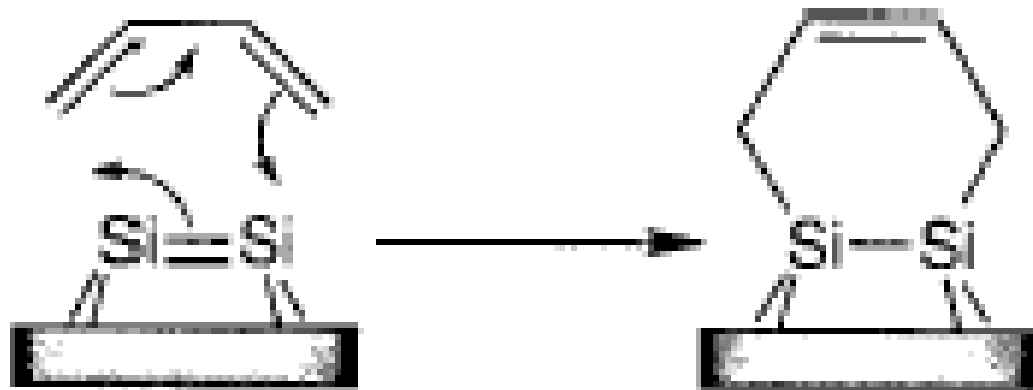


flat Si(100)-2x1



flat Si(100)-2x1

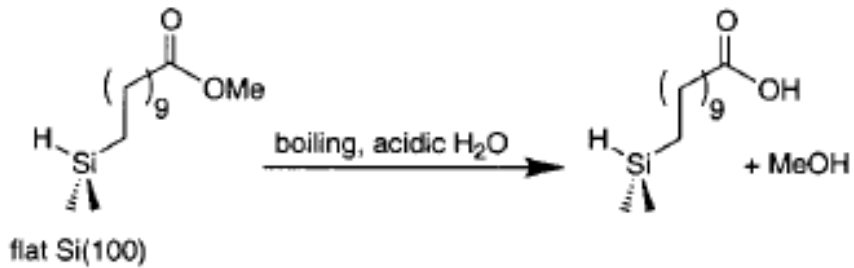
DA 4+2



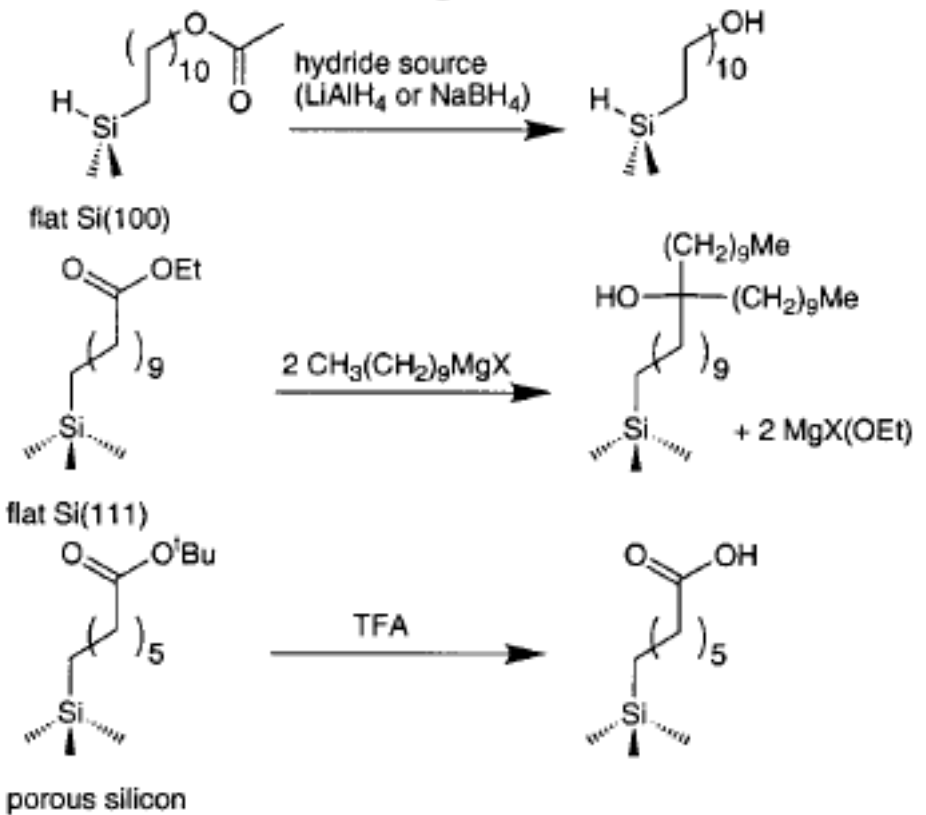
flat Si(100)-2x1

Secondary Chemistry

C. Ester hydrolysis

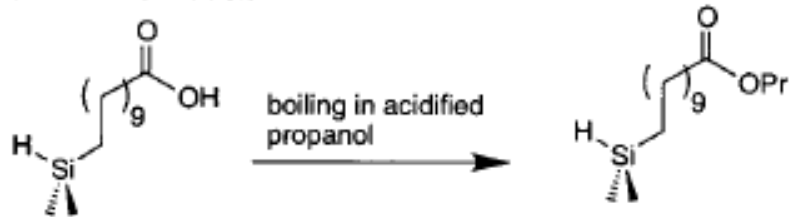


D. Ester reduction and cleavage

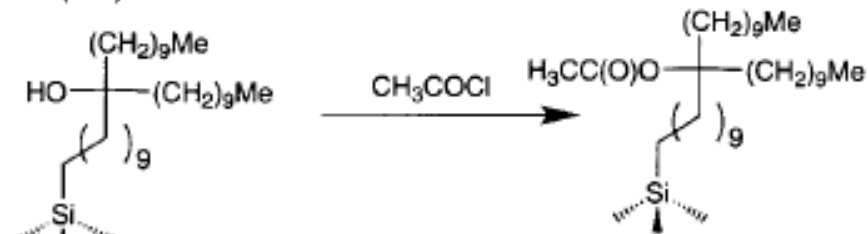


Secondary Chemistry

E. Ester Formation

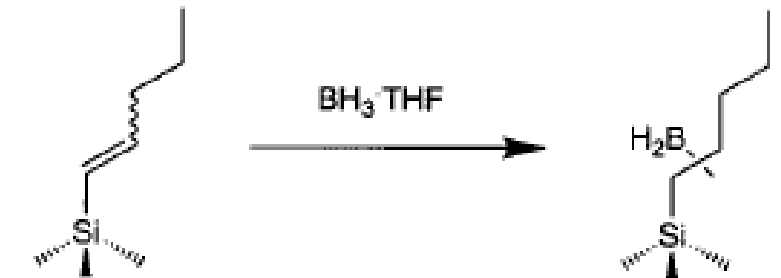


flat Si(100)

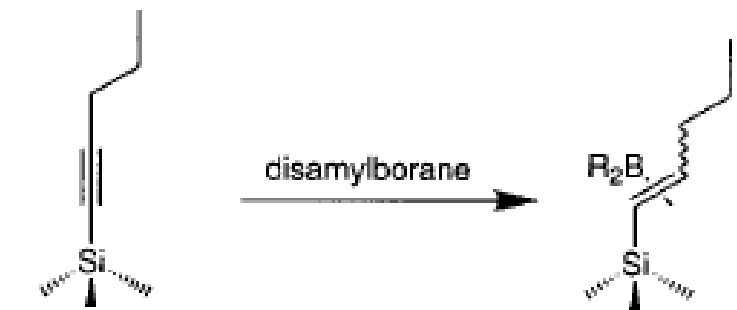


flat Si(111)

F. Hydroboration of olefins

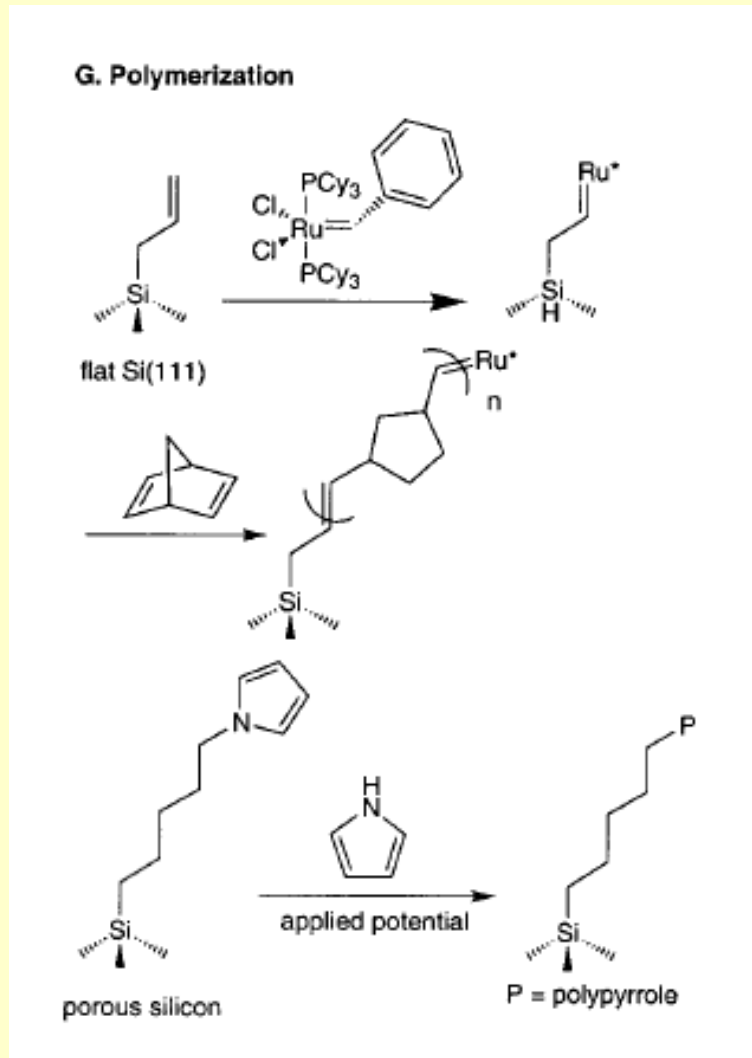


porous silicon



porous silicon

Secondary Chemistry



SELF-ASSEMBLED MONOLAYERS

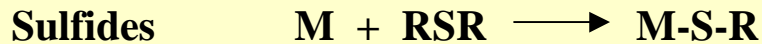
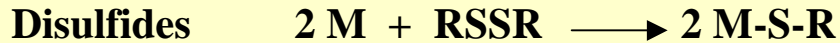
Self-assembly: spontaneous organization of molecules into stable, structurally well-defined aggregates

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

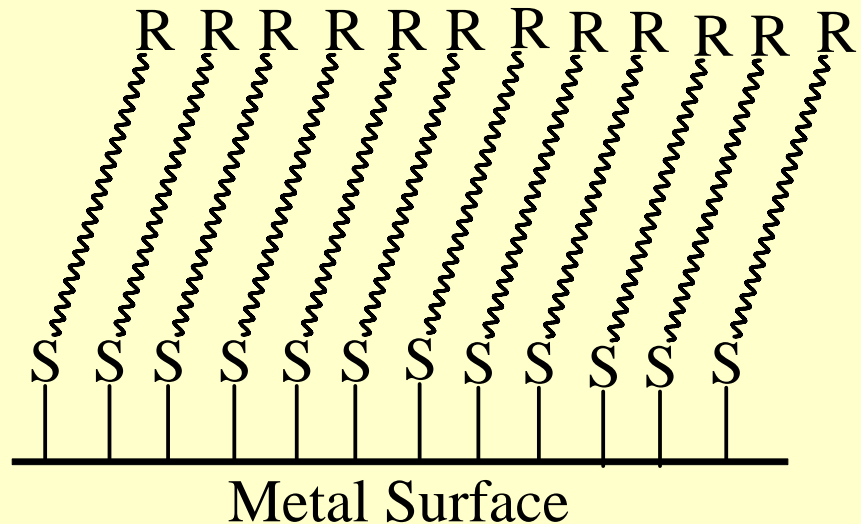


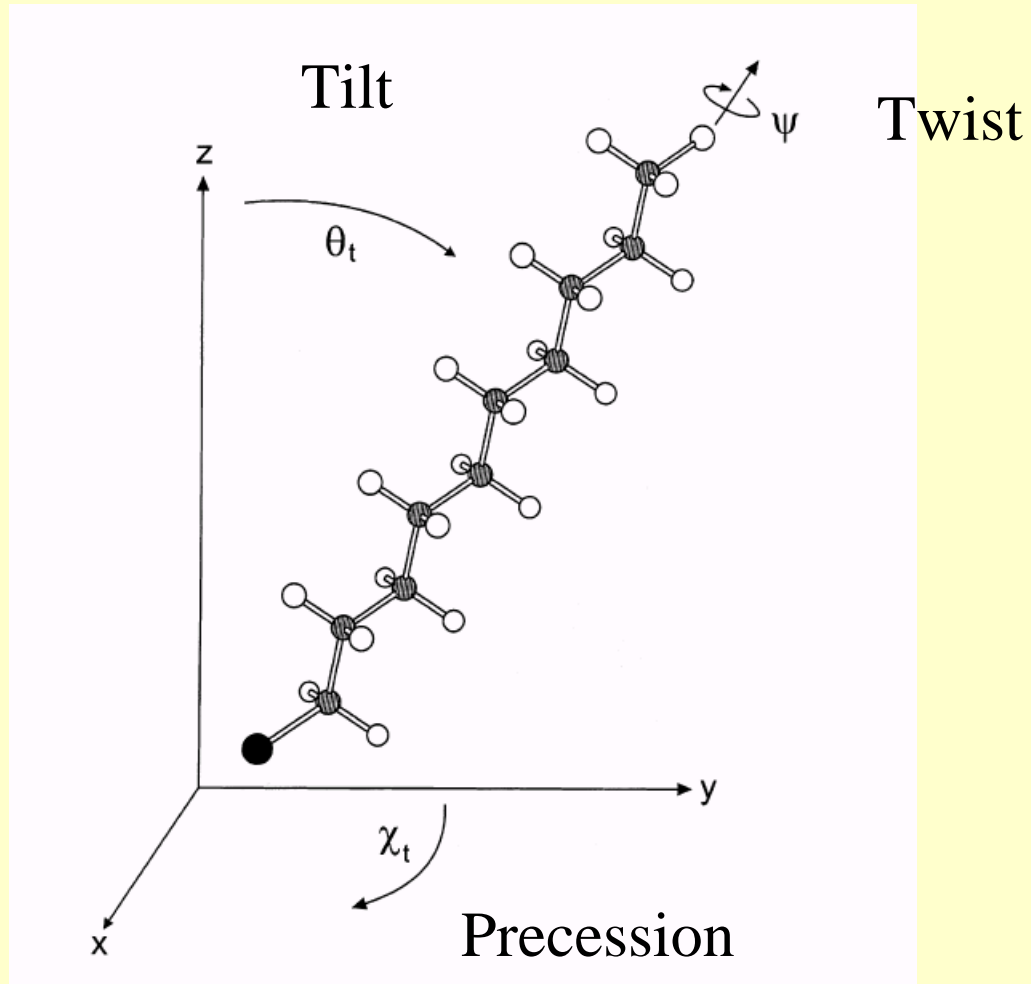
Same products formed in all three reactions: thiolates. RSH are more soluble and react 10^3 faster with Au than RSSR.

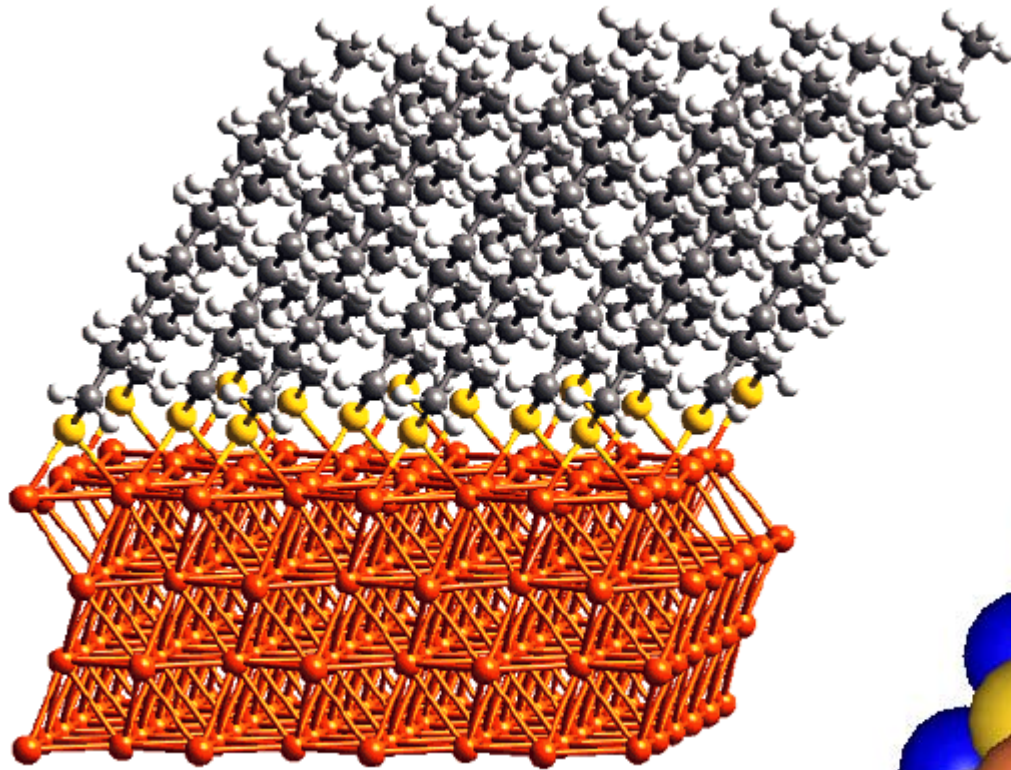
Substrates: gold polycrystalline films
on Si(SiO₂), glass, mica.

Thickness 5-300 nm, sputtering, evaporation

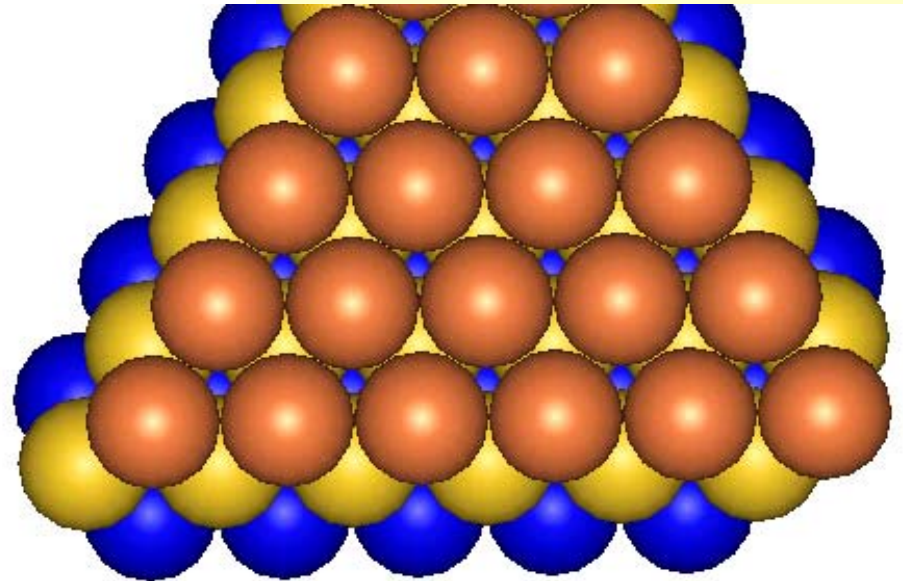
Atomically flat

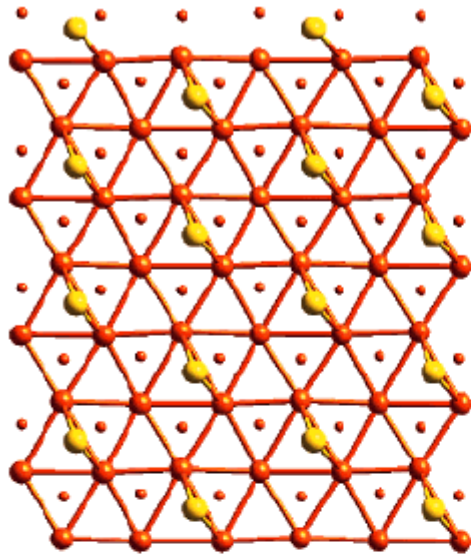




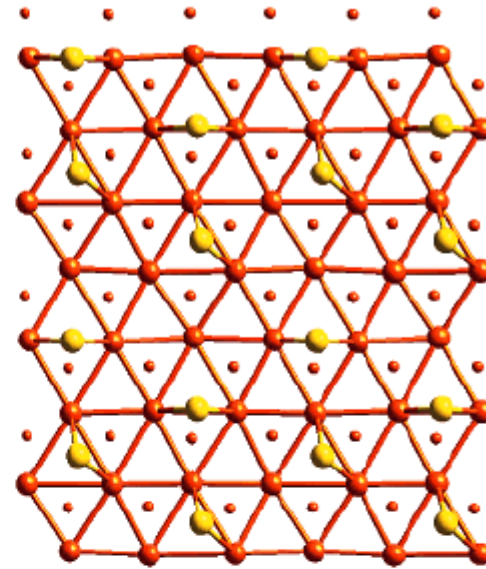


Au surface = ccp





A



A'



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 CH₂

In ^tBuSH and n-C₁₈SH competition reaction, the linear alkyl thiol binds 300 – 700 times better.

Surface coverage 10¹⁴ molecules per cm²

C₁₆ chain length ~2.2 nm, 32-40° tilted, all-trans

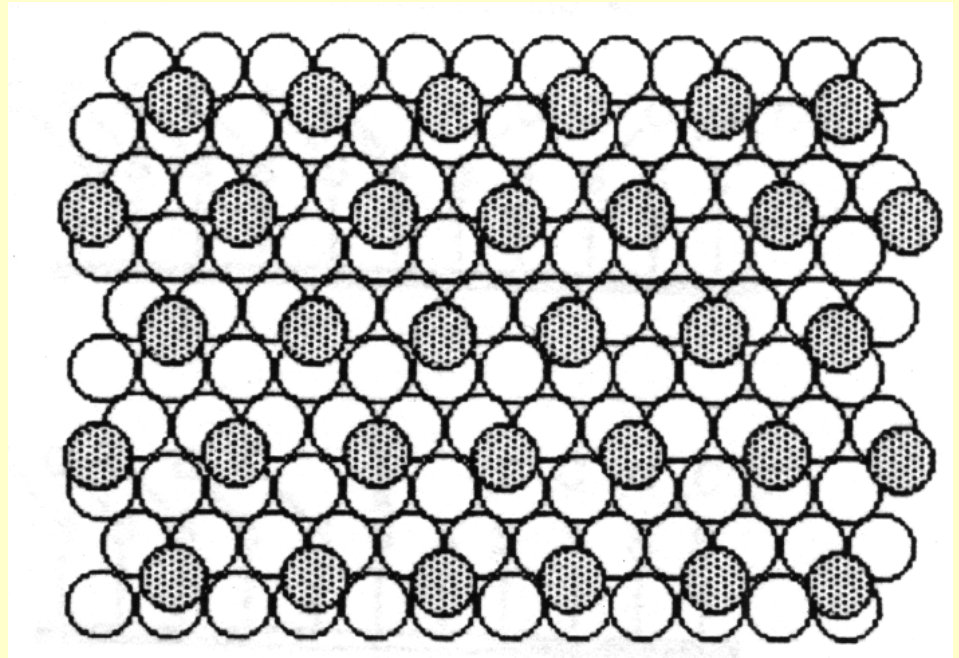
Chemical stability: Cu/C₁₈SH sustains HNO₃

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)



$\text{Au} - \text{S} - \text{C} = 180^\circ$, sp
 $\text{Au} - \text{S} - \text{C} = 104^\circ$, 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 Å² 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 μ M ~ 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



$\text{X} = \text{CH}_3, \text{CF}_3, \text{OH}, \text{NH}_2, \text{SH}, \text{COOH}, \text{COOR}, \text{CN}, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CH},$
 $\text{Cl}, \text{Br}, \text{OCH}_3, \text{SO}_3\text{H}, \text{SiMe}_3, \text{ferrocenyl}, \dots$

Microfabrication

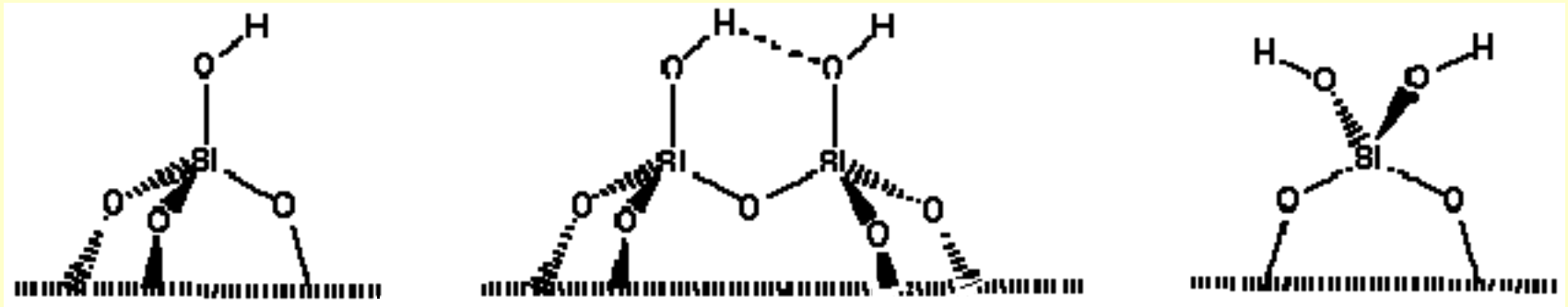
- ♠ Self-assembly, at thermodynamic minima, rejects defects, high degree of perfection.
- ♠ Dimension in the range 1 nm to 1000 μm , too large for chemical synthesis, too small for microlithography.
- ♠ High efficiency, spontaneous.

SiO₂ Surfaces

SiO₂ Surfaces

native oxide on Si
silicagel

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



isolated

vicinal

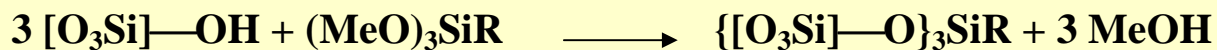
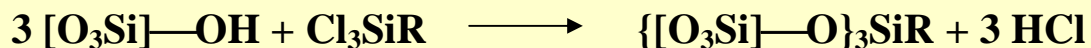
geminal

SiO₂ Surfaces

[O₃Si]—OH stands for the siliceous surface

1. Grafting

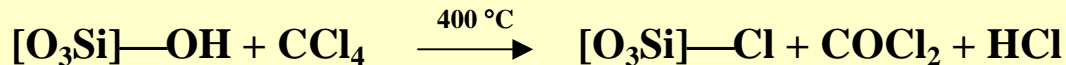
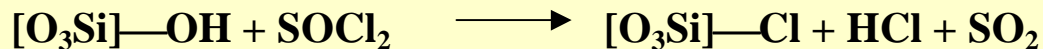
Reactions with trifunctional reagents, such as alkyltrichlorosilanes and trialkoxyalkylsilanes, lead to the three-fold attachment of the SiR groups.



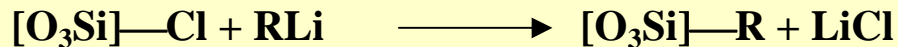
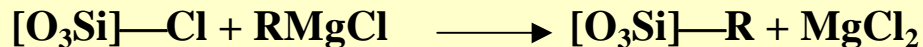
SiO₂ Surfaces

2. Chlorination/Displacement Method

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



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



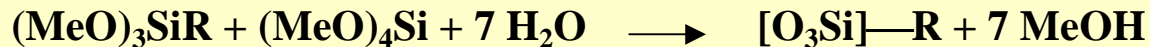
SiO₂ Surfaces

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)

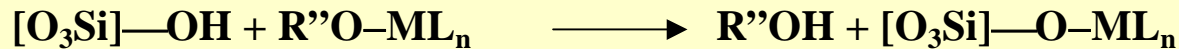
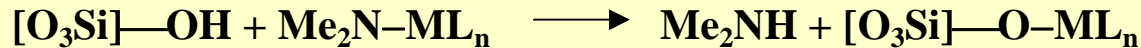
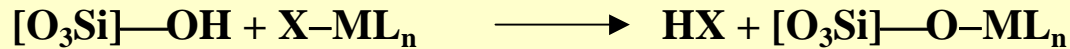
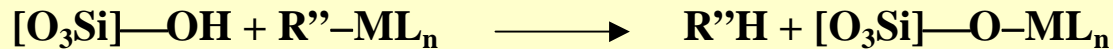
A thin layer of a hybrid (organically modified) silica gel can be deposited on the silica surface from a solution of TEOS and (MeO)₃SiR by controlled hydrolysis and condensation.



SiO₂ Surfaces

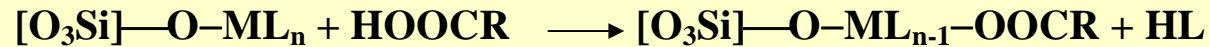
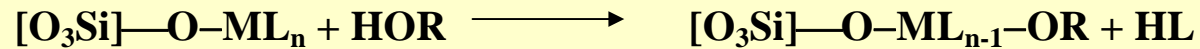
5. Organometallic modification method

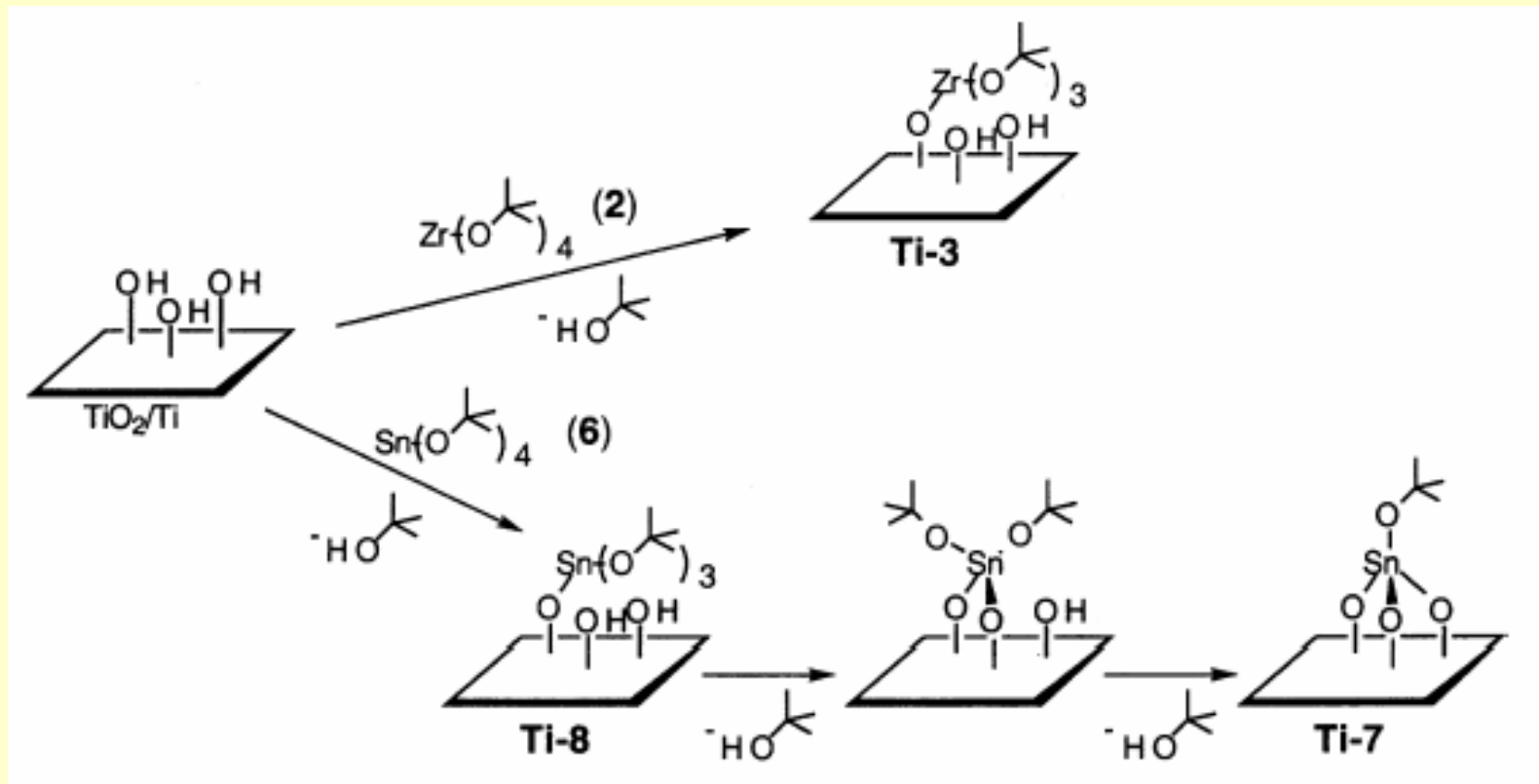
Organometallic reagents, such as metal alkyls, halides, amides, and alkoxides can be used to deposit a monolayer of metal complexes on the surface (ML_n stands for an organometallic group, M for a metal, L for a ligand, R'' for a short alkyl chain, X for halogen).



SiO₂ Surfaces

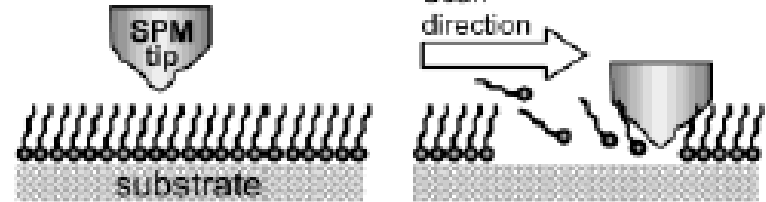
These organometallic moieties can serve as attachment points for further modification with long chain alcohols, thiols, carboxylic acids, phosphates, and diketonates.



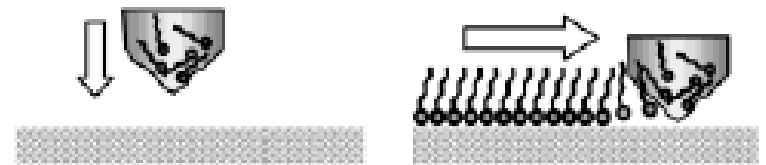


Manipulations with SAM

A. Elimination



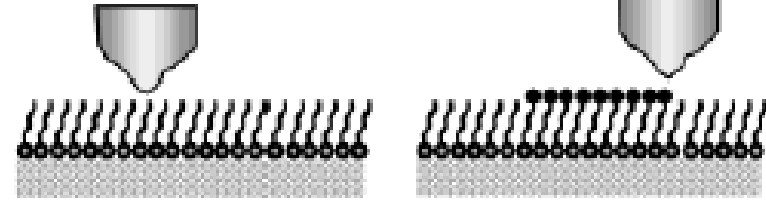
B. Addition



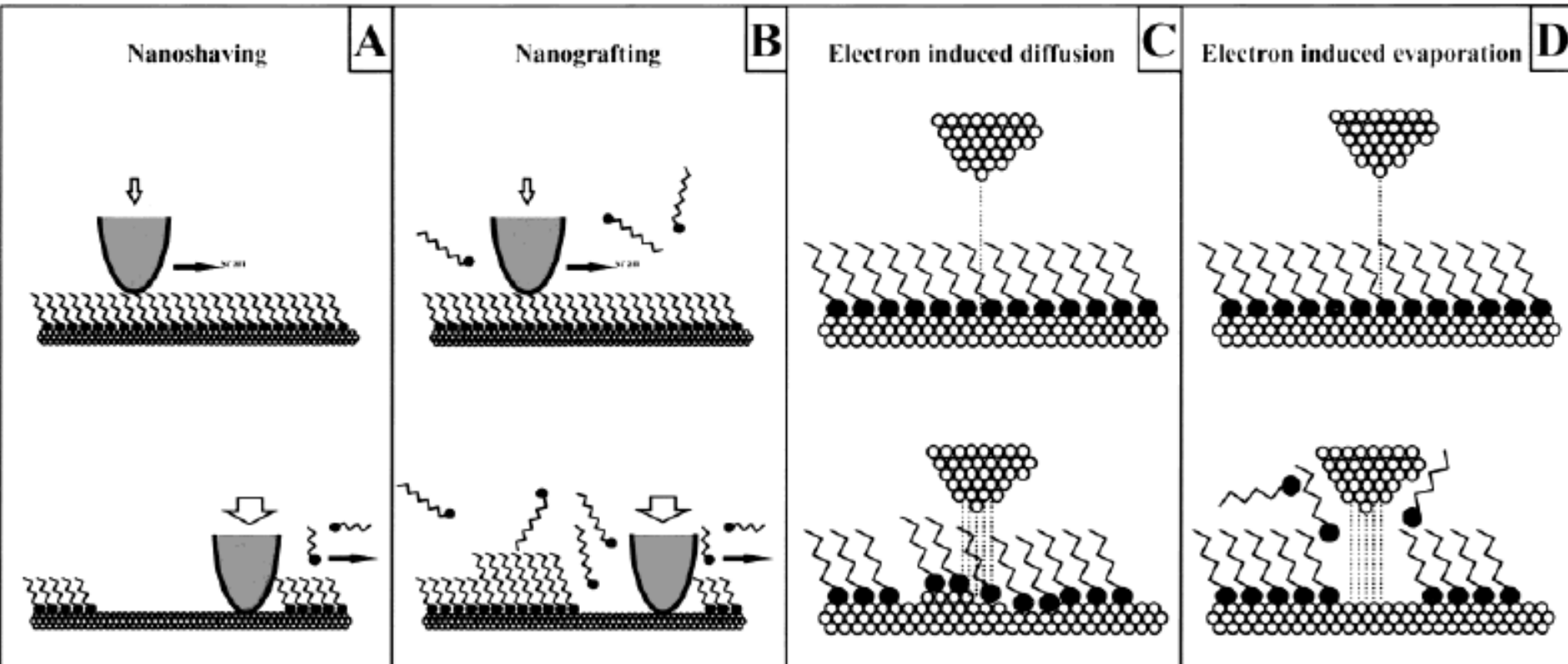
C. Substitution via *in-situ* addition



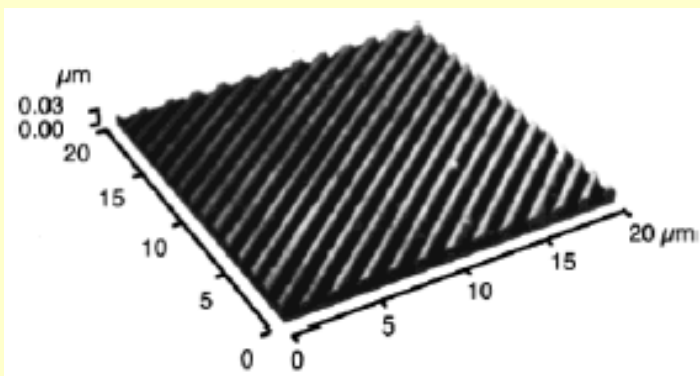
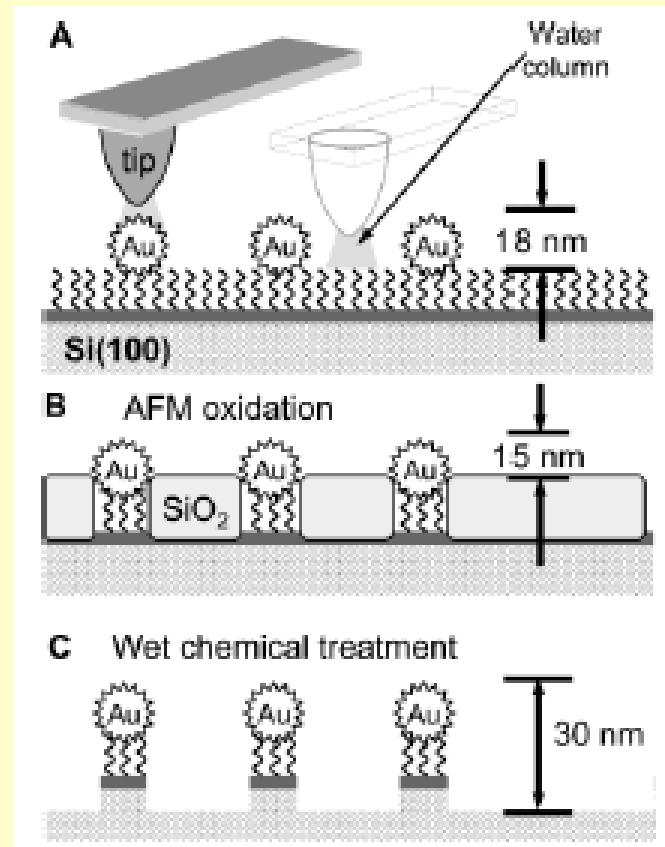
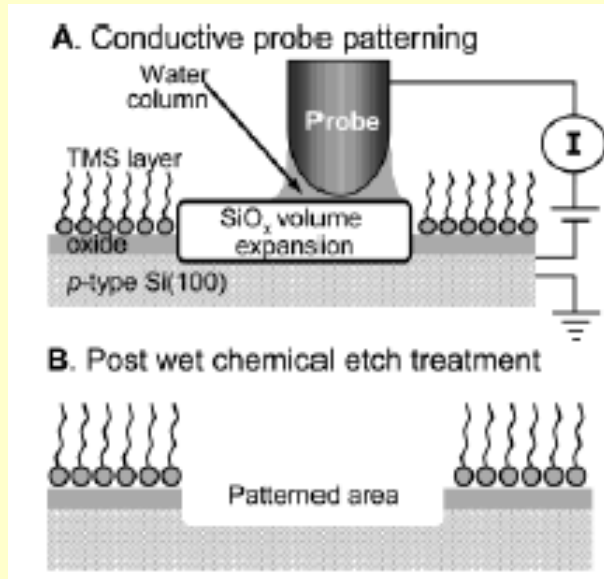
D. Substitution via terminus modification



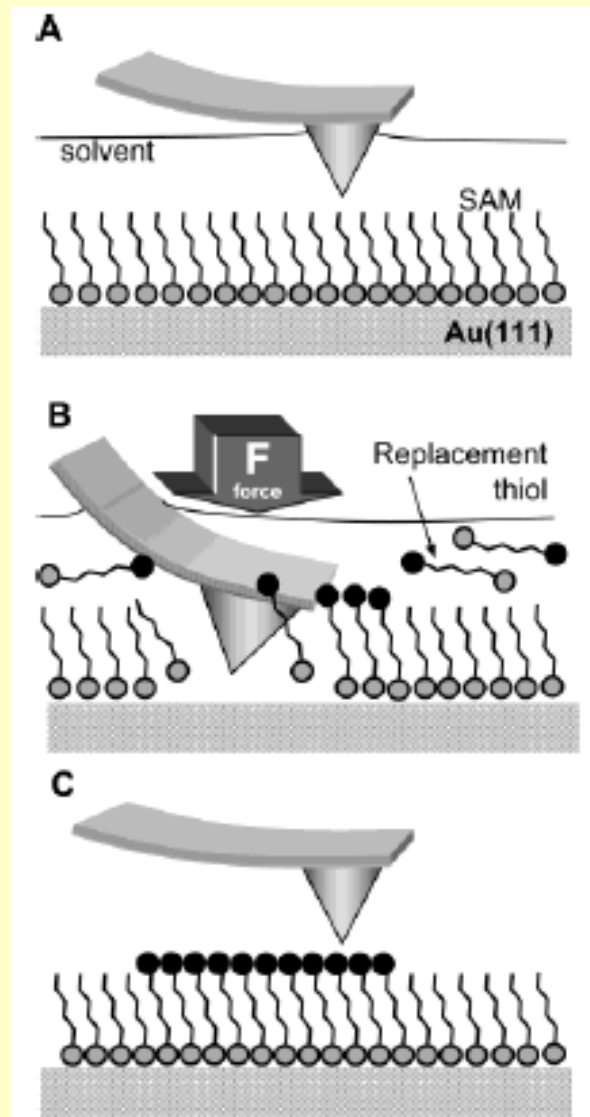
Manipulations with SAM



Manipulations with SAM



Manipulations with SAM



Manipulations with SAM

