Synthesis 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

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 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: Si (100) vs. (111)

Form: supported or unsupported, nature of substrate

Surfaces

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

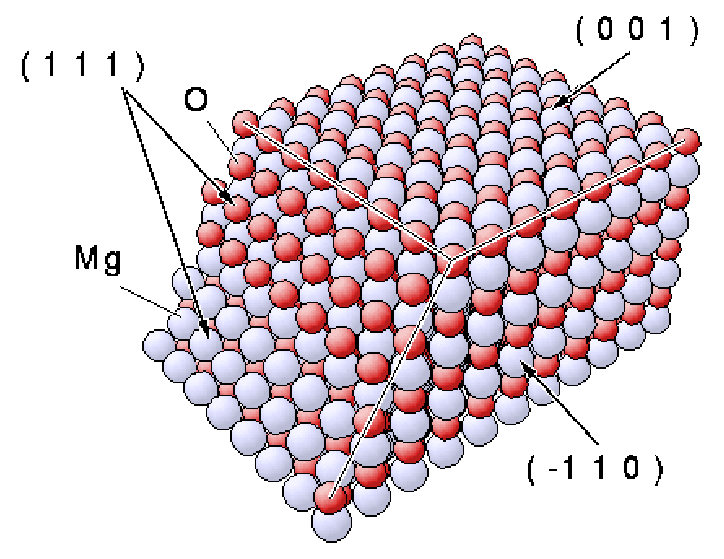
Same for liquids, different for solids

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

Surface Energy

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

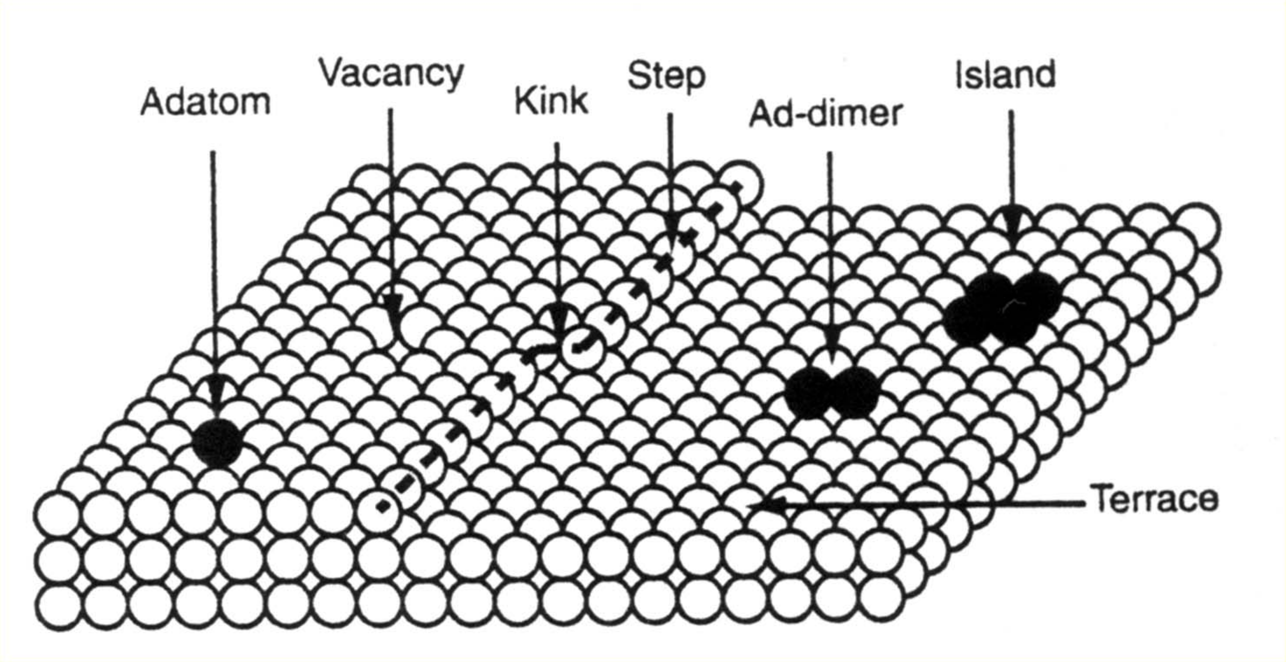


Cubic (rocksalt) MgO crystal: different netplanes

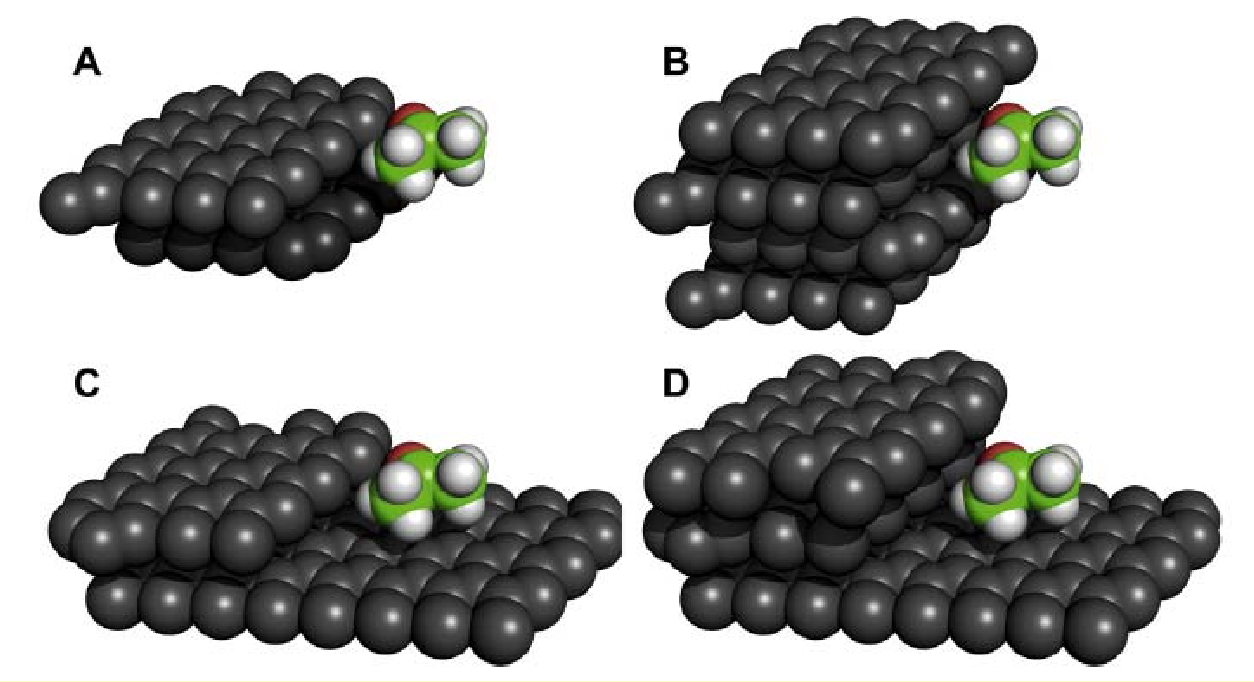
Surfaces

The TSK (TLK) Model of a Surface (Kossel/Stranski)

Terrace
Step/Ledge
Kink
Vacancy
Adatom
Island

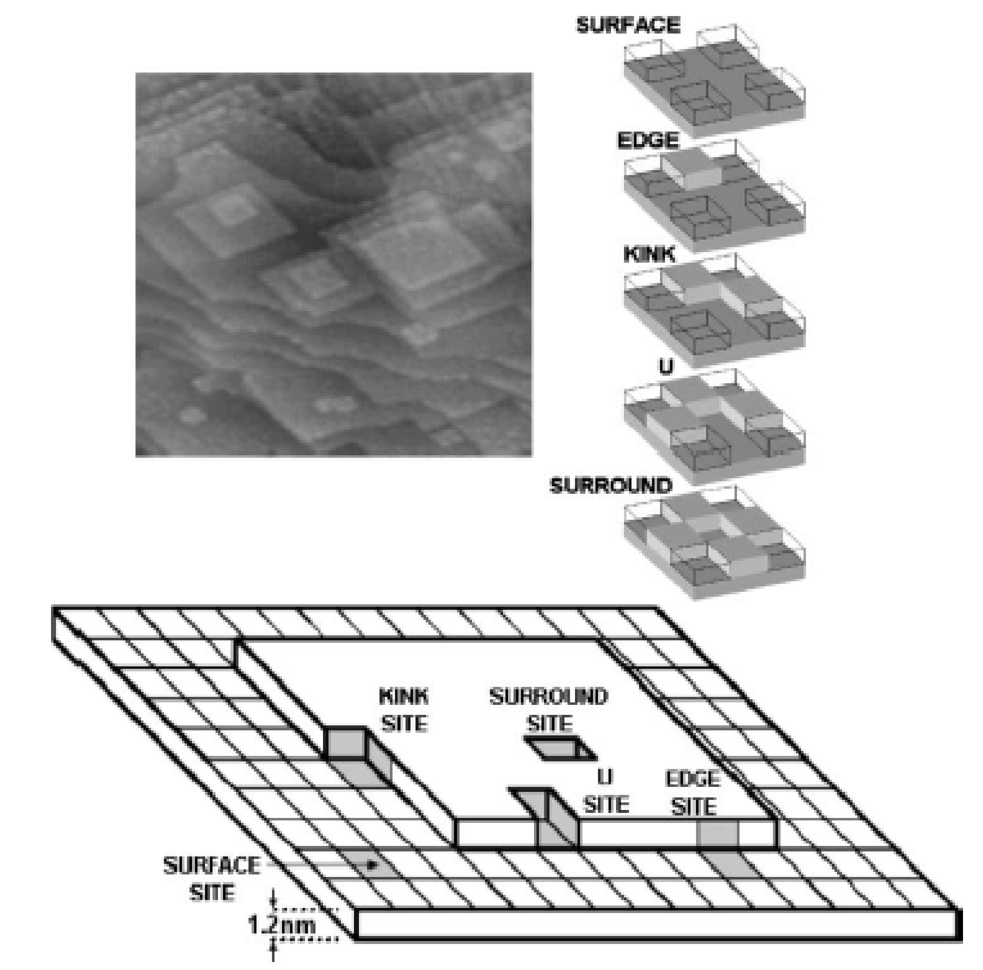


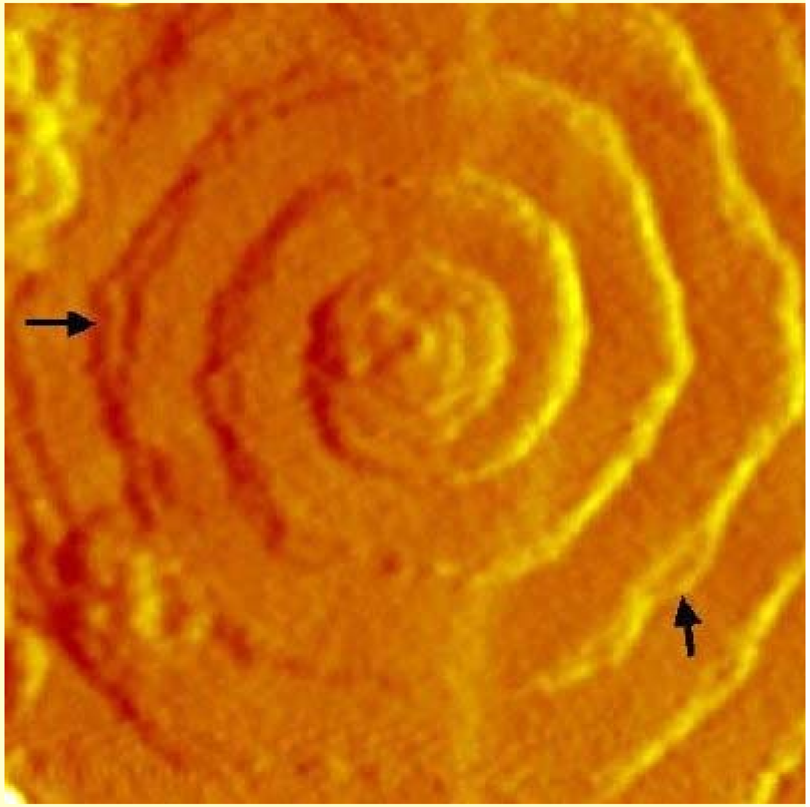
Surfaces



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

- **Stranski–Krastanov growth** - an intermediary process, both 2D layer and 3D island growth, transition from the layer-by-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

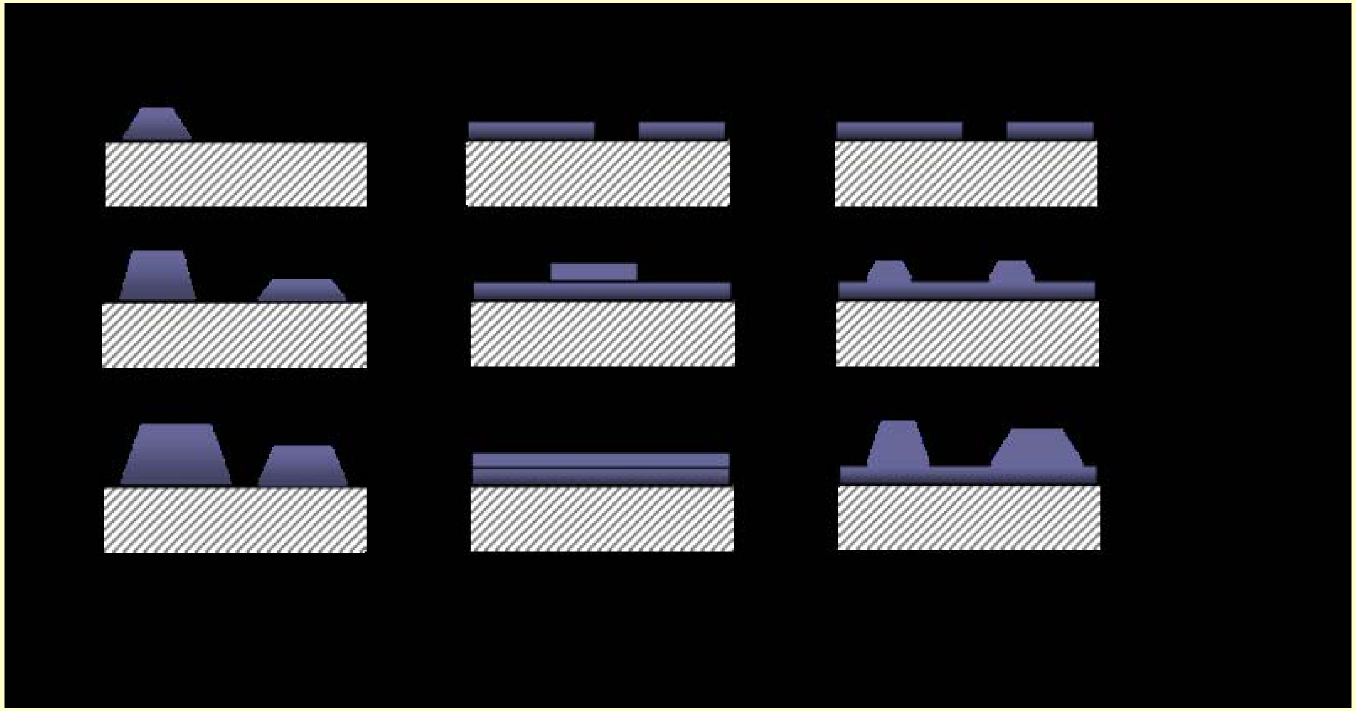
Thin-film growth mechanisms

VW
(island)

FM
(layer-by-layer)

SK
(layer-plus-island)

surface coverage, Θ

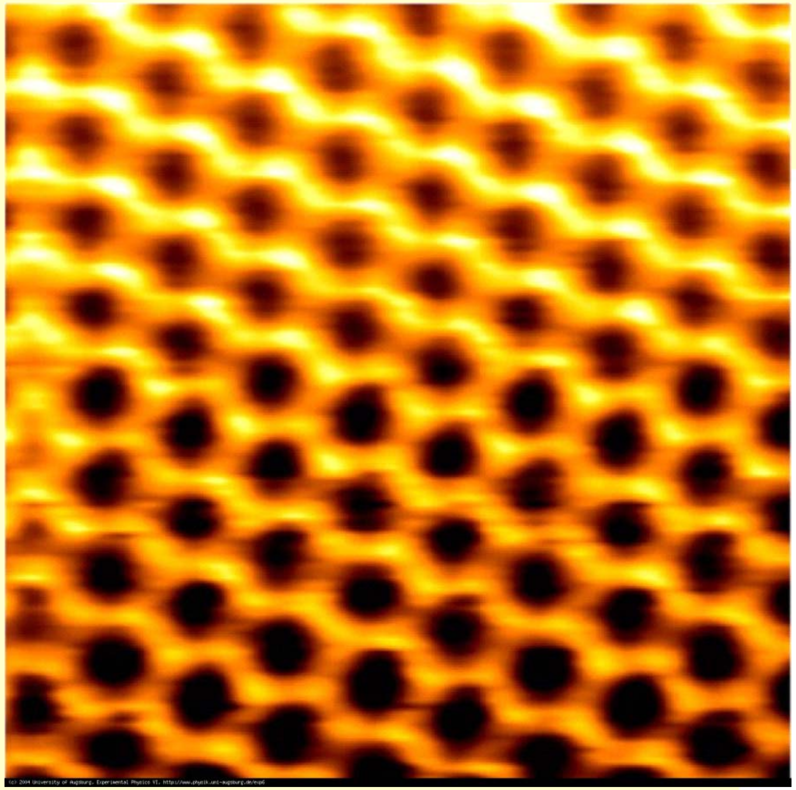


$\Theta < 1$ ML

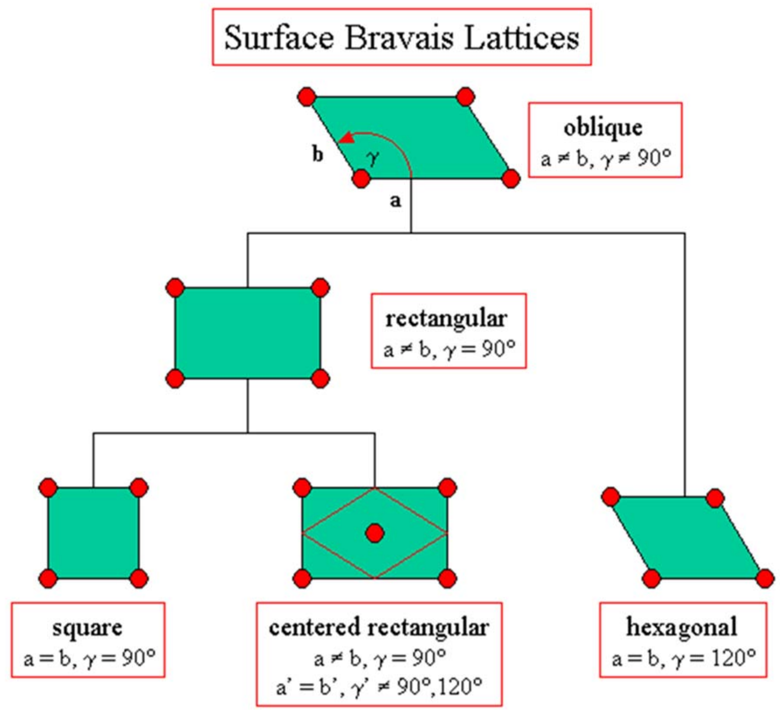
$1 < \Theta < 2$

$\Theta > 2$

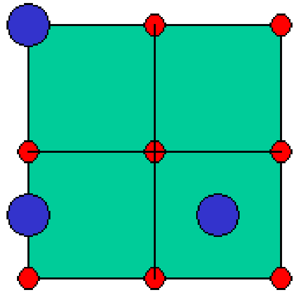
Symmetry at Surfaces



AFM of C atoms within the hexagonal graphite unit cells. Image size 2×2 nm^2.



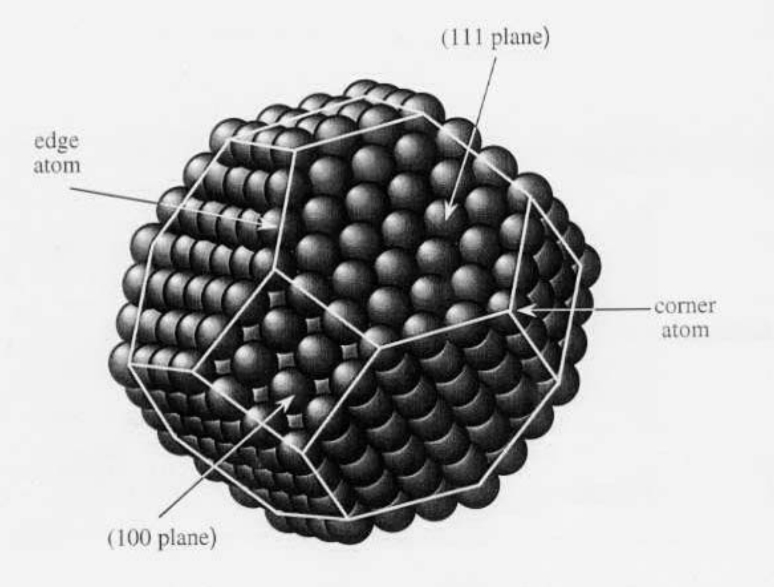
Absorption Sites

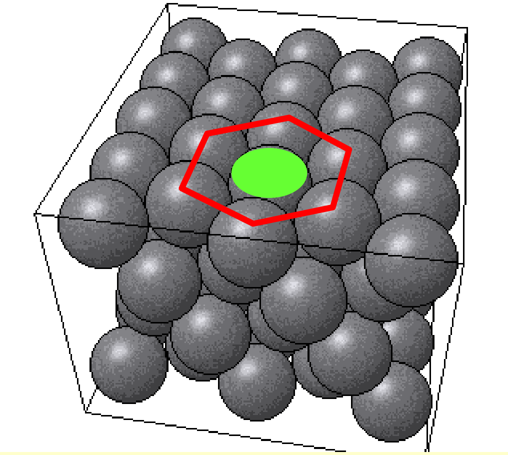


on top

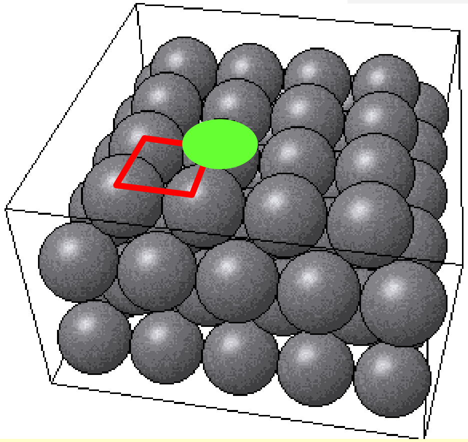
bridge

4-fold hollow

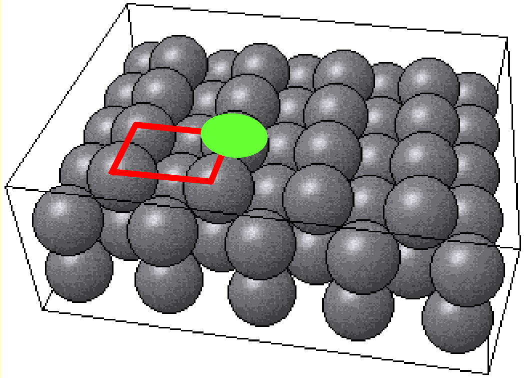




(111)



(100)



(110)

Surface Diffusion

Surface diffusion coefficient D

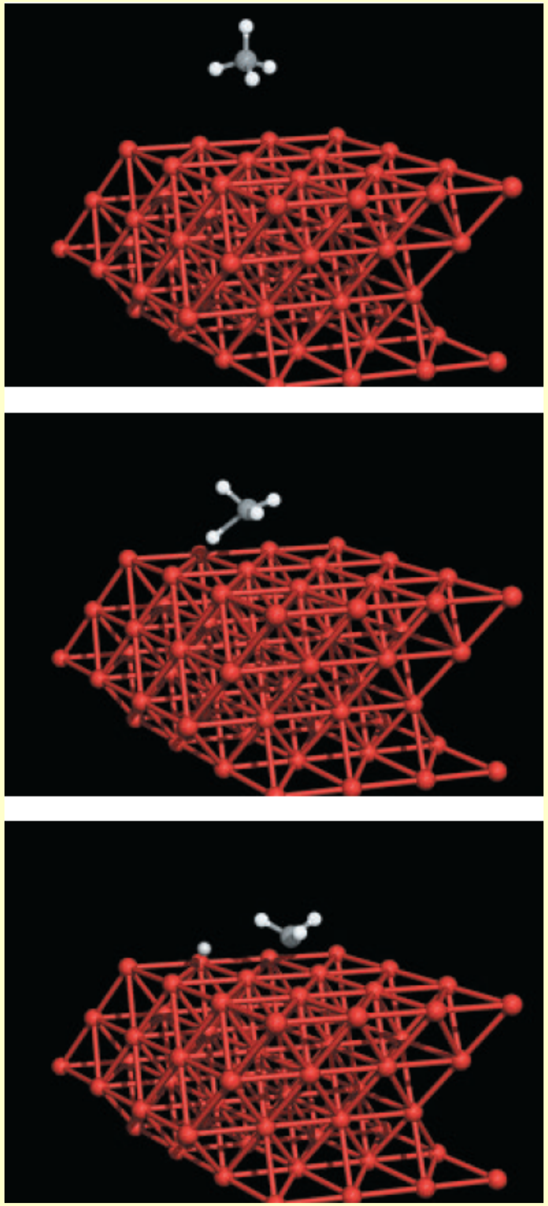
$D = a^2 k_s$ **a … effective hopping distance between sites**

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

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

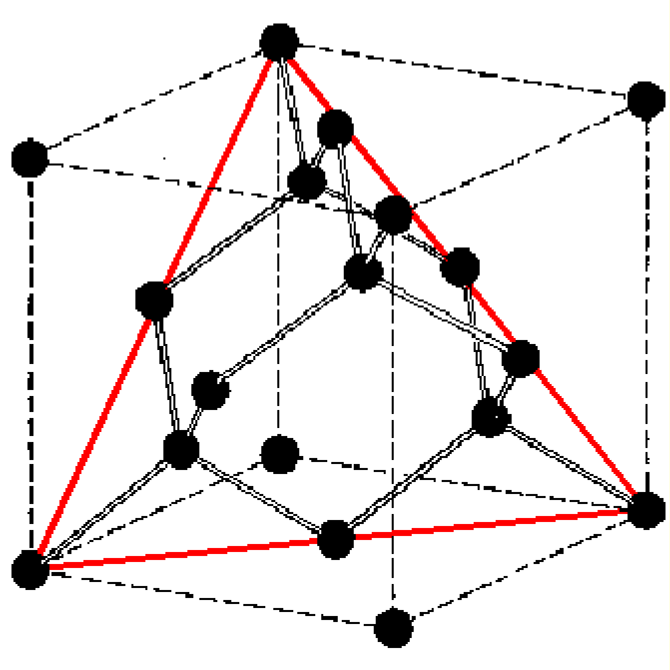
T … substrate temperature

Higher temperature = Faster 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

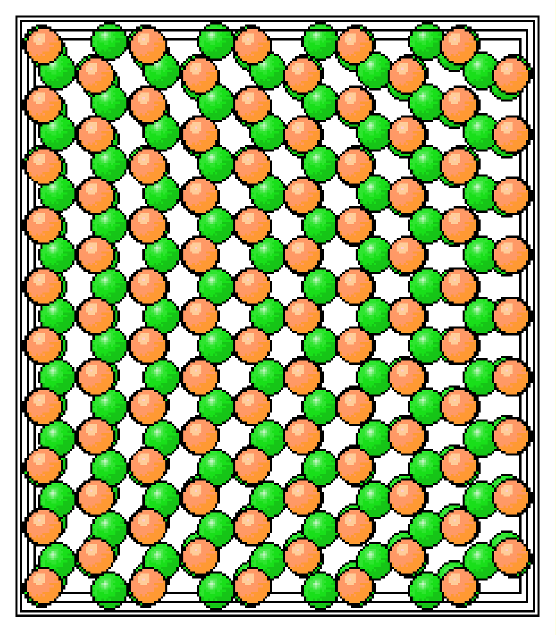
Si(111) = a set of atomic planes

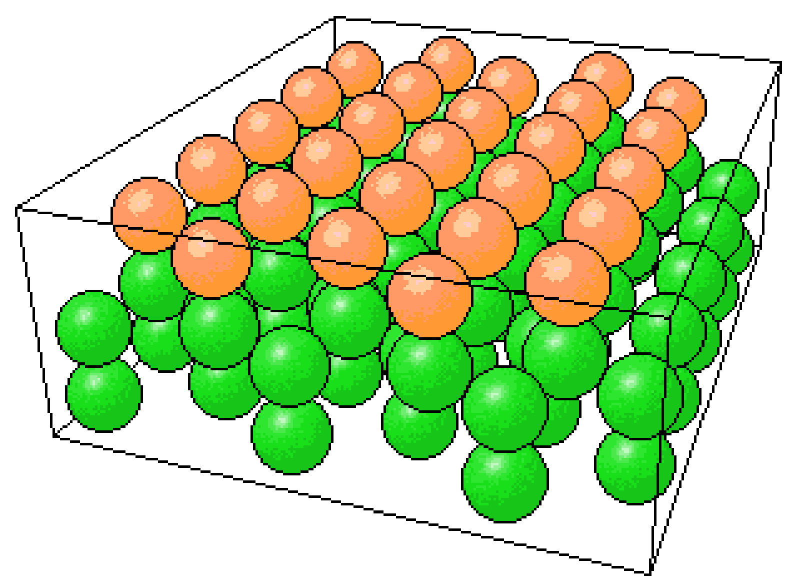
One plane outlined with red

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

Si(111) Surface

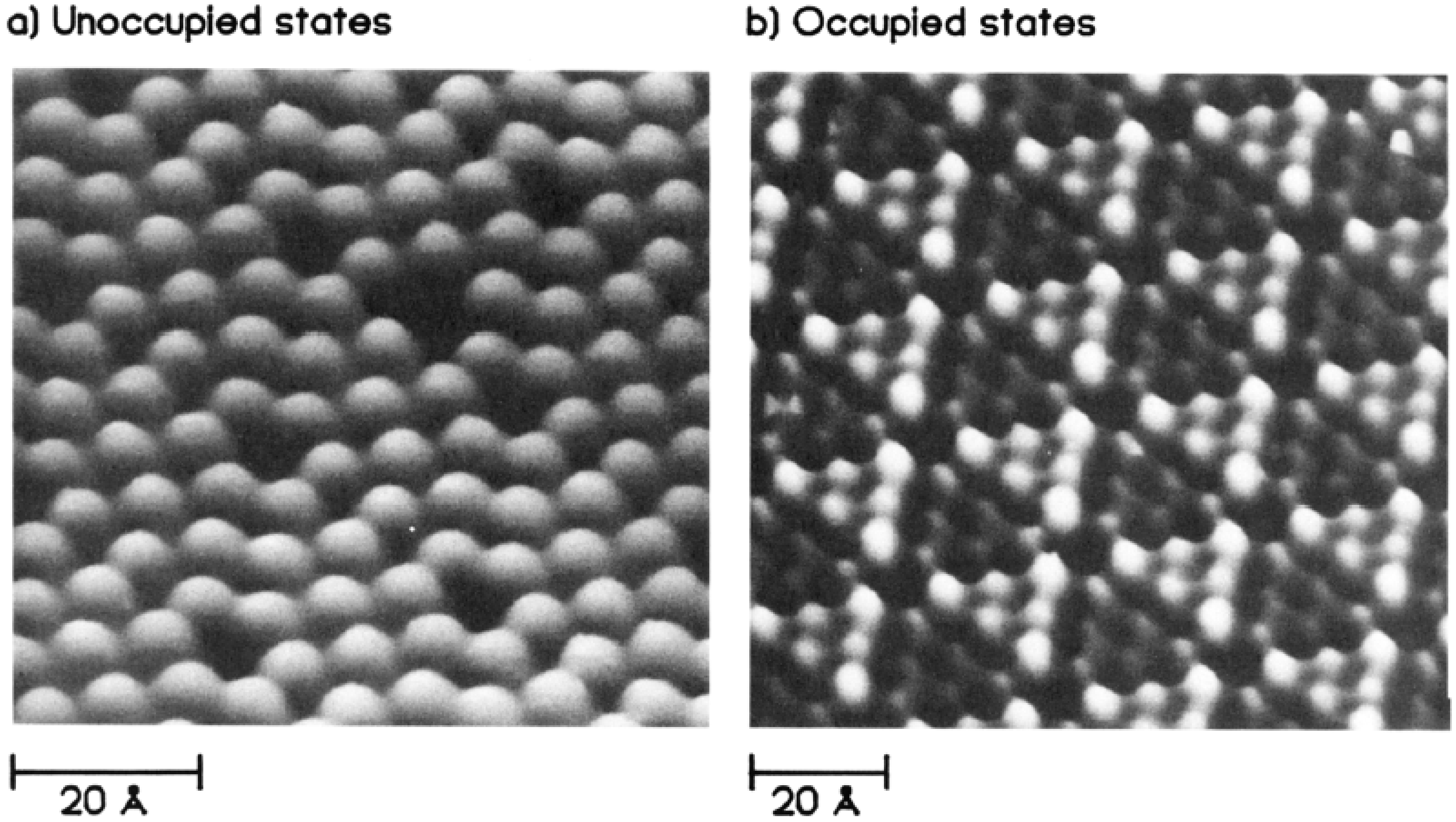
A top view of the atomic arrangement for the (111) plane





orange = the top layer
green = deeper layers

Si(111) Surface



a) Unoccupied states

b) Occupied states

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

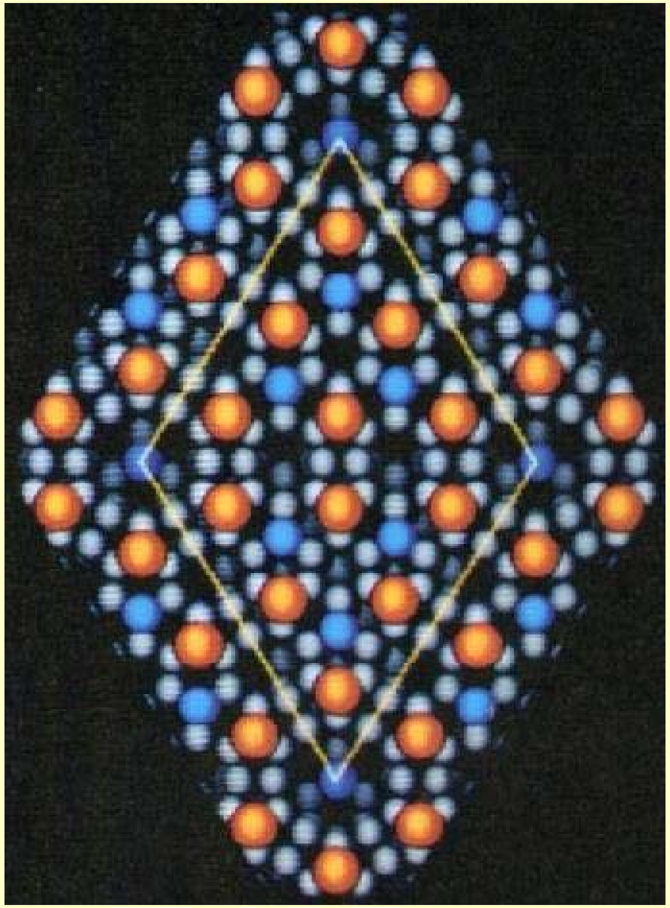
Relaxation = energy lowering, no change in symmetry

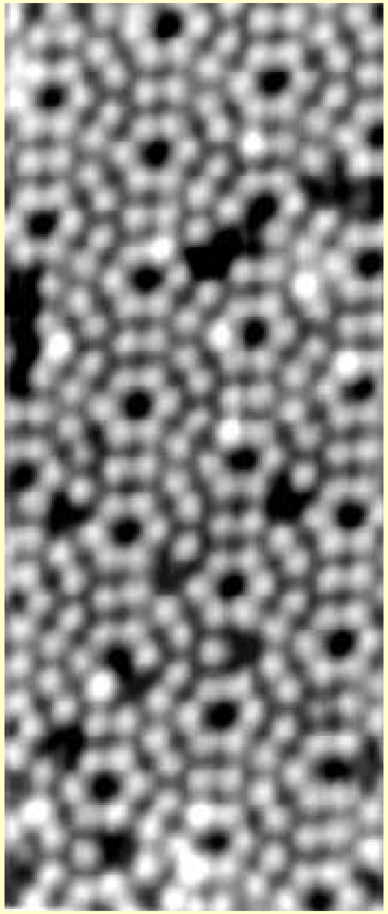
Reconstruction = the surface atoms rearrange to a more energetically stable configuration.

Symmetry lowering
2D symmetry – 17 plane groups / 230 bulk space groups

7x7 Reconstruction

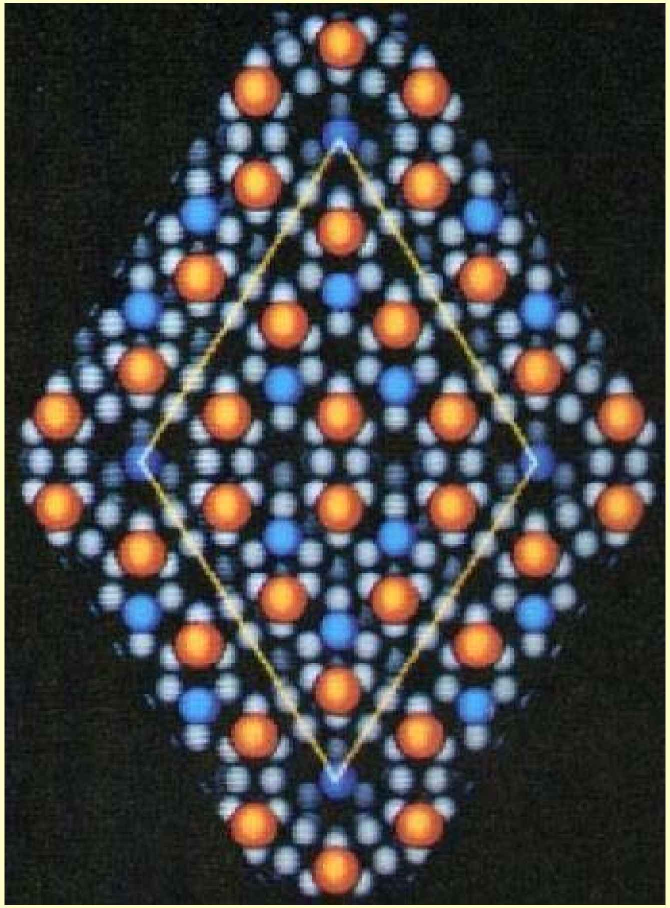
When (111) surface of Si is heated to high temperatures under the Ultra-High Vacuum conditions the surface atoms rearrange to a more energetically stable configuration called 7x7 reconstruction.

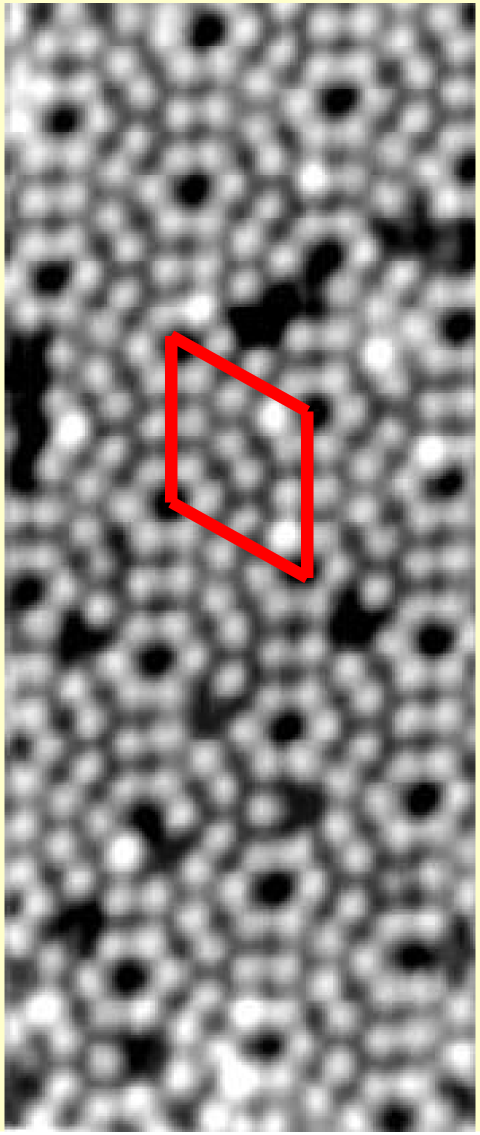




STM image of Si(111) surface

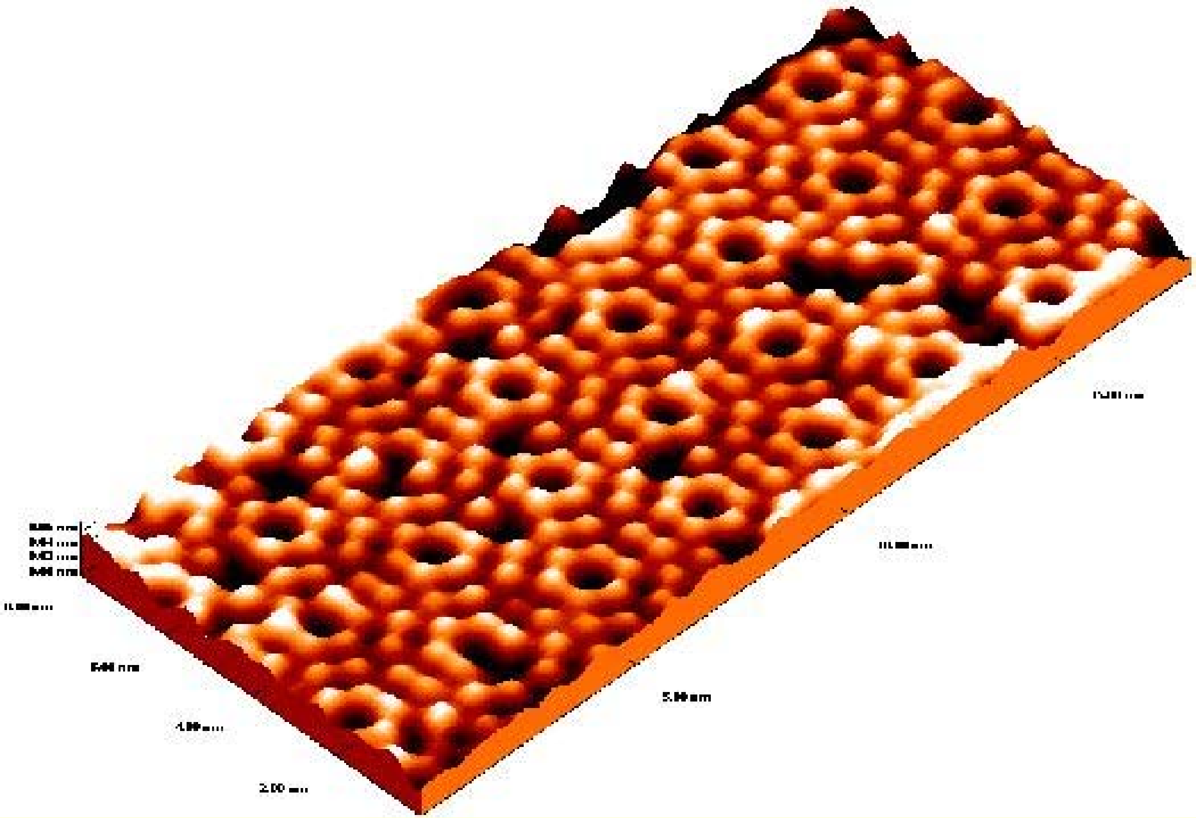
7x7 Reconstruction



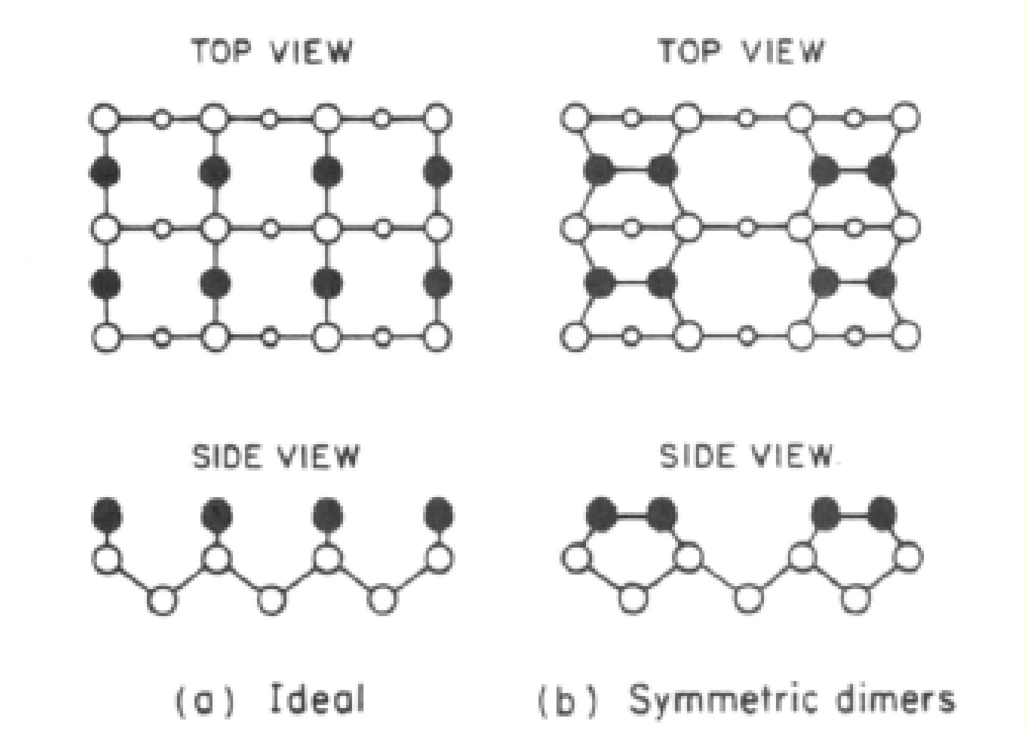


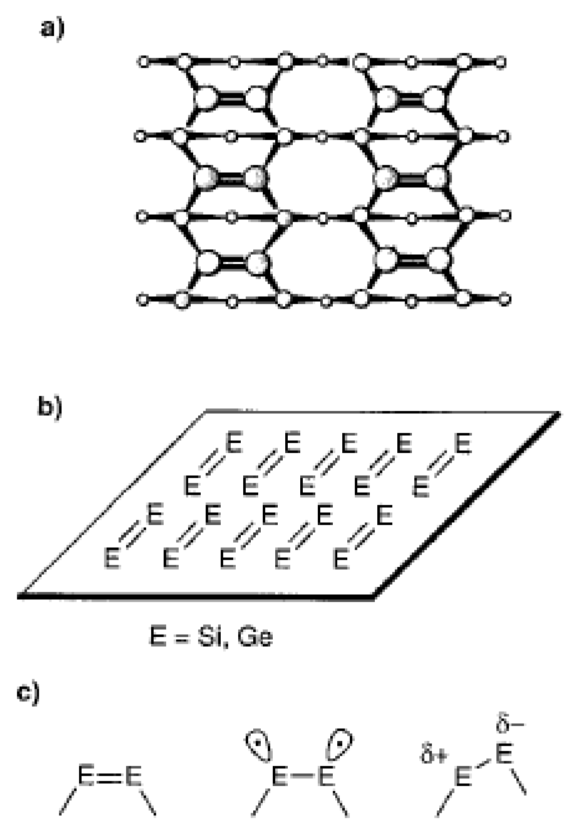
7x7 Reconstruction

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





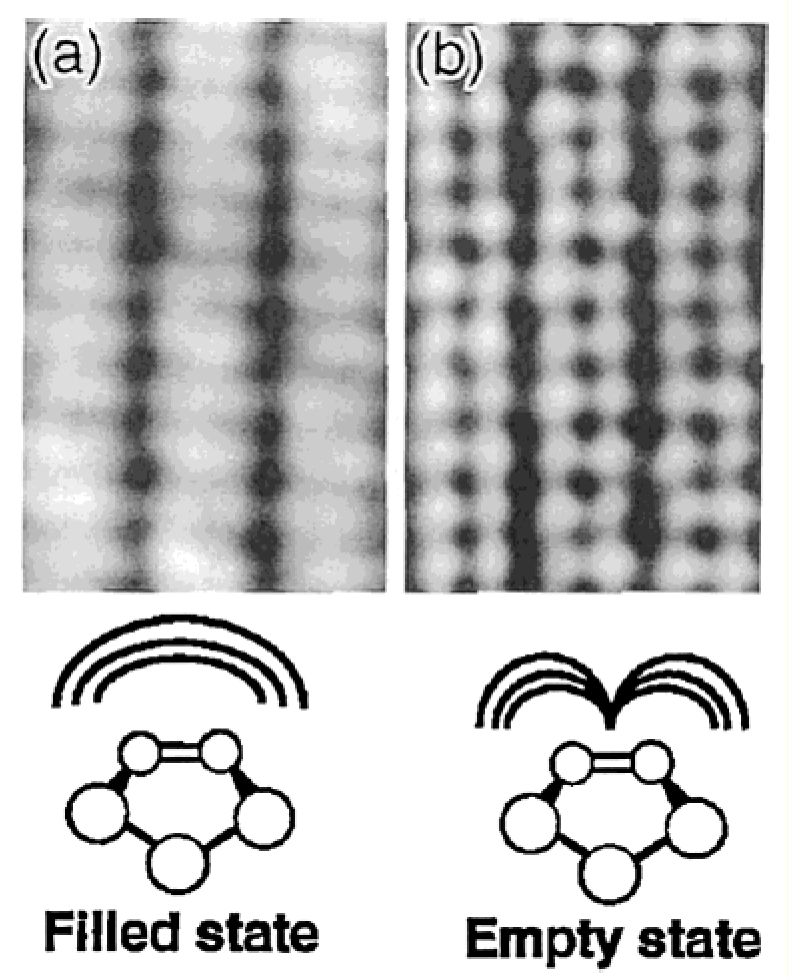
ideal reconstructed

STM images of the silicon-silicon dimers imaged with

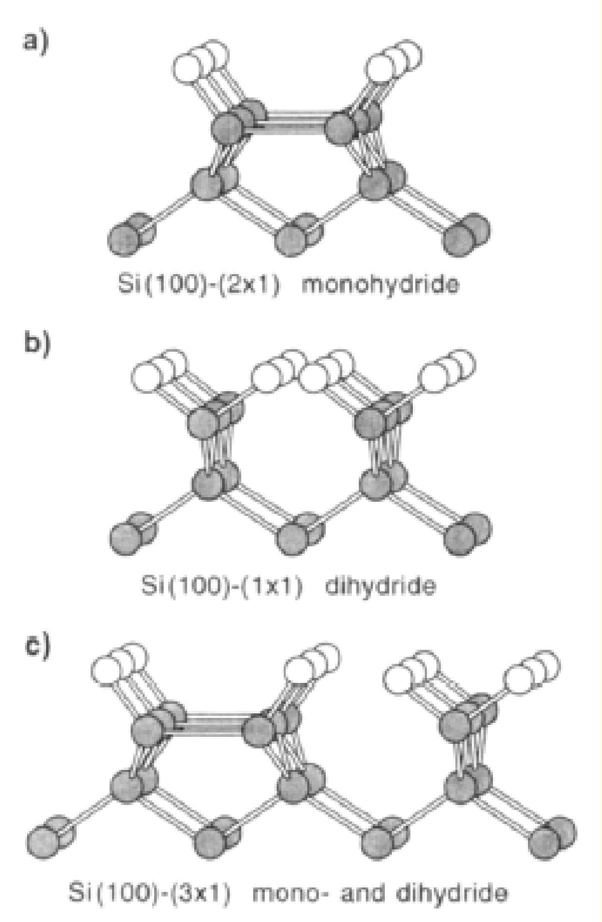
(a) V_{sample} = -2.0 V
(b) V_{sample} = 2.3 V

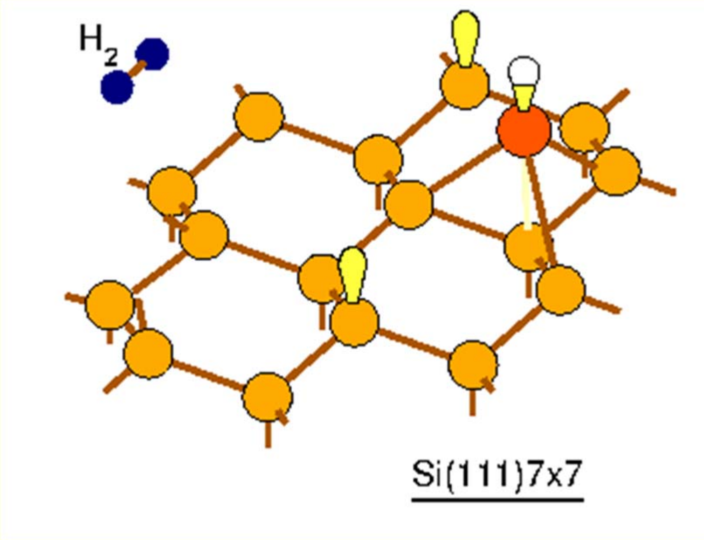
The filled and empty states of these highly ordered dimers can be probed by biasing the surface in the opposite directions

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



H-terminated Si(100) Surface




H$_2$
Si(111)7x7

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

Porous Alumina Films

Example:

Anodic oxidation of aluminum in oxalic or phosphoric acid

$Pt|H_3PO_4, H_2O|Al$

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

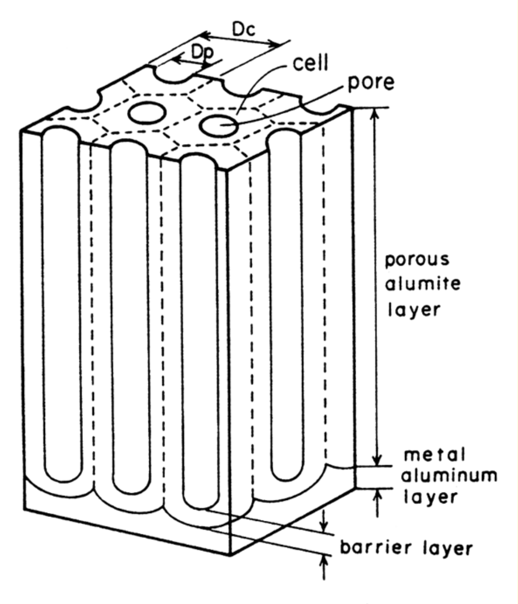
$PO_4^{3-} + 2e^- \rightarrow PO_3^{3-} + O^{2-}$ cathode

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

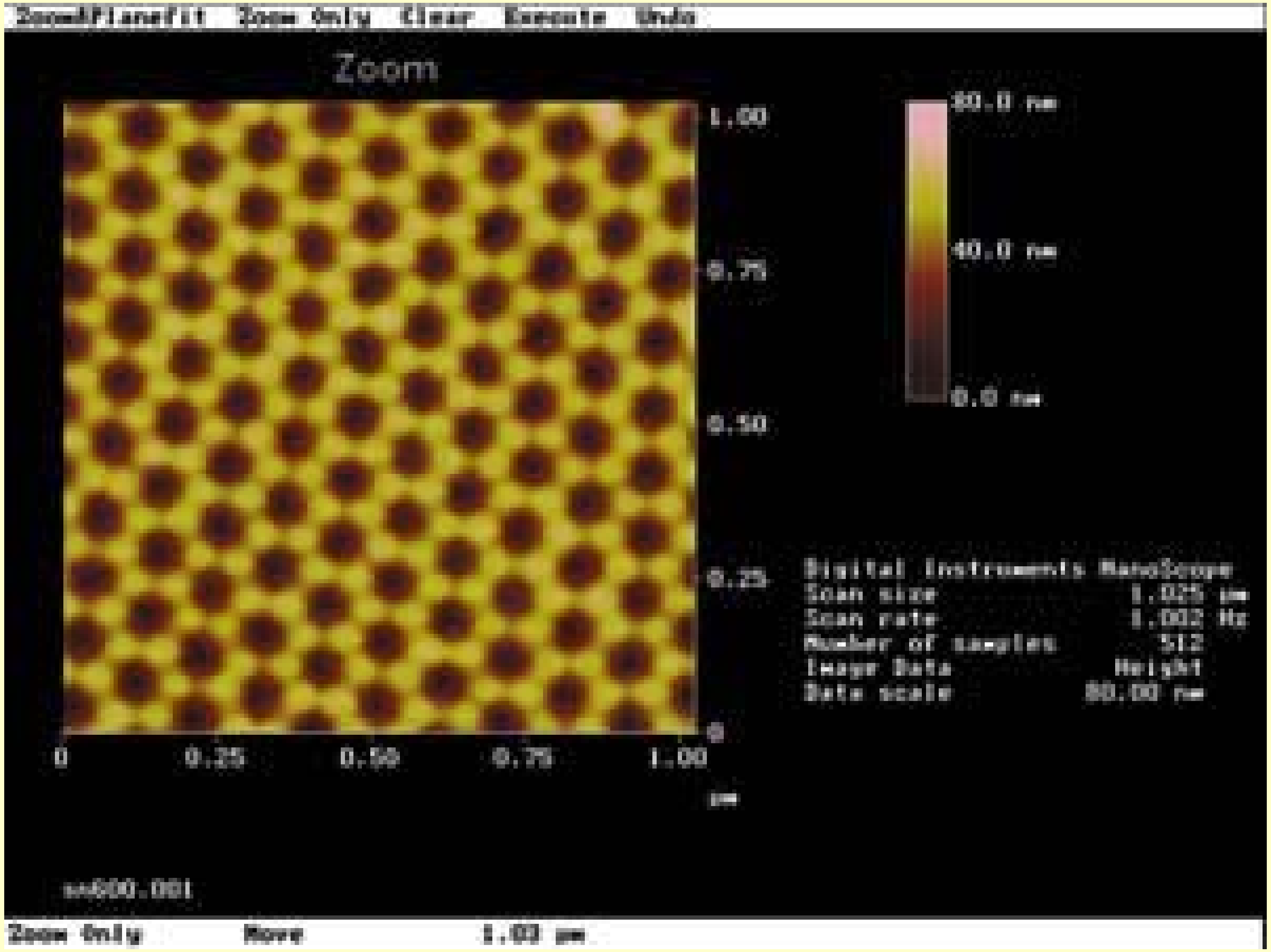
Porous Alumina Films



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

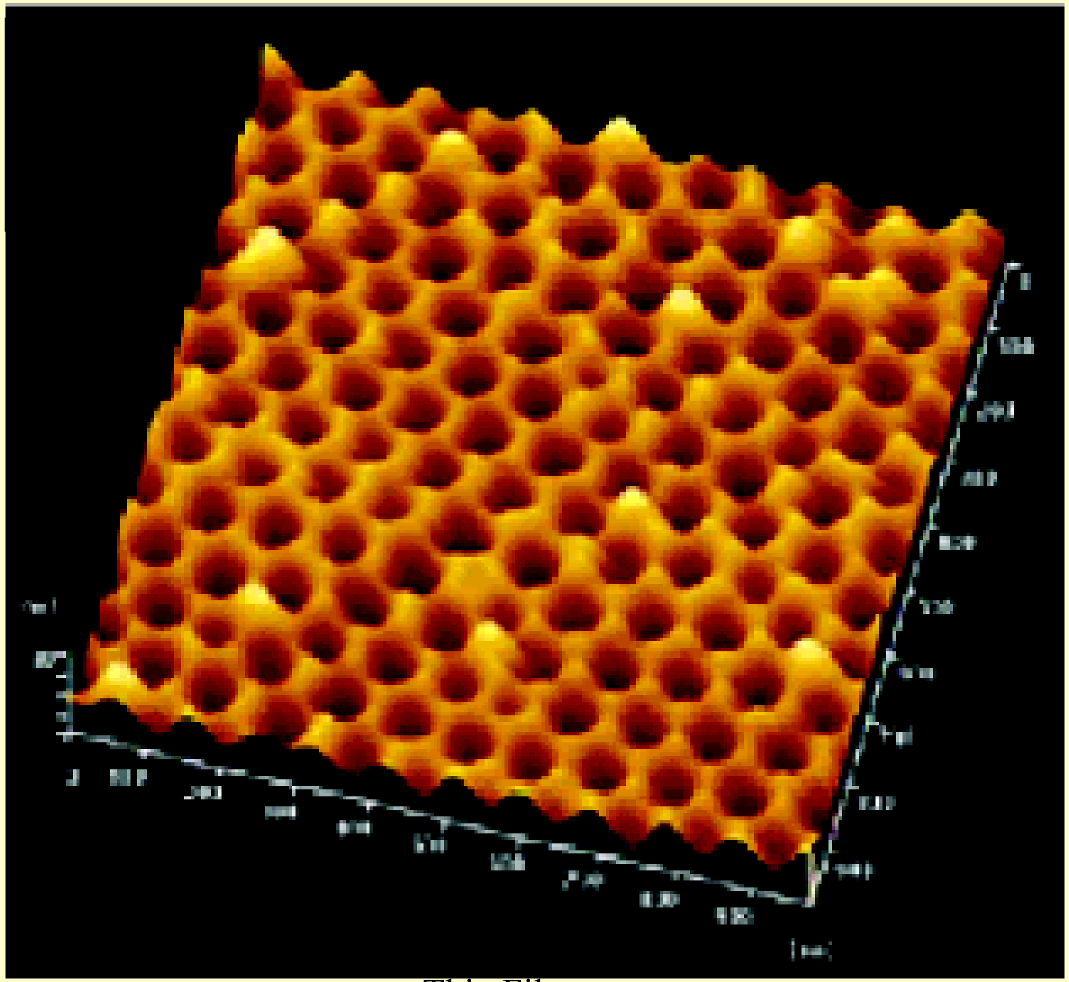
Exceptionally useful process for creating controlled porosity membranes, photonic gap materials, template for synthesizing semiconductor nanostructures, host for synthesizing and organizing aligned carbon nanotubes for high intensity electron emission displays, and last but not least, fuel cell electrode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

AFM Image of Porous Alumina Film

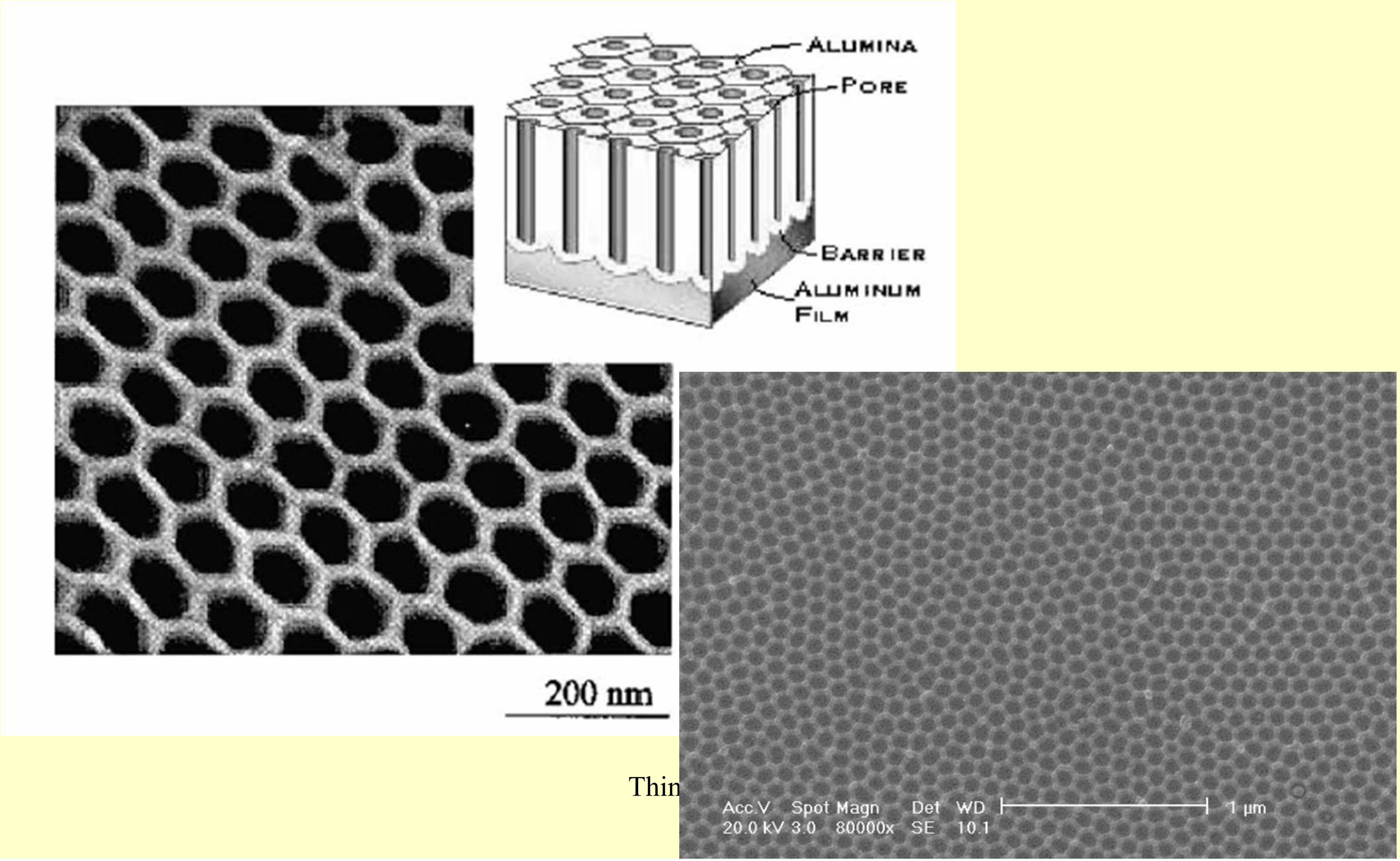


```
Digital Instruments NanoScope
Scan size            1.025 µm
Scan rate            1.002 Hz
Number of samples      512
Image Data           Height
Data scale          80.00 nm
```

AFM Image of Porous Alumina Film



Porous Alumina Films



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

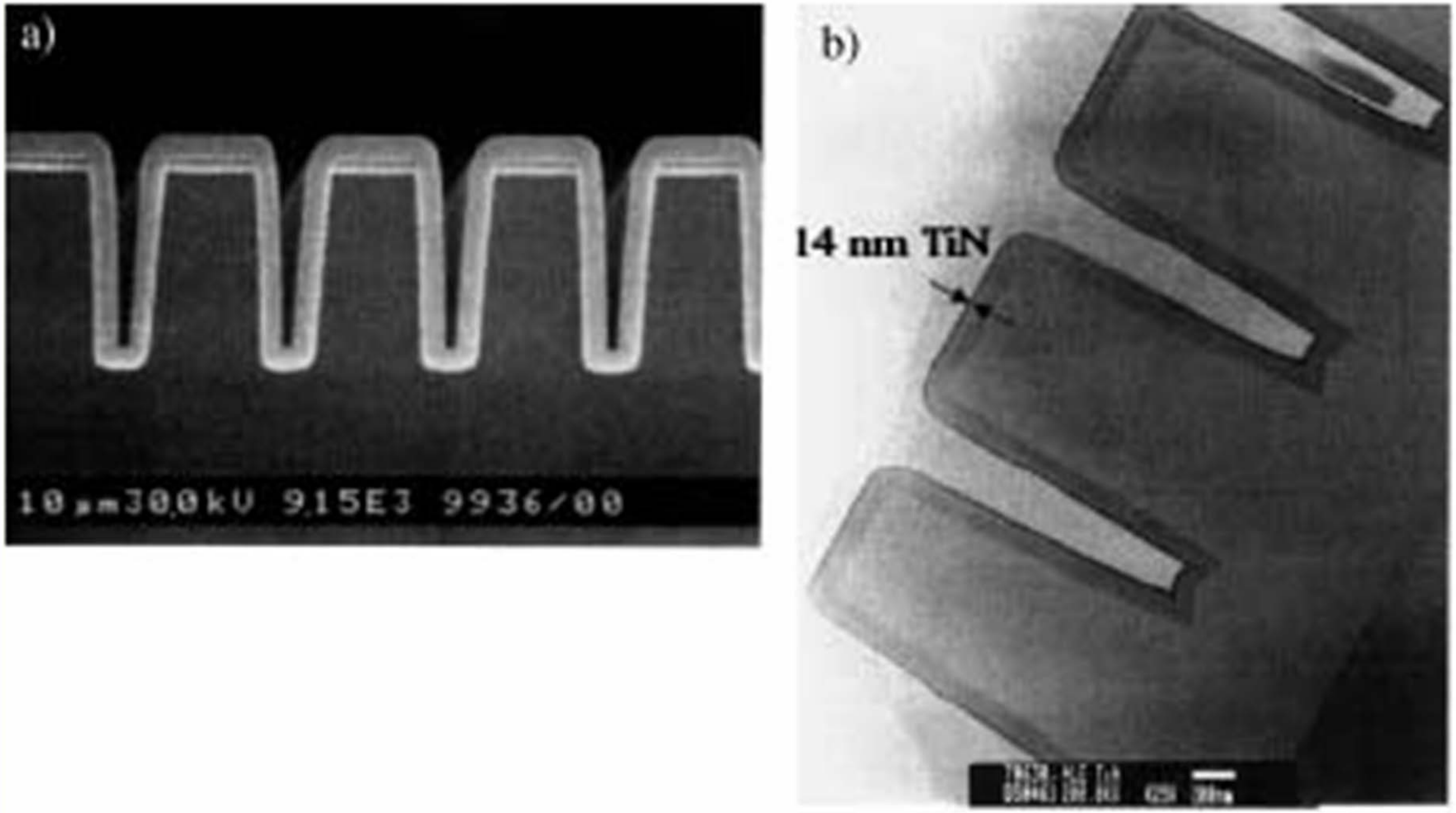
$CH_4 + H_2$ **(RF, MW) → C, diamond films**

Et_4Si **(thermal, air) →** SiO_2

$SiCl_4$ **or** SiH_4 **(thermal,** H_2**) → a-HSi**

$SiH_4 + PH_3$ **(RF) → n-Si**

$Si_2H_6 + B_2H_6$ **(RF) → 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) → n-Si

Me_3Ga (laser photolysis, heating) → Ga

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

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

Synthesis of Thin Films

Specially designed MOCVD reactors
Controlled flow of precursors to single crystal heated substrate
Most reactions occur in range 400-1300^{o}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^{o}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

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

Epitaxy

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

Kinetic control – TD metastable phases

$YMnO_3$
•hexagognal in bulk
•cubic perovskite film on $NdGaO_3$ substrates

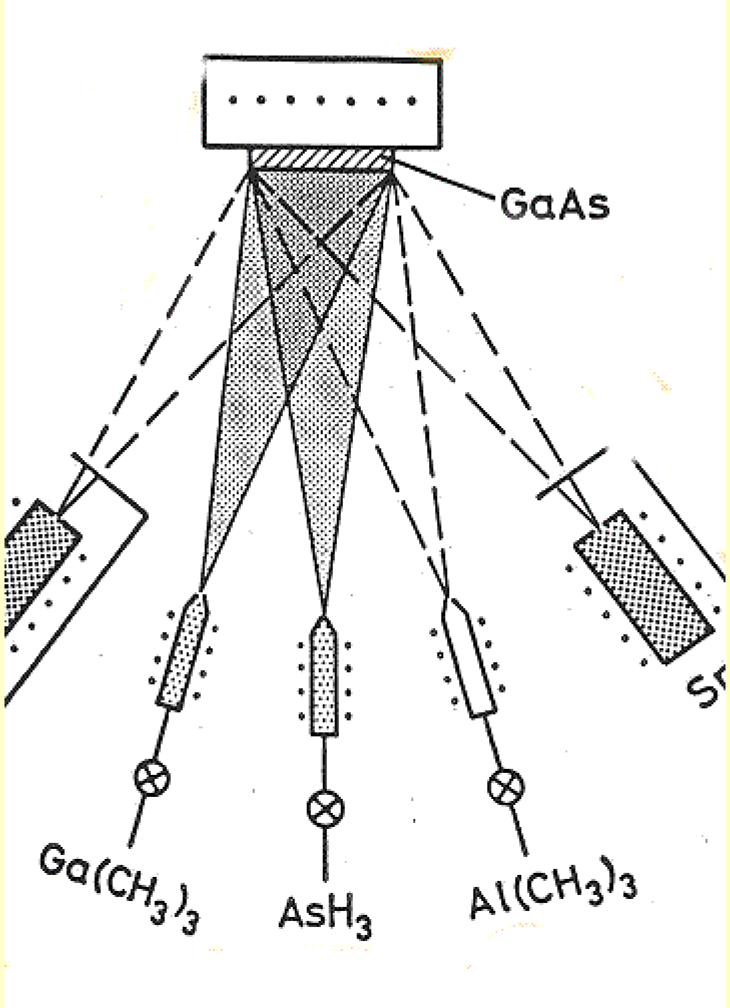
Homoepitaxy – same compound/orientation in substrate and film
Heteroepitaxy – different compounds in the substrate and film

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



SYNTHESIS OF THIN FILMS

☂ PHOTOEPITAXY

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

$Et_2Te + Hg\ (pool) + H_2\ (h\nu\ ,\ 200\ ^oC) \rightarrow HgTe + 2C_2H_6$

MOCVD preparation requires 500 ^{o}C 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 ^{o}C even with a 14% lattice mismatch
GaAs is susceptible to damage under MOCVD conditions 650-750 ^{o}C

SYNTHESIS OF THIN FILMS

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

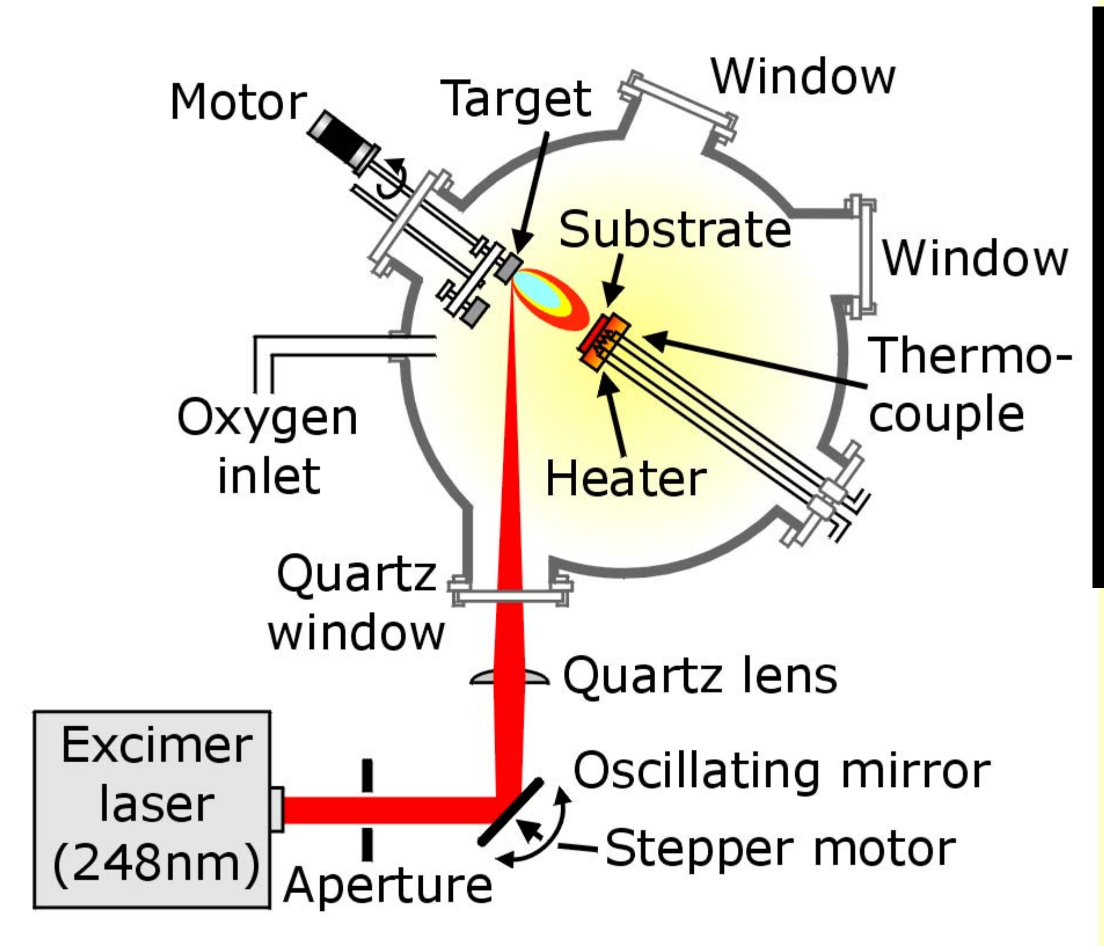
$CH_3Br(g)\ (h\nu\ ) \rightarrow CH_3(g) + Br(g)$

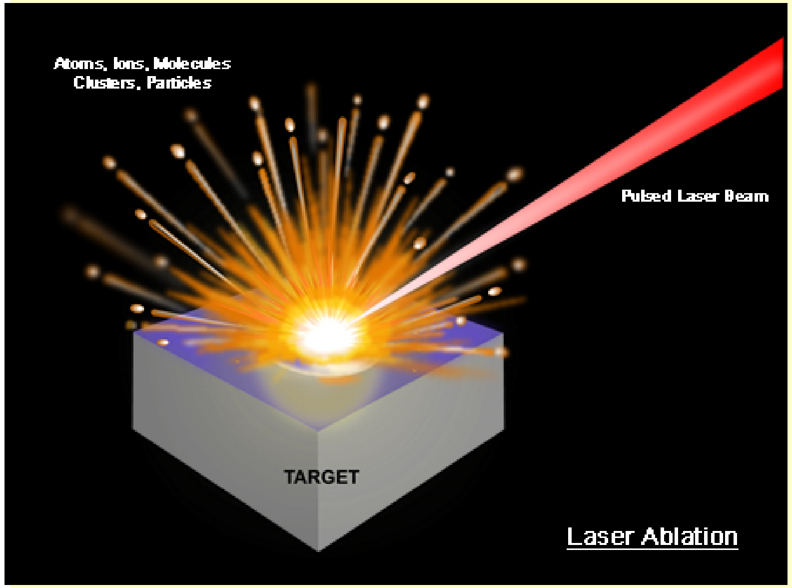
$Br(g) + GaAs(s) \rightarrow GaAs\ldots Br_n(ad)$

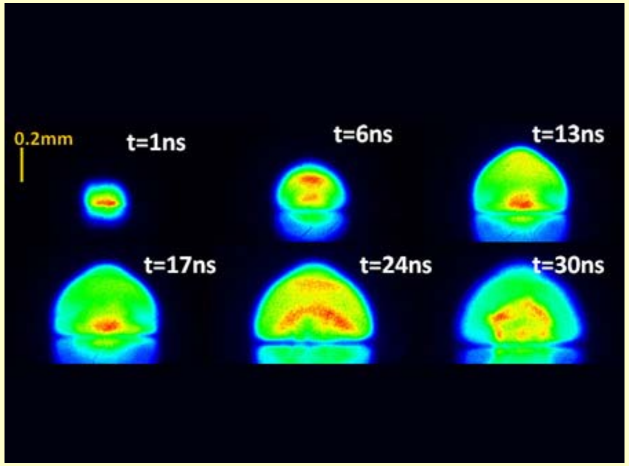
$GaAs\ldots Br_n(ad) \rightarrow GaBr_n(g) + AsBr_n(g)$

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

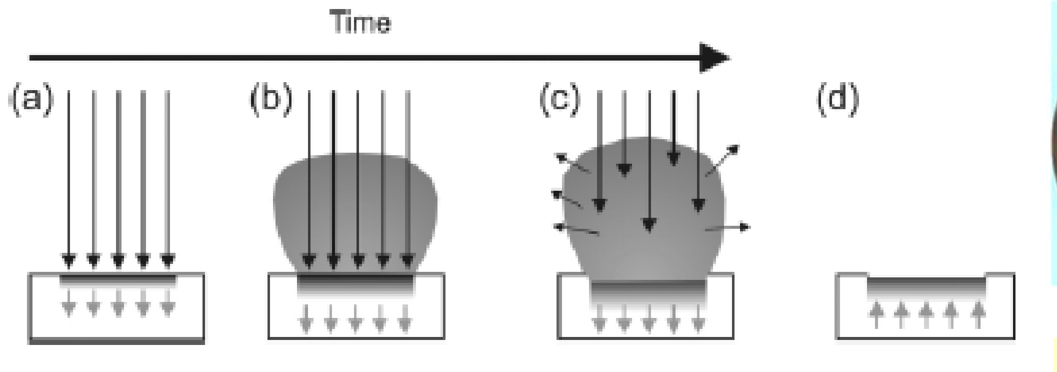
Pulsed Laser Ablation

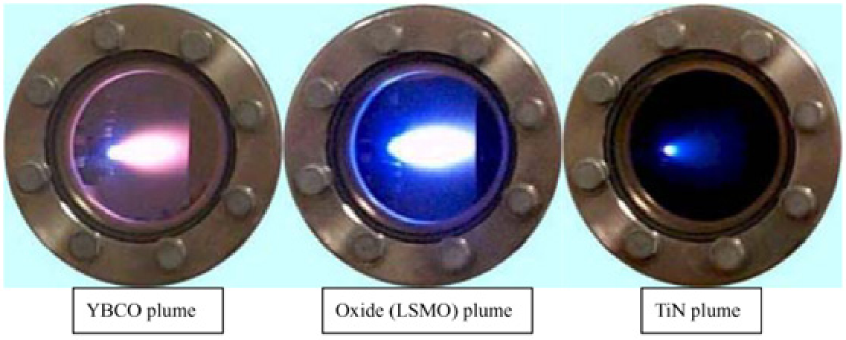






Pulsed Laser Ablation





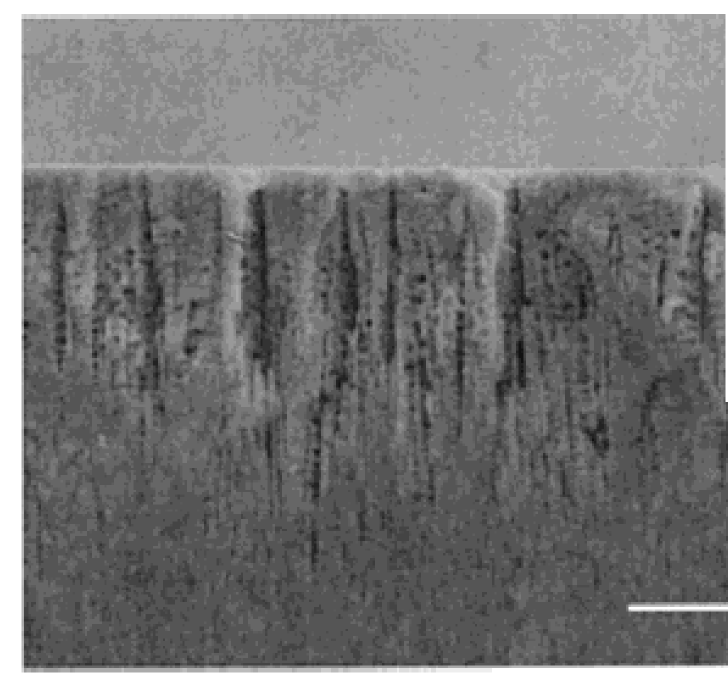
(a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid–liquid interface)

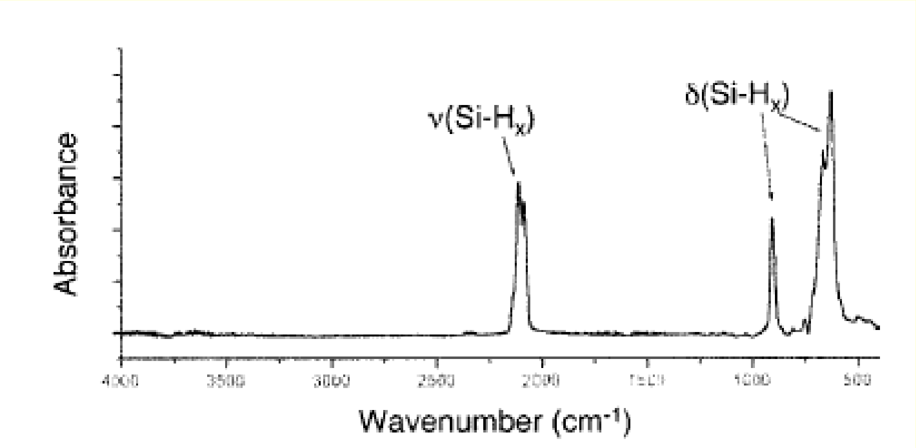
(b) Melt front propagates into the solid, vaporization continues and laser-plume interactions start to become important

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

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

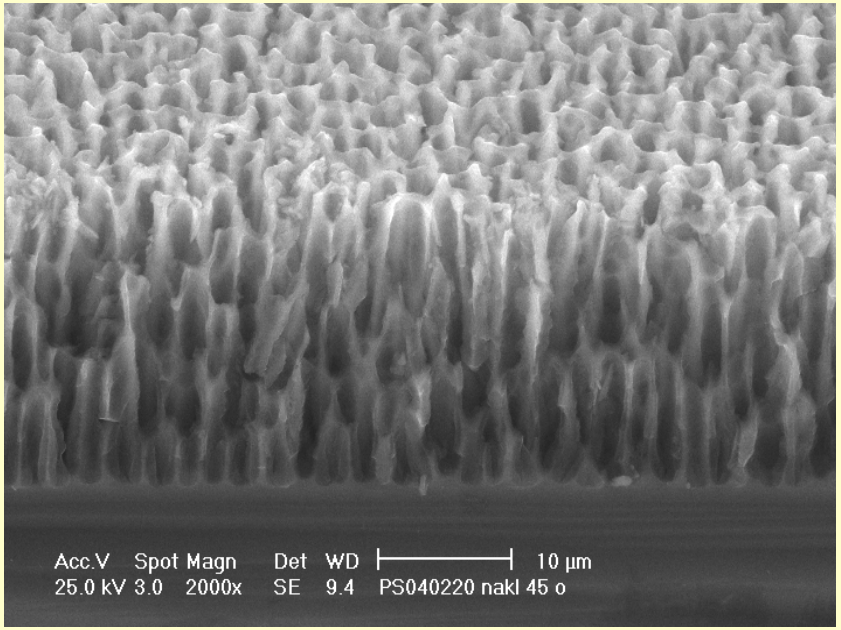
Porous Si

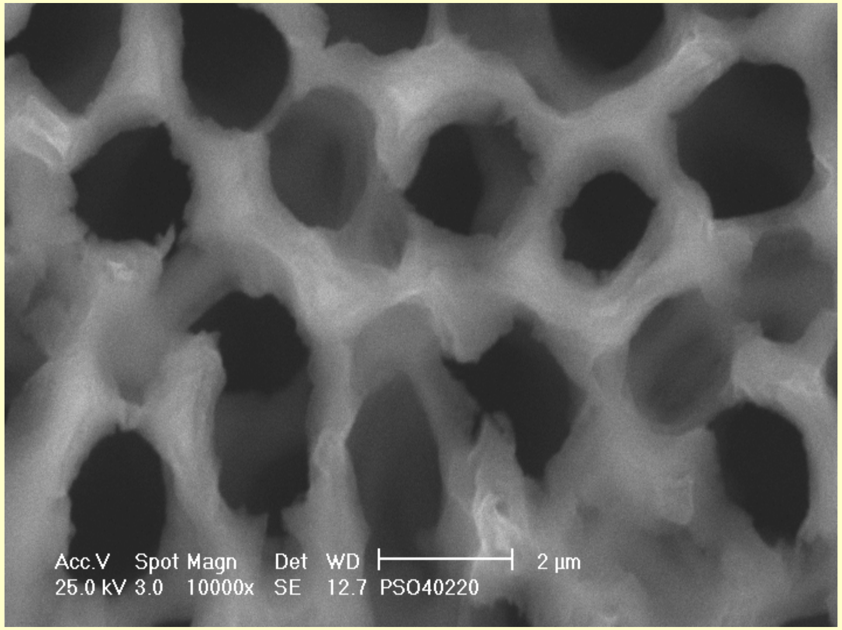




SEM of a porous silicon, the pores extending from the surface of the Si(100) wafer down into the bulk, etched from n-type Si(100) (P-doped, 0.75-0.95 ø,cm) at 77.2 mA cm^{-2} for 1 min with a 1:1 solution of 49% HF(aq)/ EtOH. Scale bar is 10 μm.

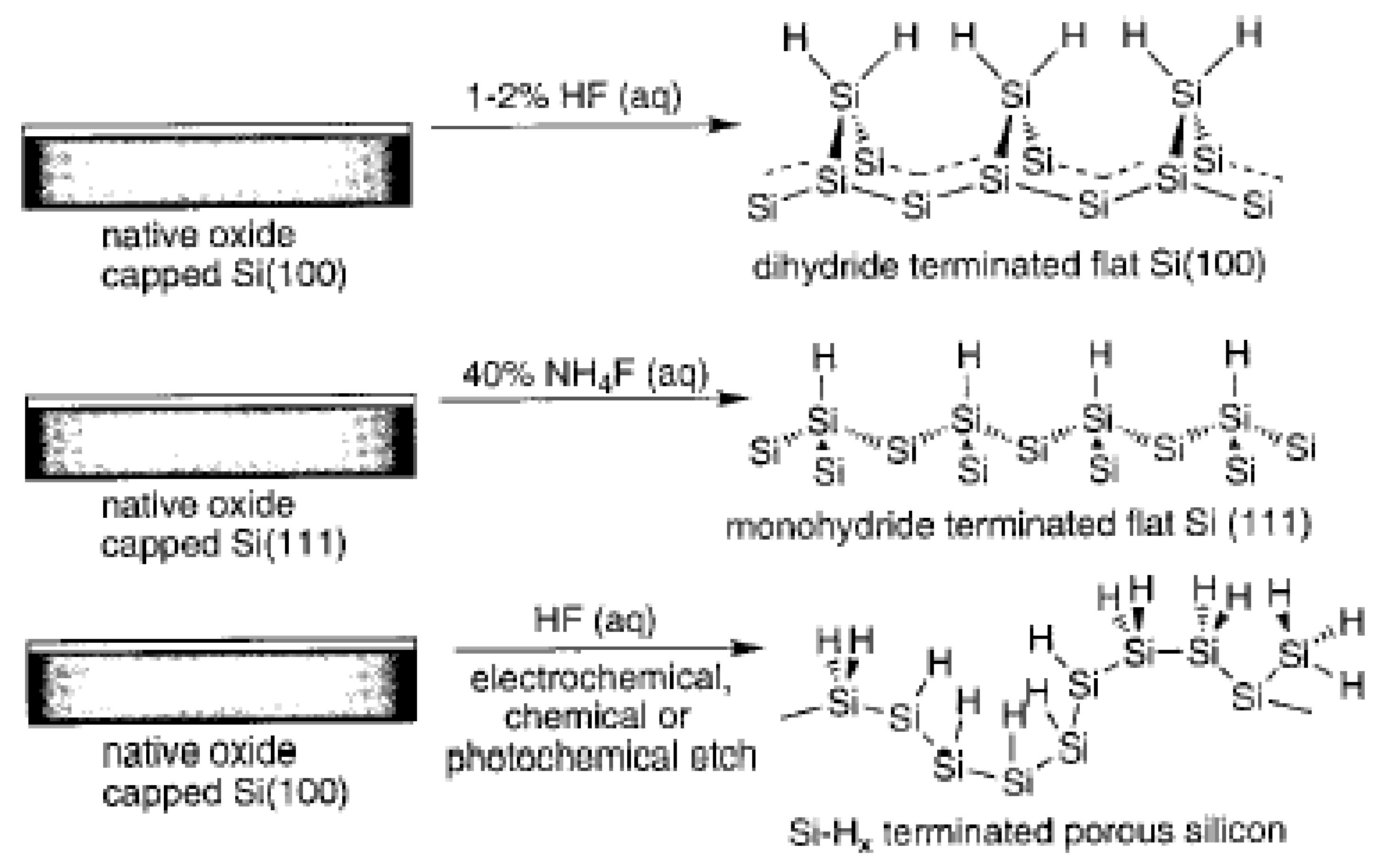
Porous Si





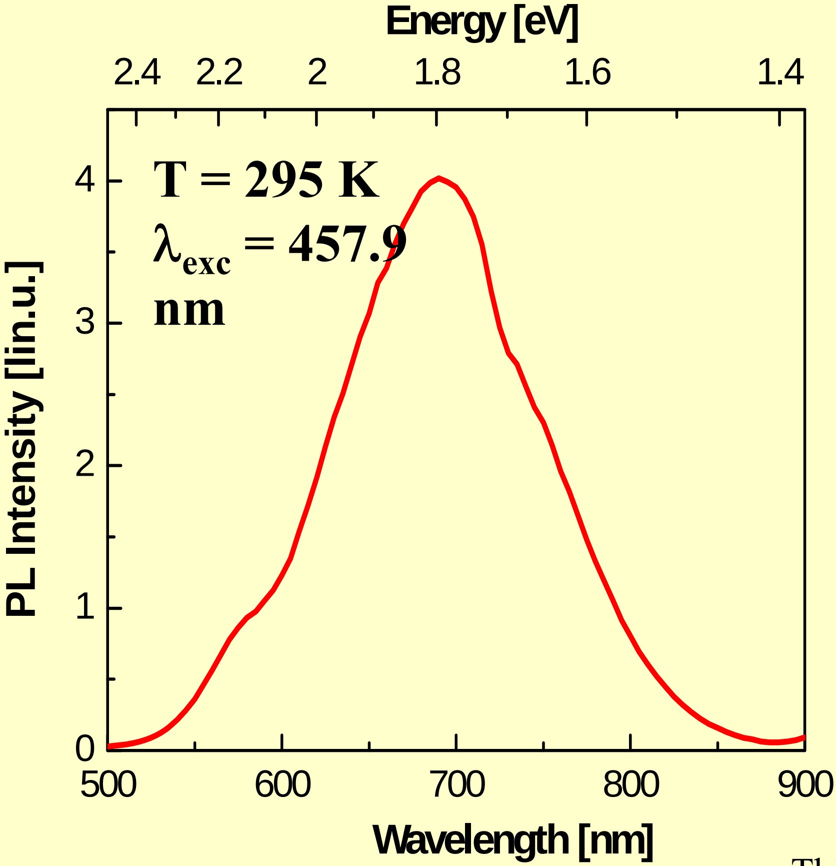
HF:EtOH = 1:2.5
$j = 10\ \mathrm{mA/cm^2}$
$t = 30$ min

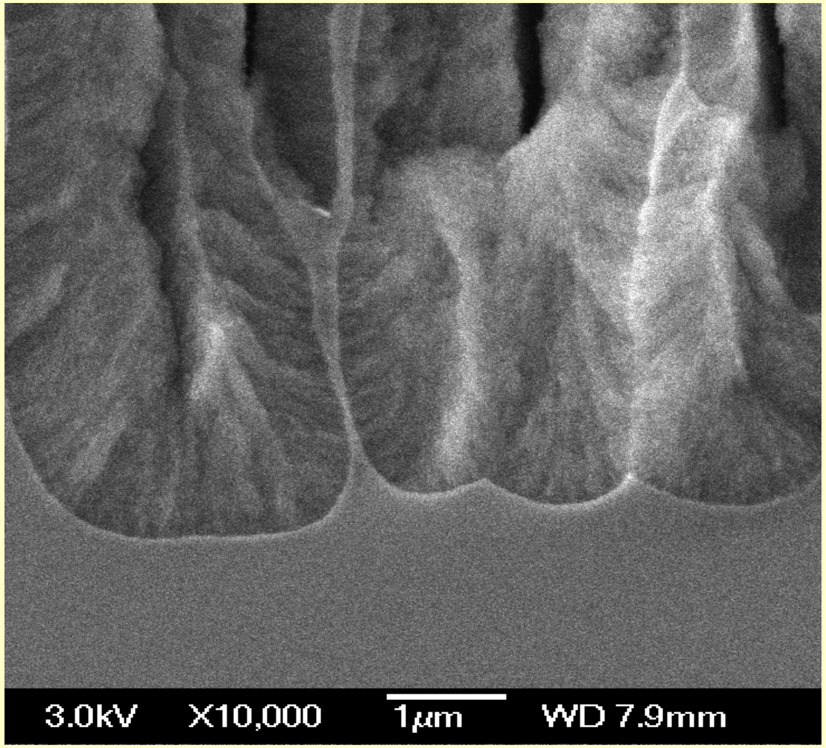
Chemistry on Si Surface



Porous Si

Luminiscence of p-Si





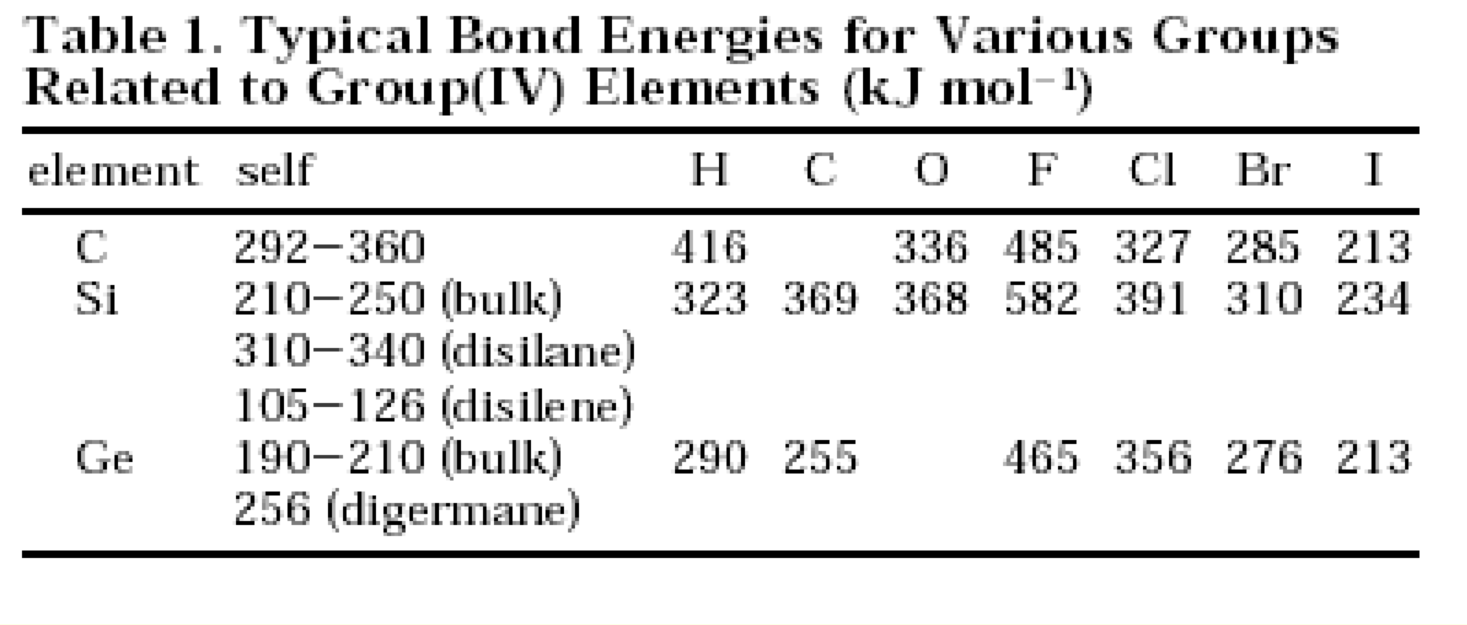
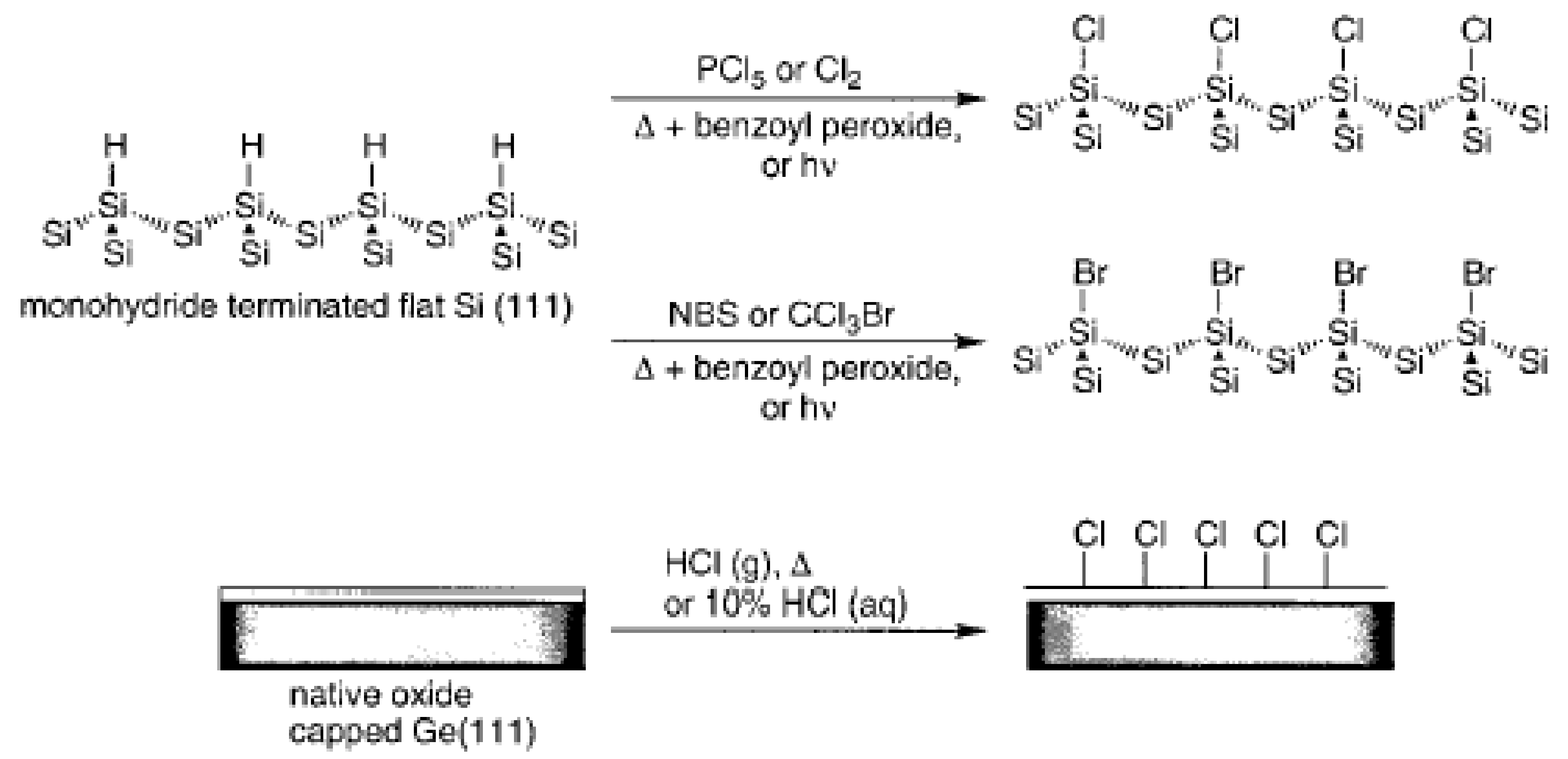


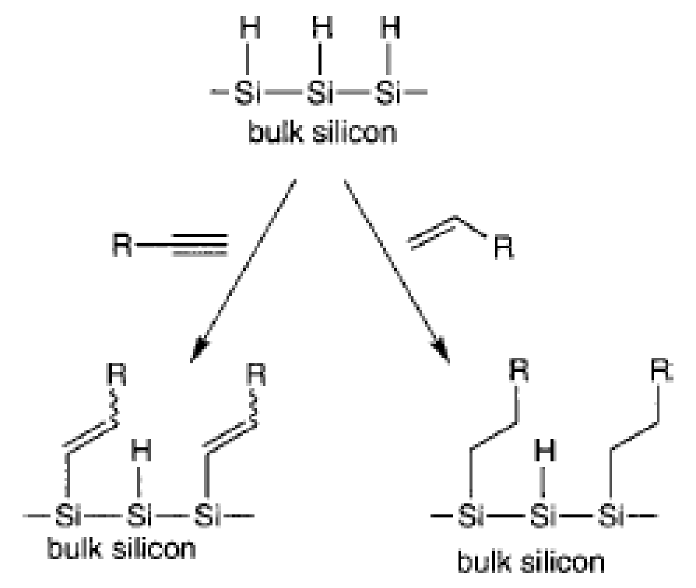
Table 1. Typical Bond Energies for Various Groups Related to Group(IV) Elements (kJ mol^{-1})

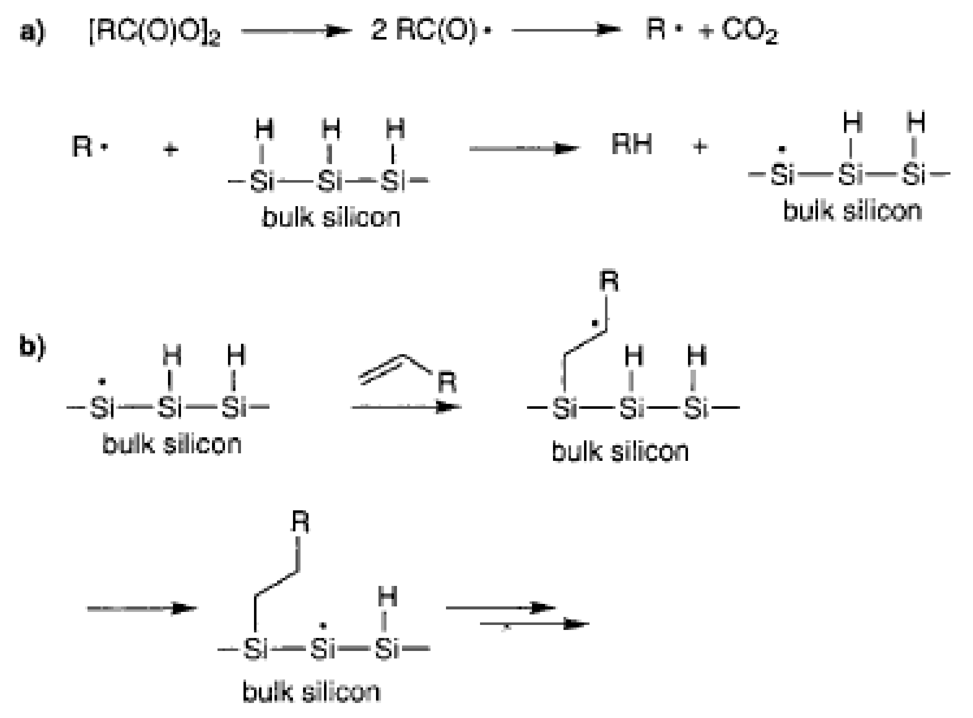
element	self	H	C	O	F	Cl	Br	I
C	292−360	416		336	485	327	285	213
Si	210−250 (bulk)	323	369	368	582	391	310	234
	310−340 (disilane)							
	105−126 (disilene)							
Ge	190−210 (bulk)	290	255		465	356	276	213
	256 (digermane)							

Chemistry on Si Surface

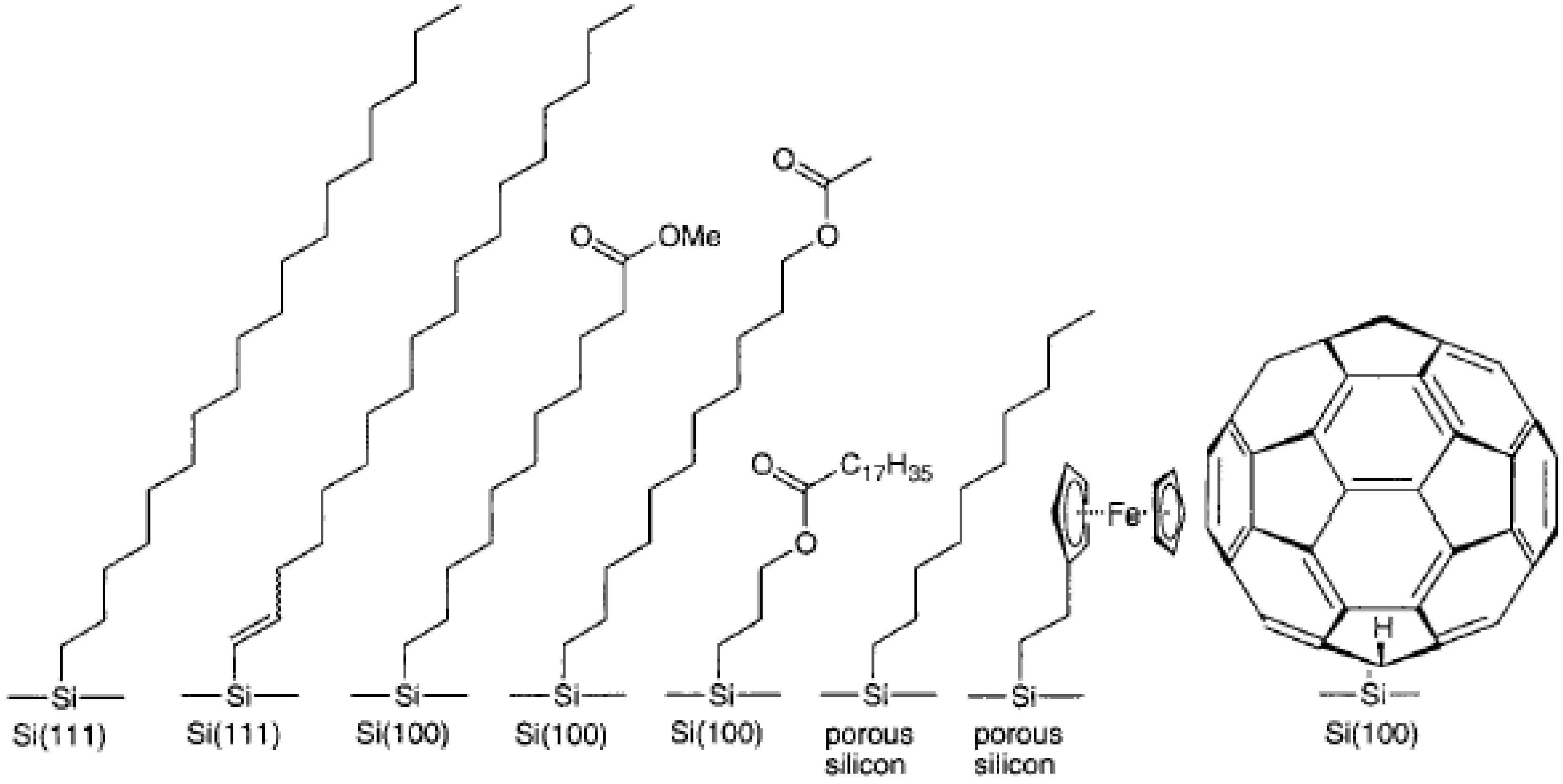


Hydrosilylation

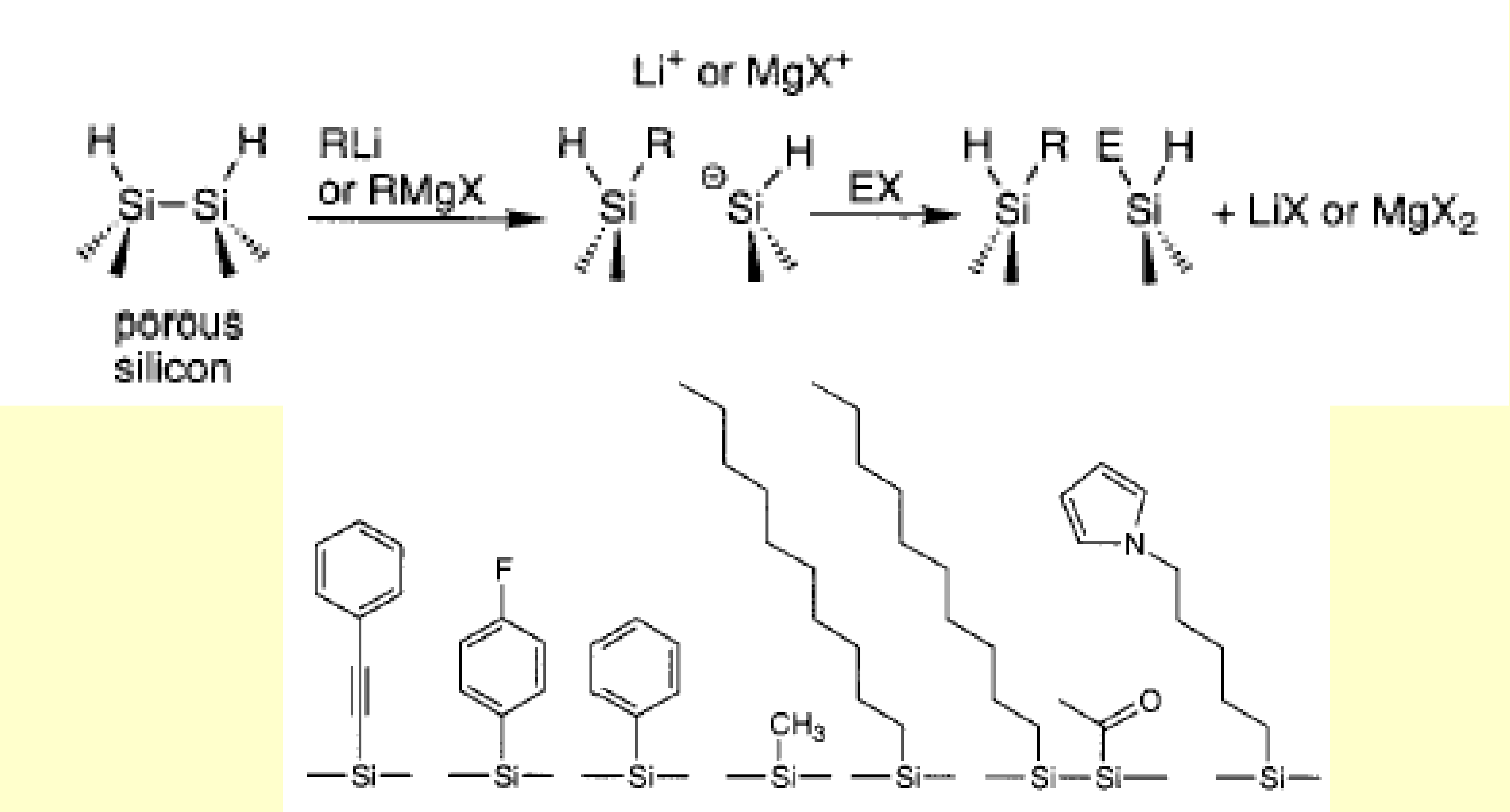




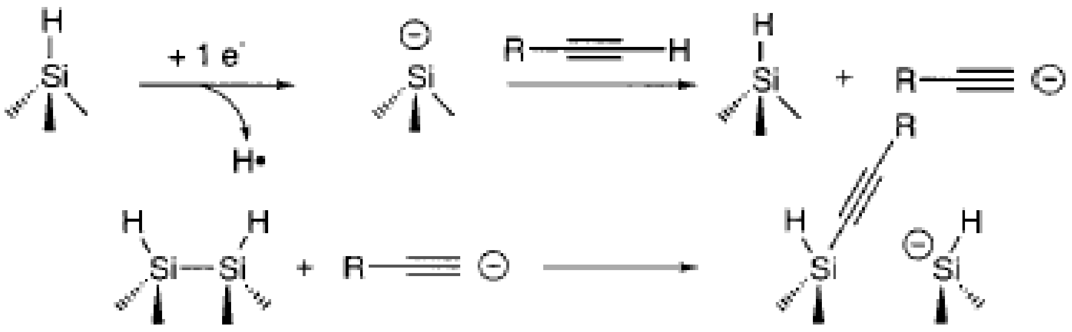
Chemistry on Si Surface



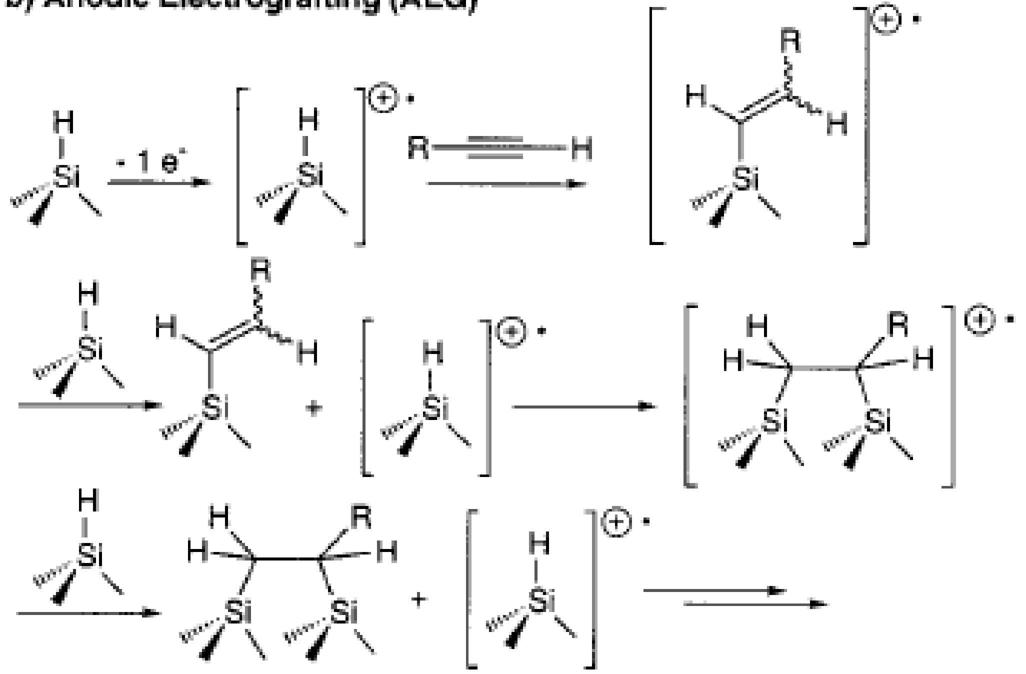
Carbaanion LiR, RMgX



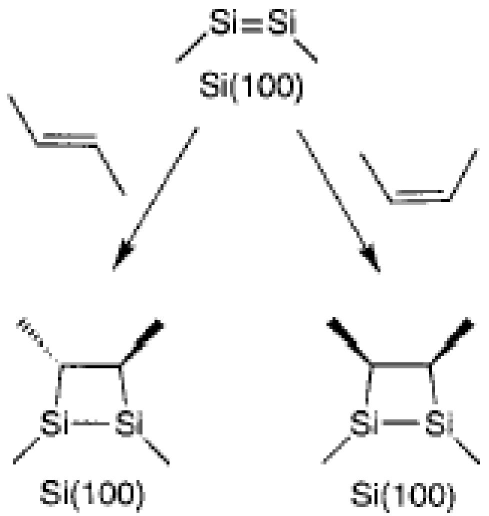
a) Cathodic Electrografting (CEG)

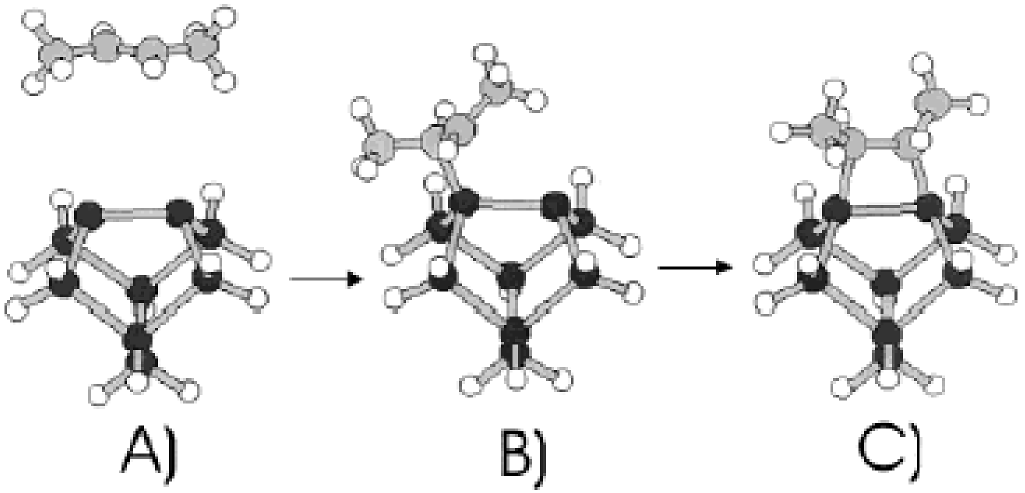


b) Anodic Electrografting (AEG)

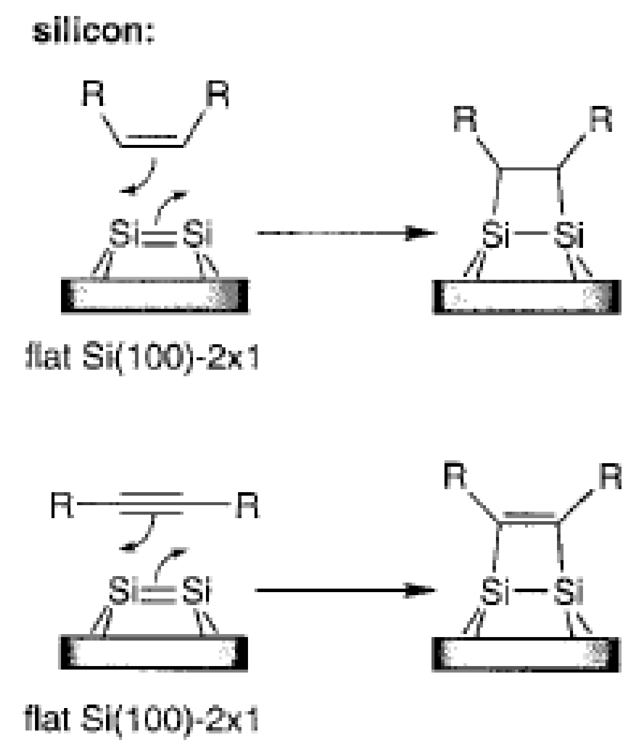


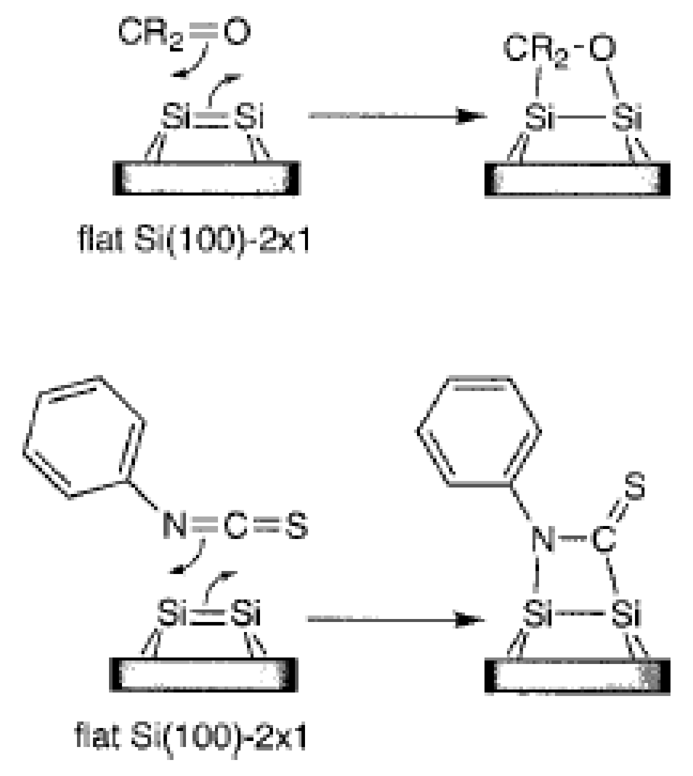
2+2 Cycloaddition



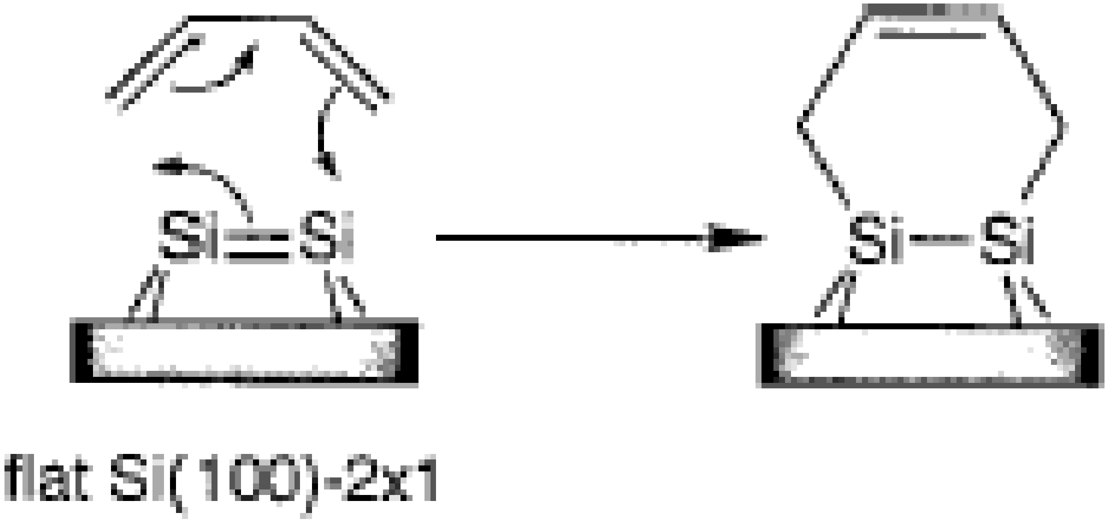


2+2 Cycloaddition

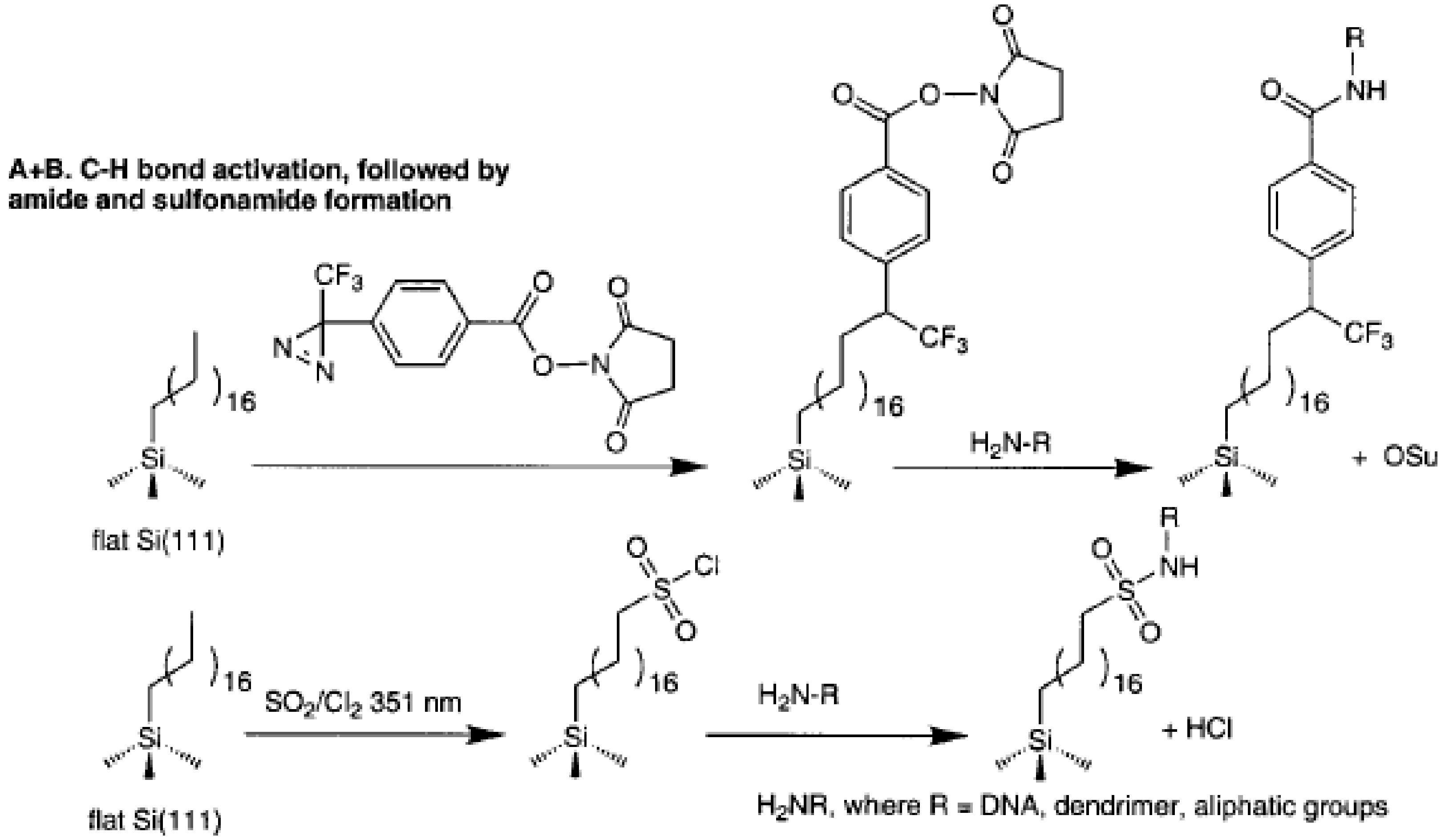




DA 4+2



Secondary Chemistry

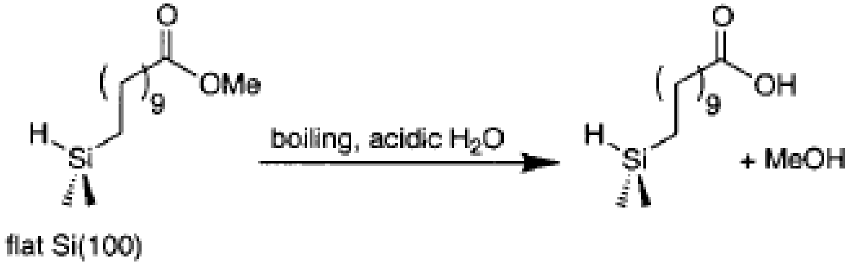


A+B. C-H bond activation, followed by amide and sulfonamide formation

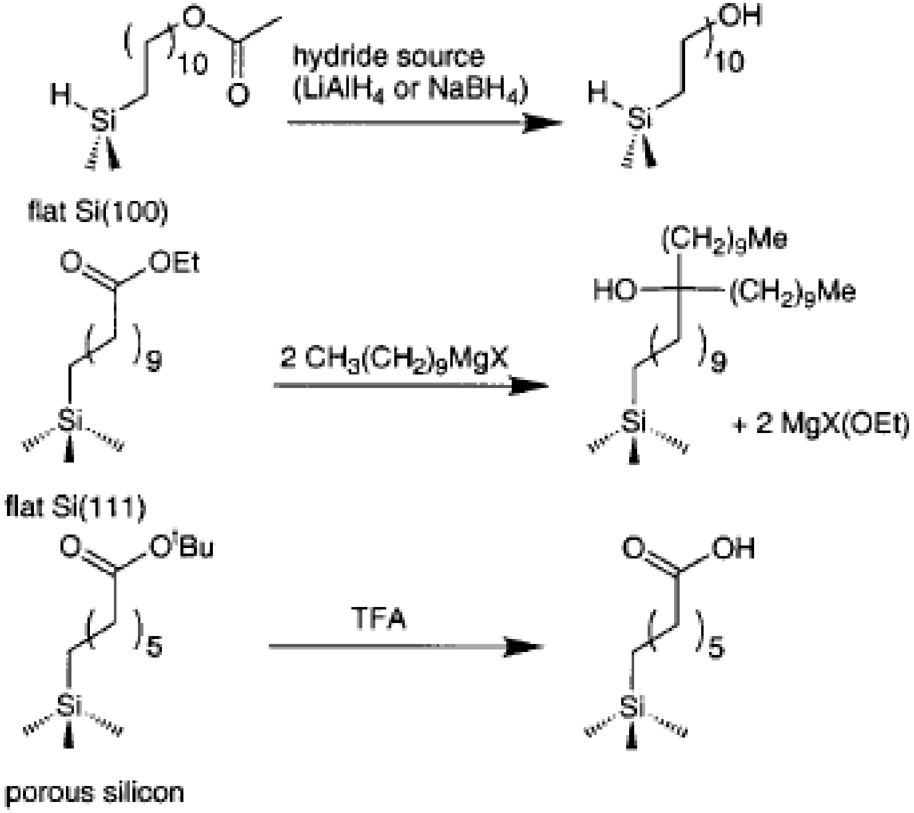
H_2NR, where R = DNA, dendrimer, aliphatic groups

Secondary Chemistry

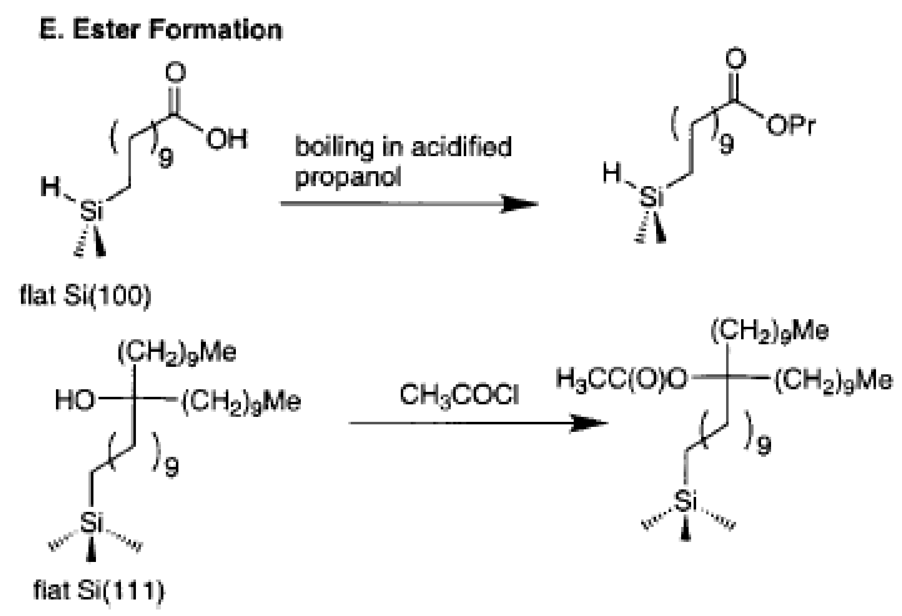
C. Ester hydrolysis

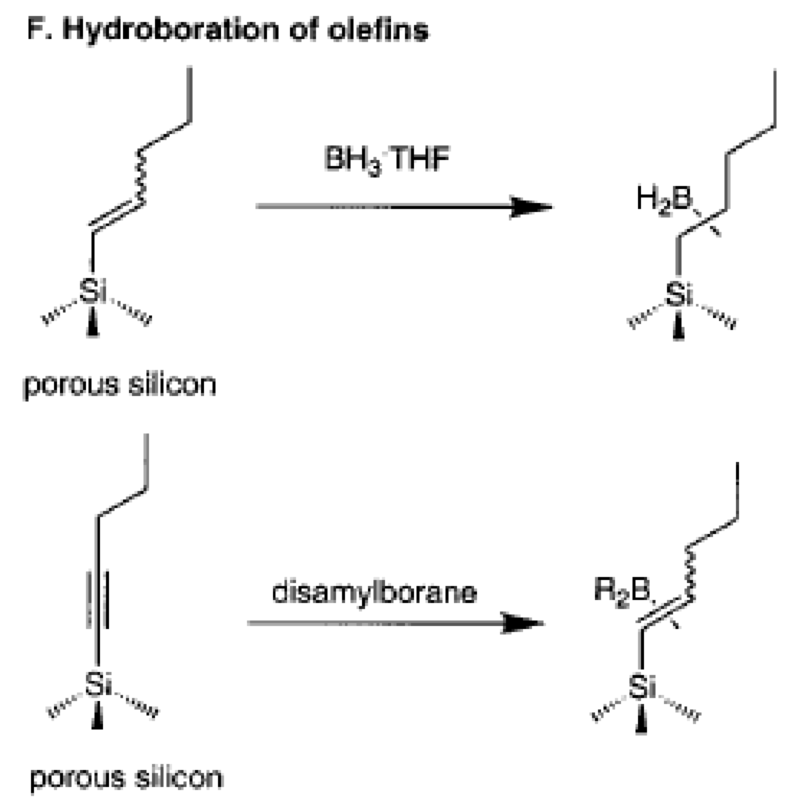


D. Ester reduction and cleavage

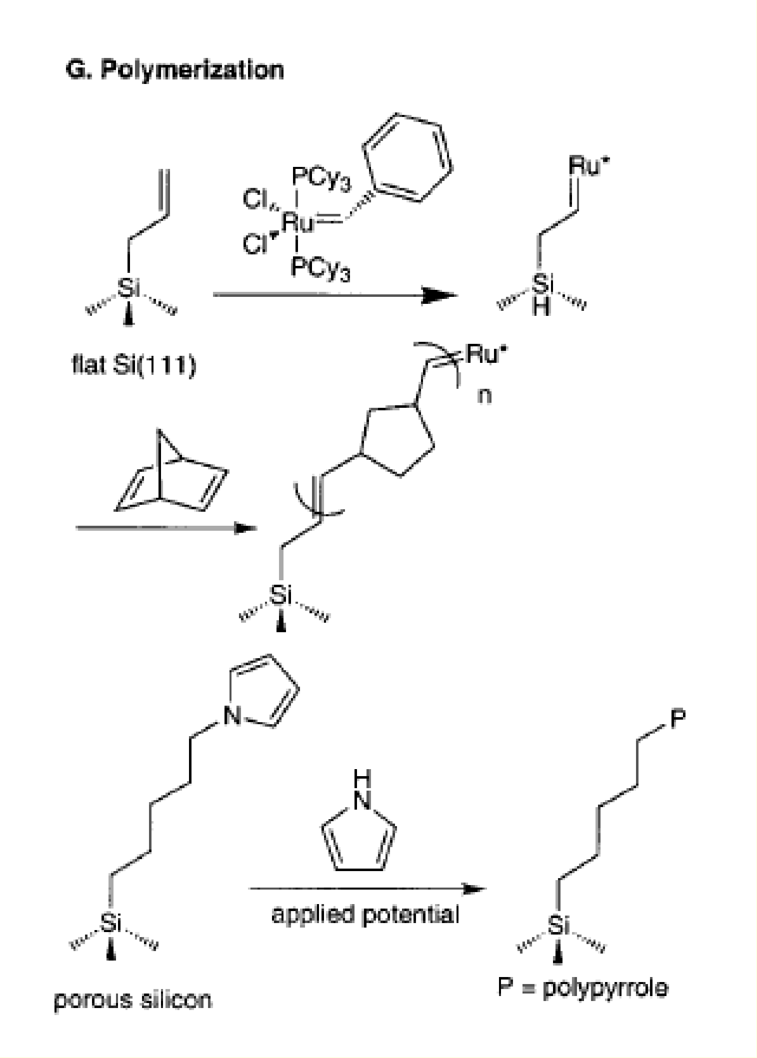


Secondary Chemistry


E. Ester Formation


F. Hydroboration of olefins

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

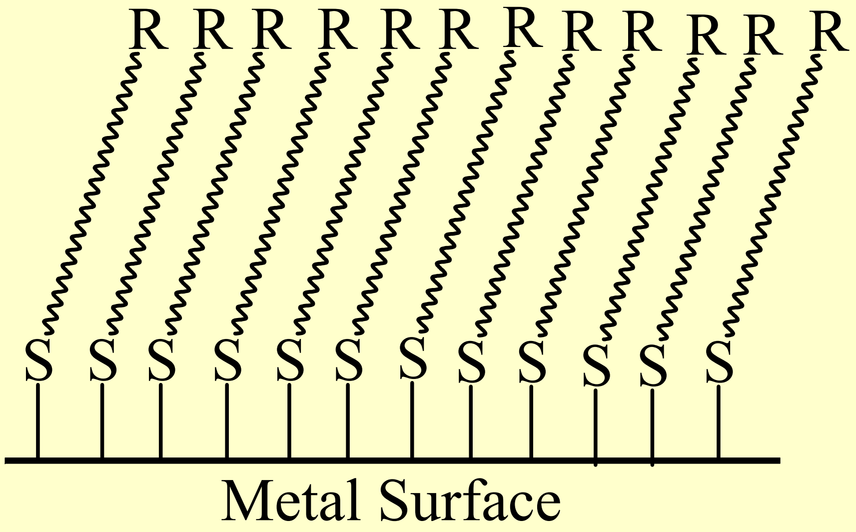
Thiols	$M + RSH \longrightarrow M\text{-}S\text{-}R + 1/2\ H_2$
Disulfides	$2\ M + RSSR \longrightarrow 2\ M\text{-}S\text{-}R$
Sulfides	$M + RSR \longrightarrow M\text{-}S\text{-}R$

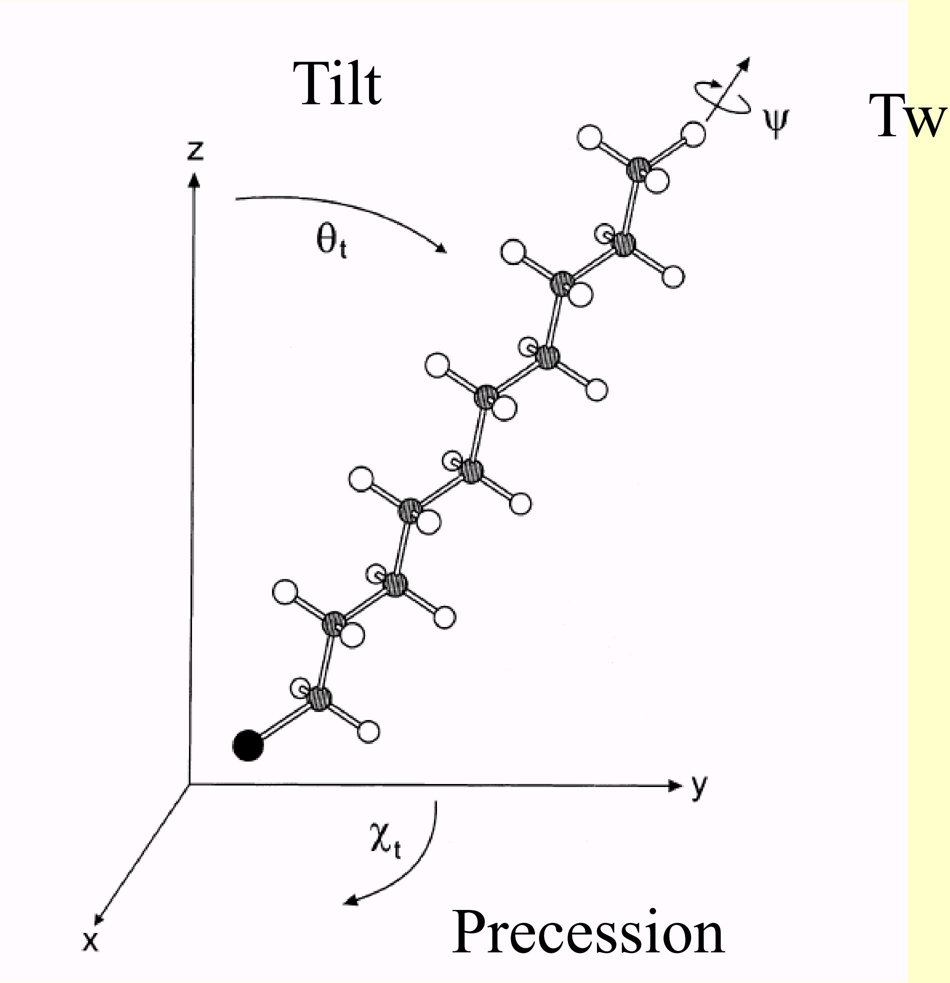
Same products formed in all three reactions: thiolates. RSH are more soluble and react 10^3 faster with Au than RSSR.

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

Thickness 5-300 nm, sputtering, evaporation

Atomically flat

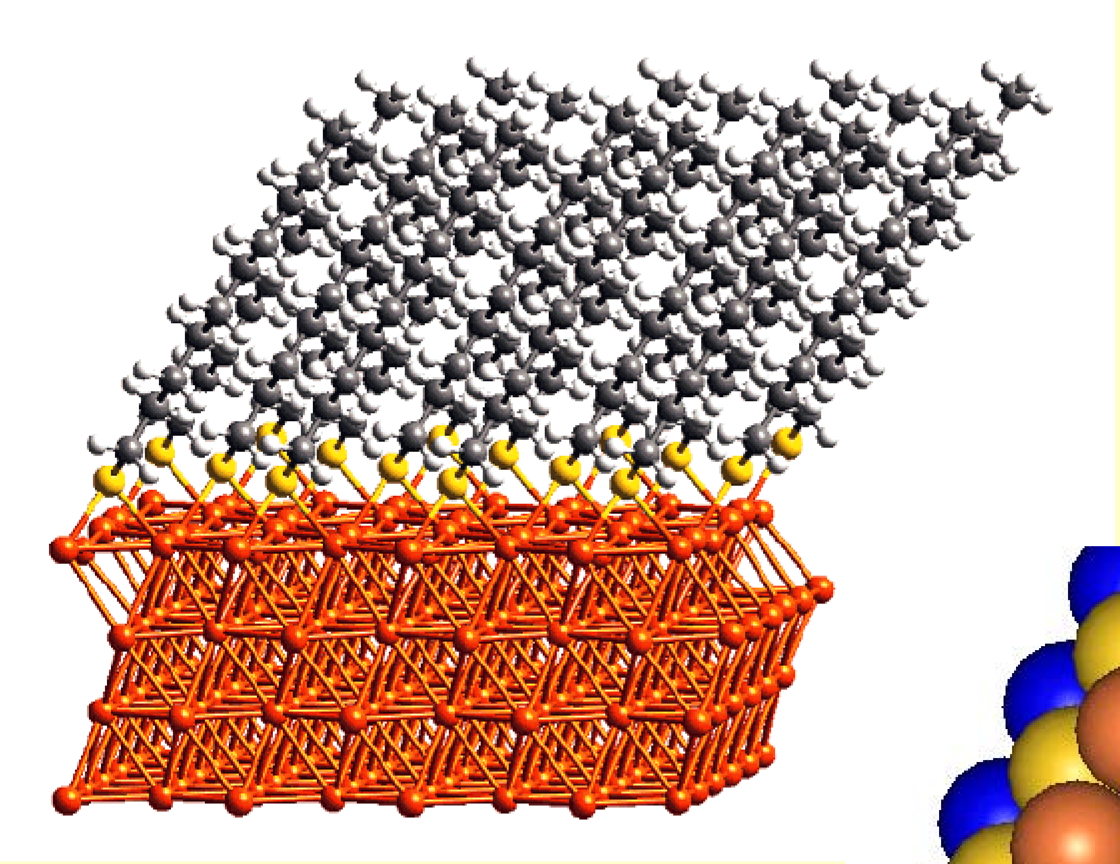


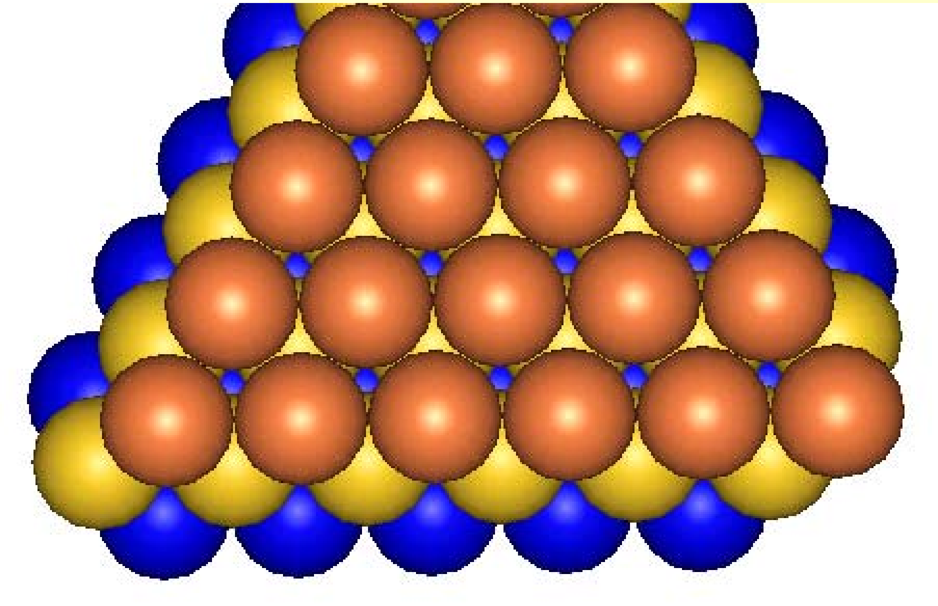


Tilt

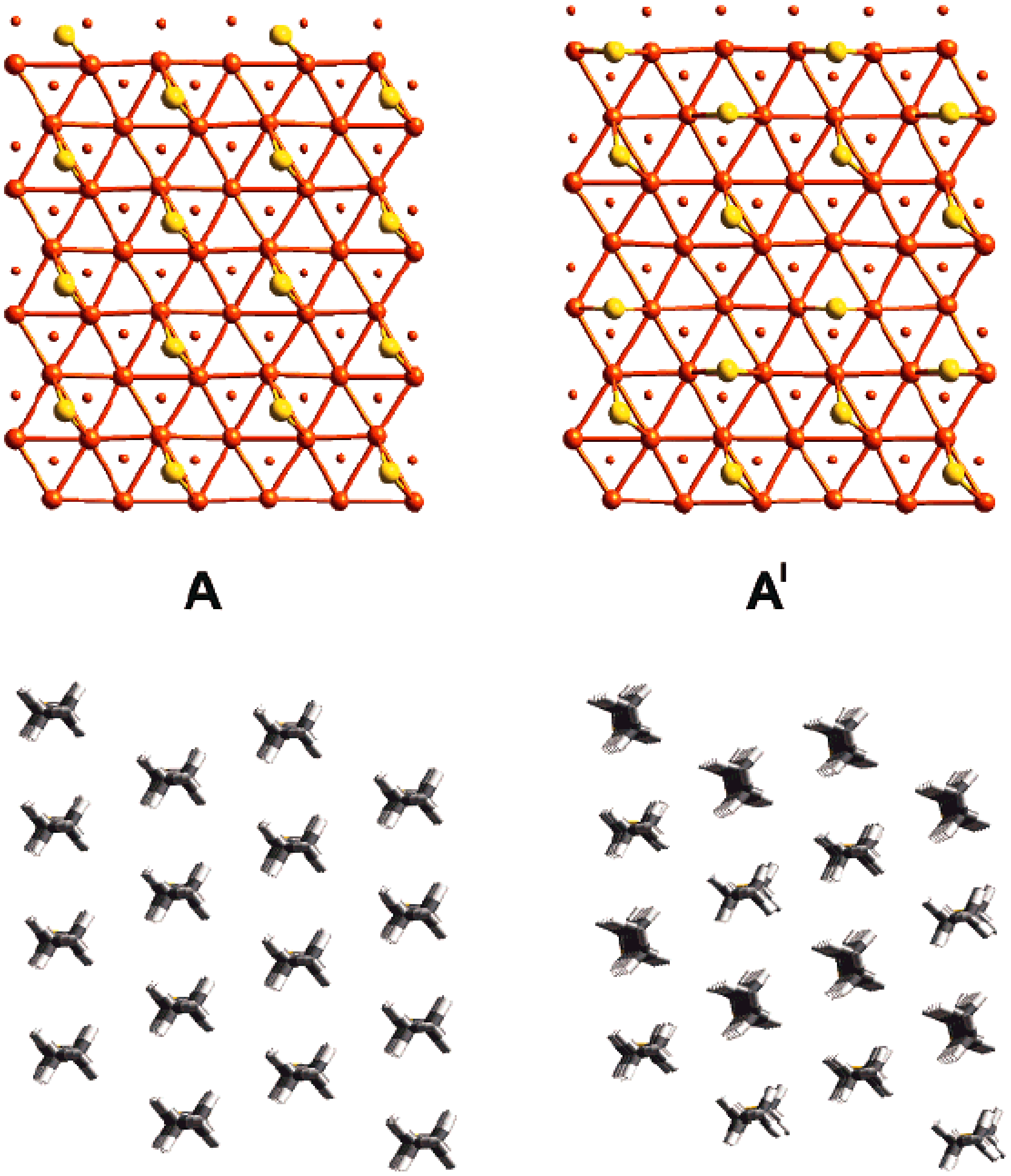
Twist

Precession





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 CH_2**

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

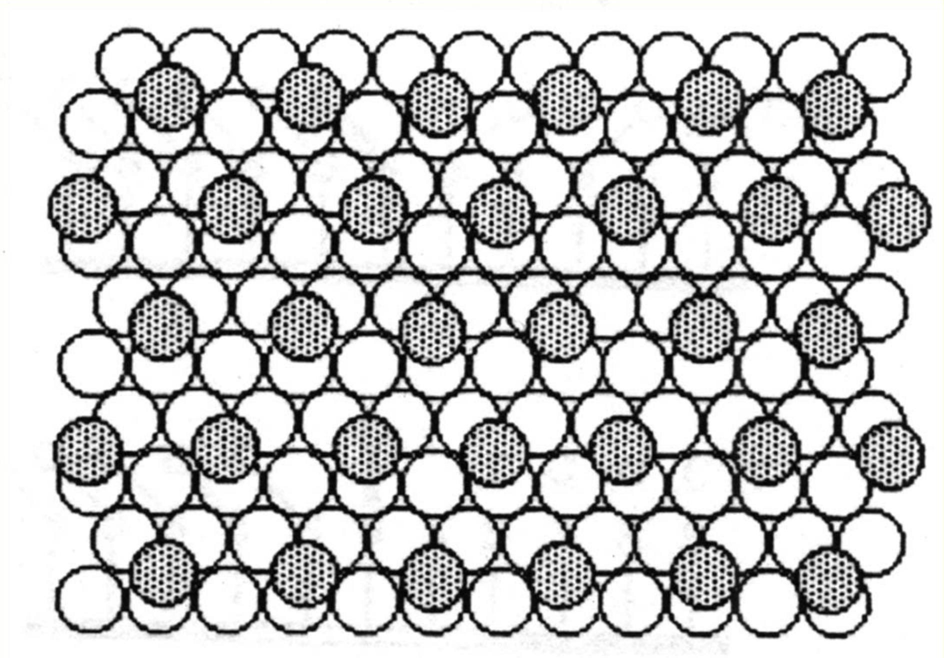
Surface coverage 10^{14} molecules per cm^2
C_{16} chain length ~2.2 nm, 32-40° tilted, all-trans

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

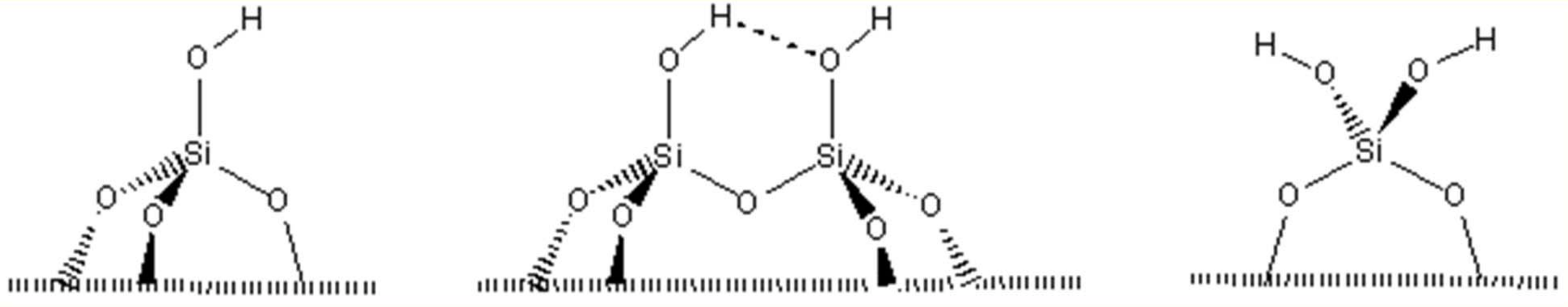
♠ Self-assembly, at thermodynamic minima, rejects defects, high degree of perfection.
♠ Dimension in the range 1 nm to 1000 μm, too large for chemical synthesis, too small for microlithography.
♠ High efficiency, spontaneous.

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

$[O_3Si]$—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.

$$3\,[O_3Si]\text{—}OH + Cl_3SiR \longrightarrow \{[O_3Si]\text{—}O\}_3SiR + 3\,HCl$$

$$3\,[O_3Si]\text{—}OH + (MeO)_3SiR \longrightarrow \{[O_3Si]\text{—}O\}_3SiR + 3\,MeOH$$

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.

$$[O_3Si]\text{—}OH + SOCl_2 \longrightarrow [O_3Si]\text{—}Cl + HCl + SO_2$$

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

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

$$[O_3Si]\text{—}Cl + RMgCl \longrightarrow [O_3Si]\text{—}R + MgCl_2$$

$$[O_3Si]\text{—}Cl + RLi \longrightarrow [O_3Si]\text{—}R + LiCl$$

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 $(MeO)_3SiR$ by controlled hydrolysis and condensation.

$$(MeO)_3SiR + (MeO)_4Si + 7\ H_2O \longrightarrow [O_3Si]\text{—}R + 7\ MeOH$$

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).

$$[O_3Si]\text{—}OH + R''\text{–}ML_n \longrightarrow R''H + [O_3Si]\text{—}O\text{–}ML_n$$

$$[O_3Si]\text{—}OH + X\text{–}ML_n \longrightarrow HX + [O_3Si]\text{—}O\text{–}ML_n$$

$$[O_3Si]\text{—}OH + Me_2N\text{–}ML_n \longrightarrow Me_2NH + [O_3Si]\text{—}O\text{–}ML_n$$

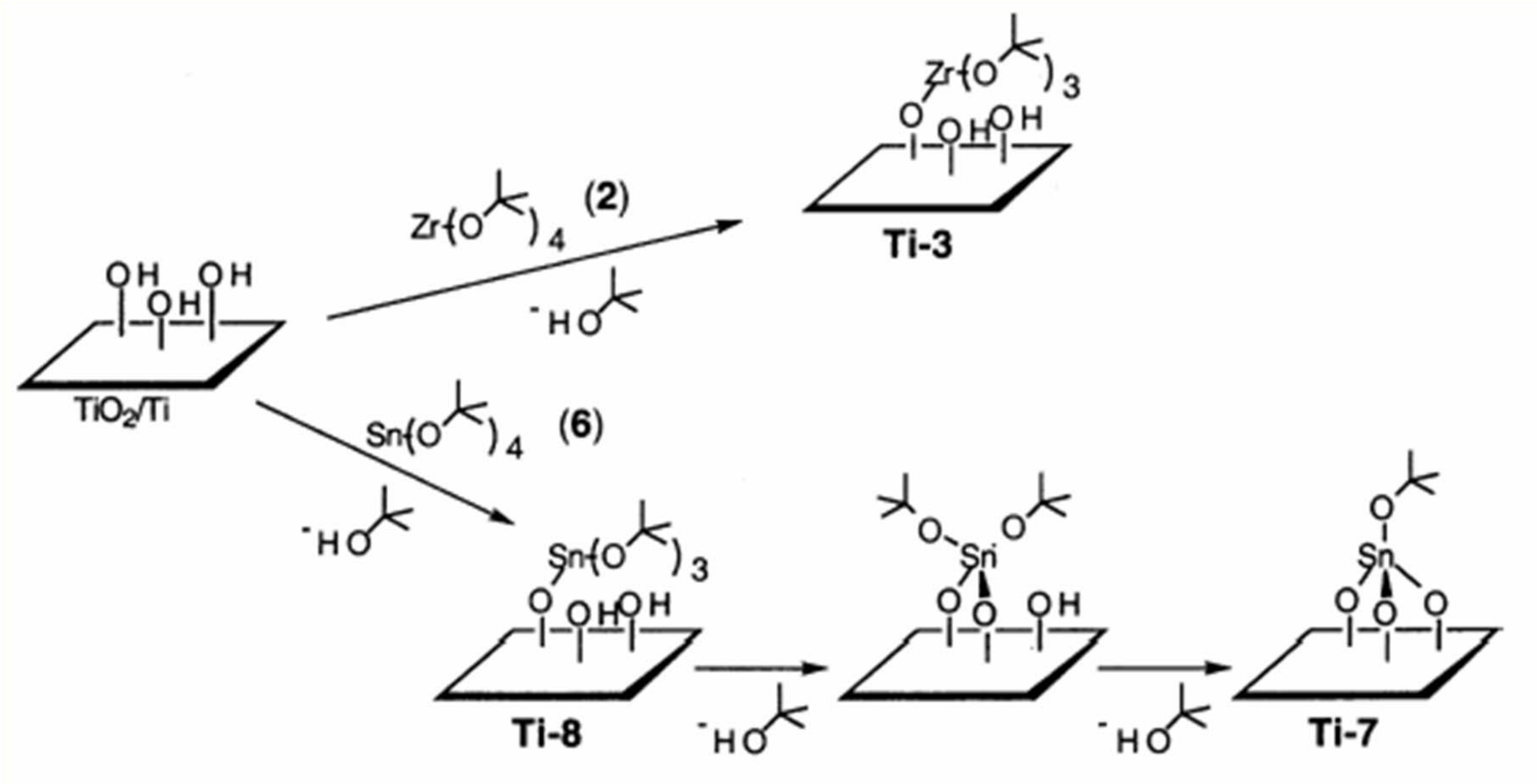
$$[O_3Si]\text{—}OH + R''O\text{–}ML_n \longrightarrow R''OH + [O_3Si]\text{—}O\text{–}ML_n$$

SiO_2 Surfaces

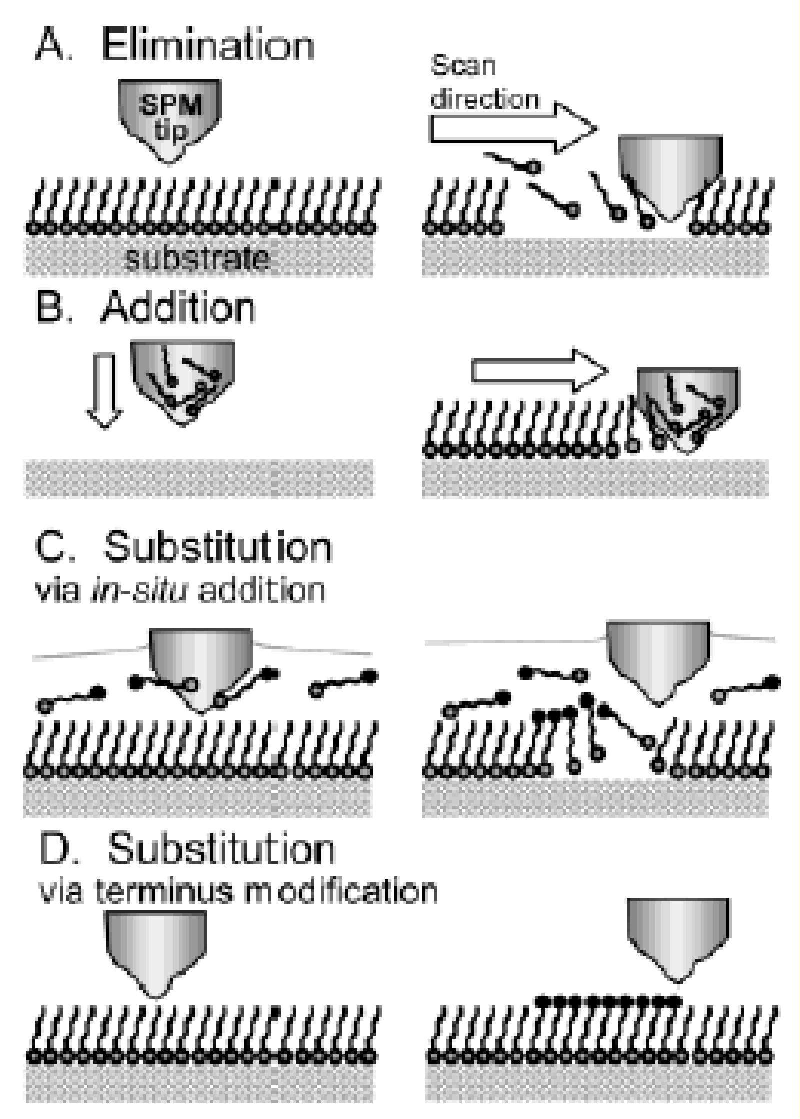
These organometallic moieties can serve as attachment points for further modification with long chain alcohols, thiols, carboxylic acids, phosphates, and diketonates.

$$[O_3Si]\text{—}O\text{–}ML_n + HOR \longrightarrow [O_3Si]\text{—}O\text{–}ML_{n-1}\text{–}OR + HL$$

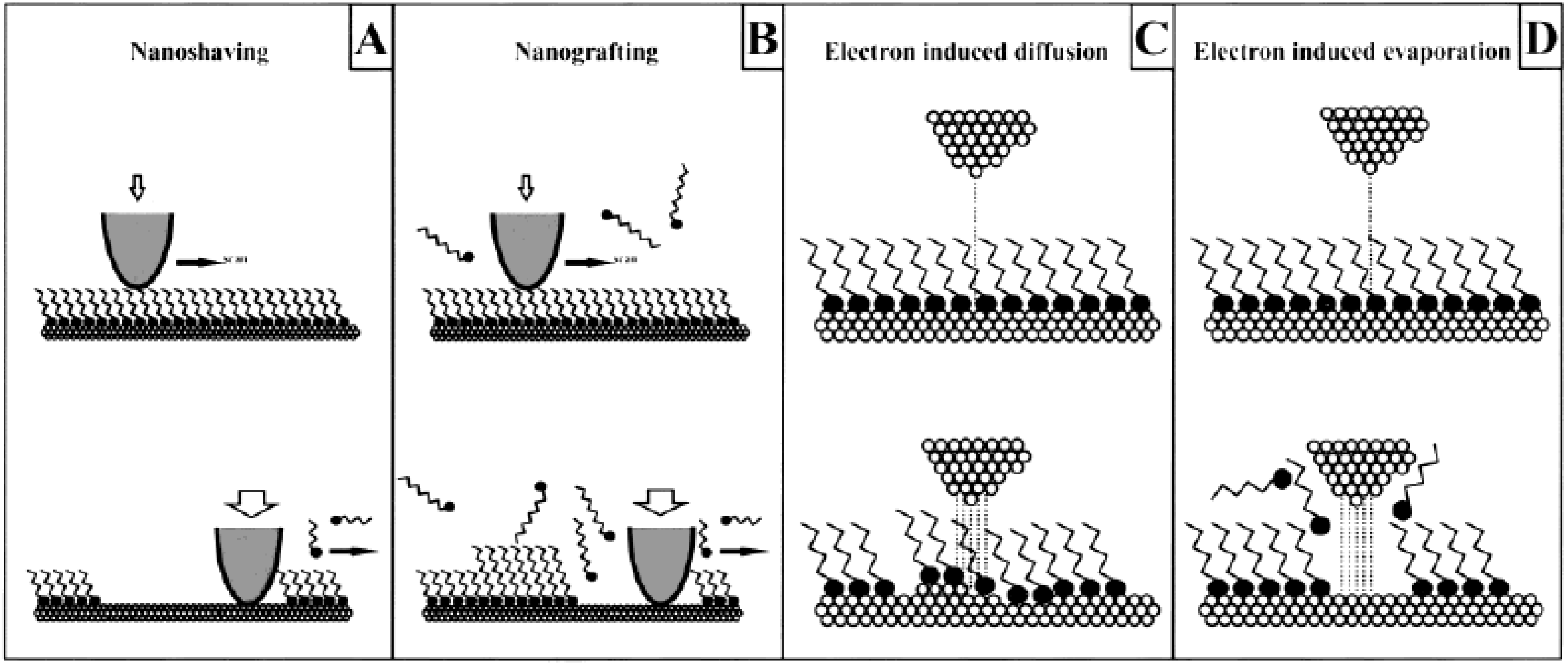
$$[O_3Si]\text{—}O\text{–}ML_n + HOOCR \longrightarrow [O_3Si]\text{—}O\text{–}ML_{n-1}\text{–}OOCR + HL$$



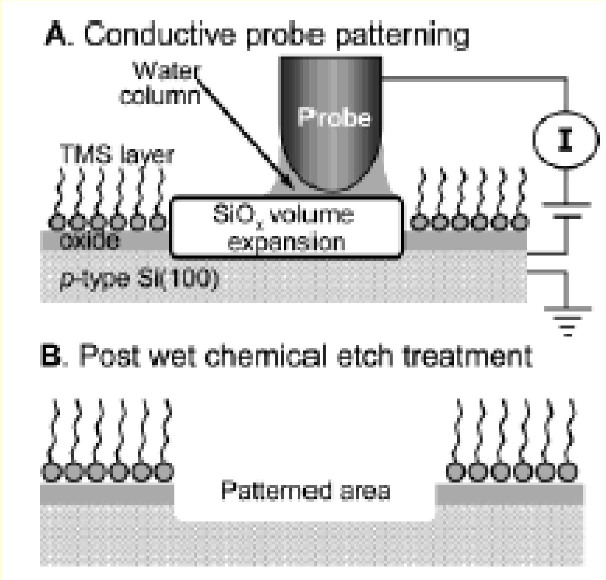
Manipulations with SAM

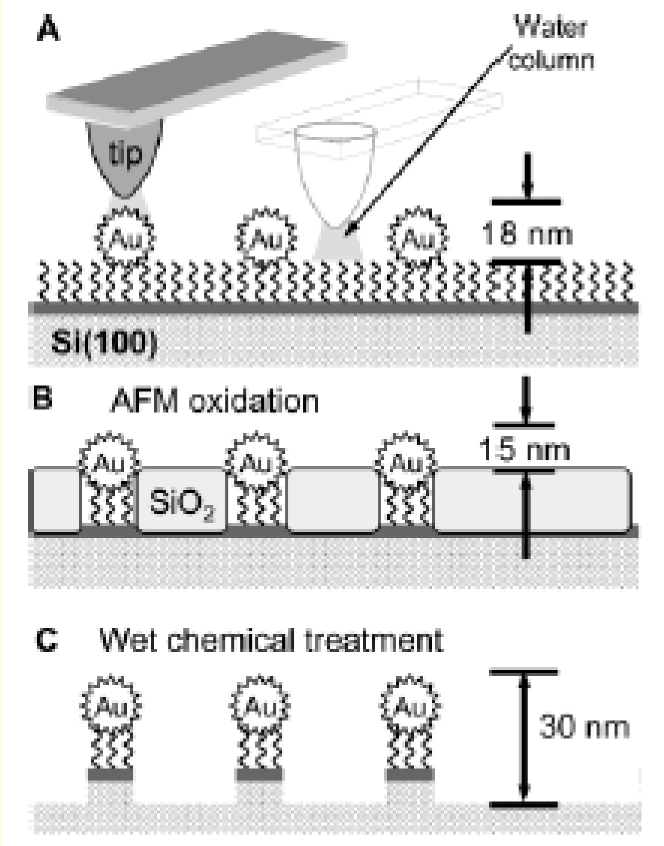


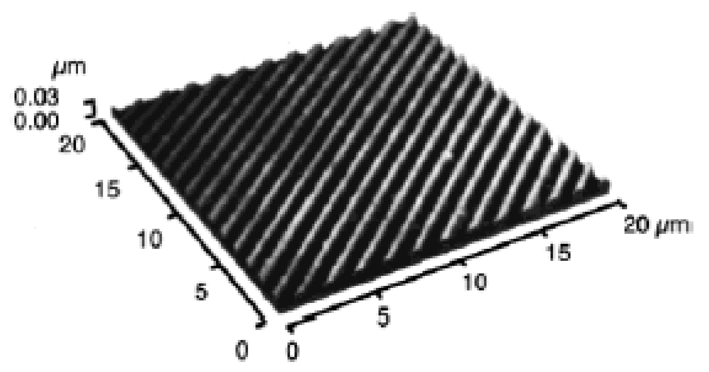
Manipulations with SAM



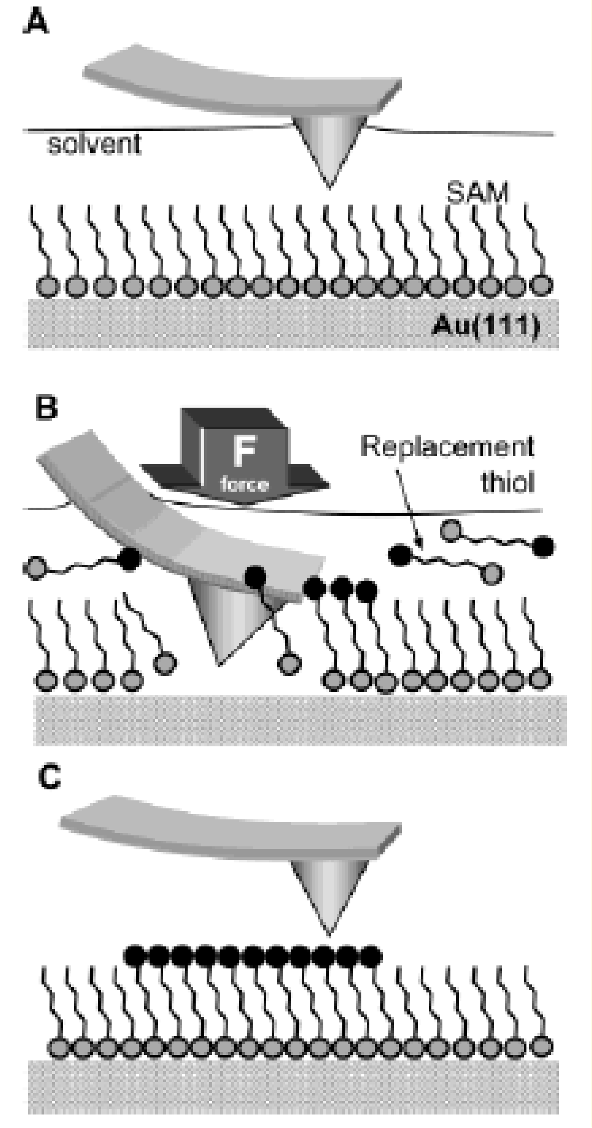
Manipulations with SAM



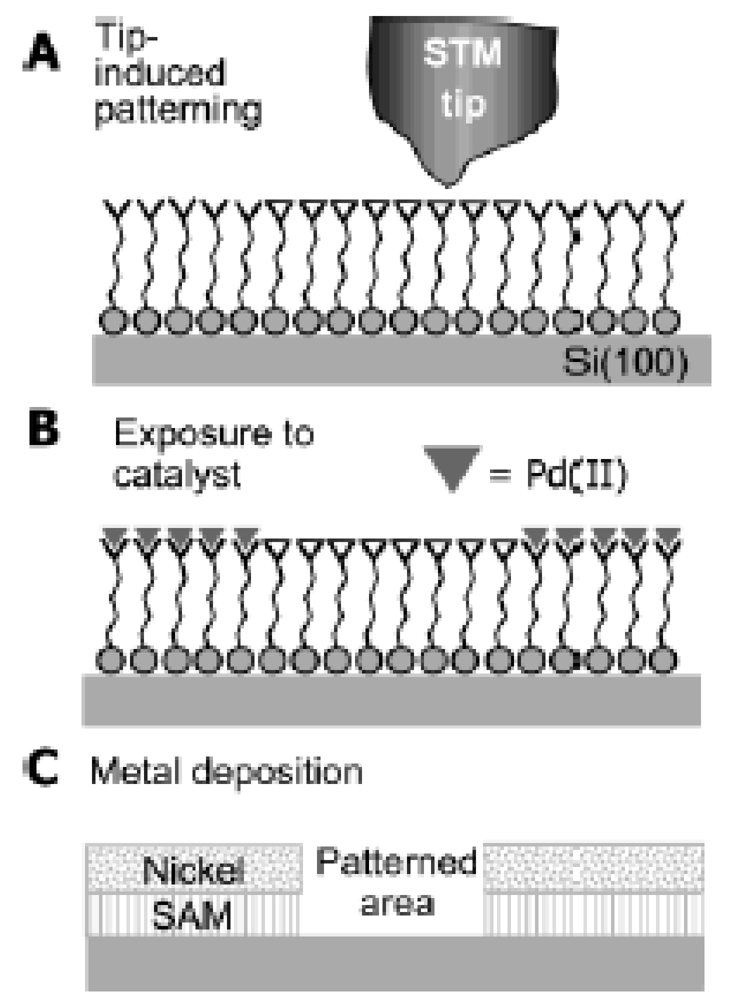




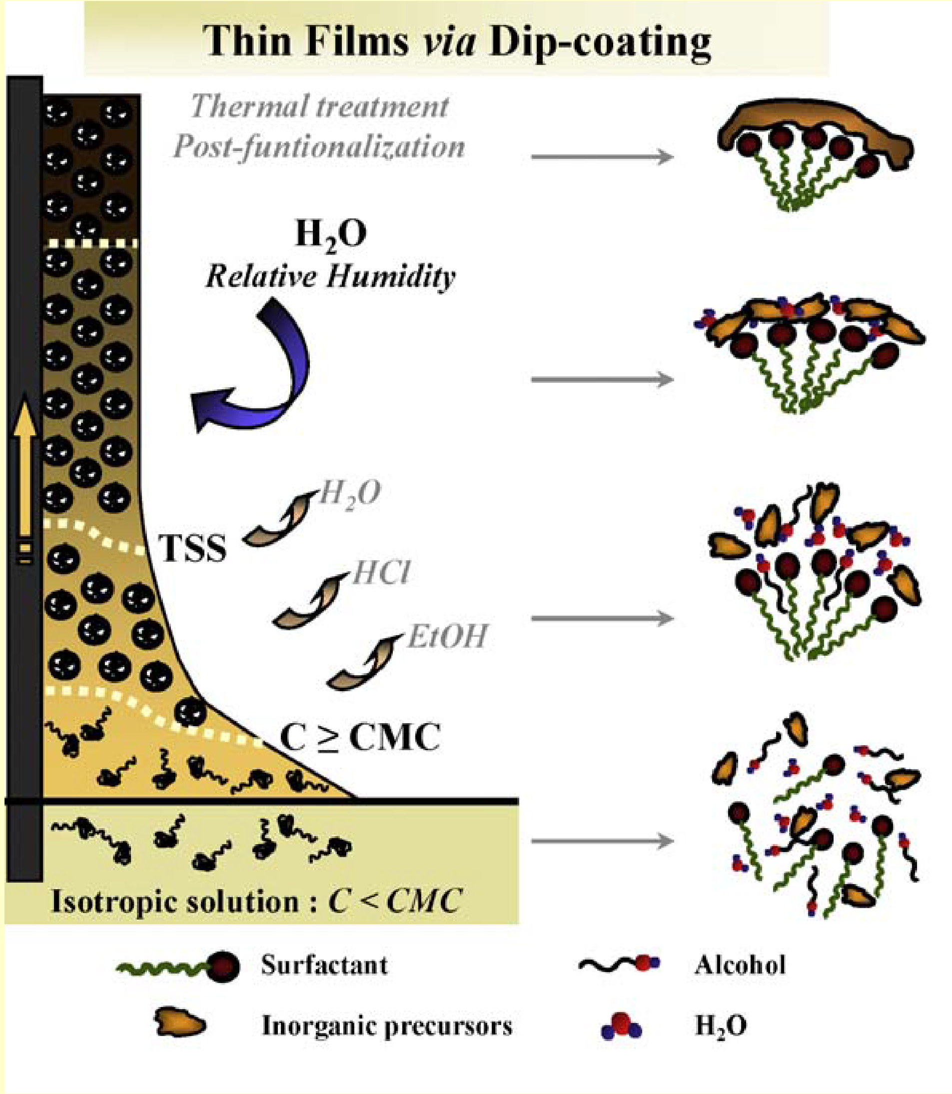
Manipulations with SAM



Manipulations with SAM

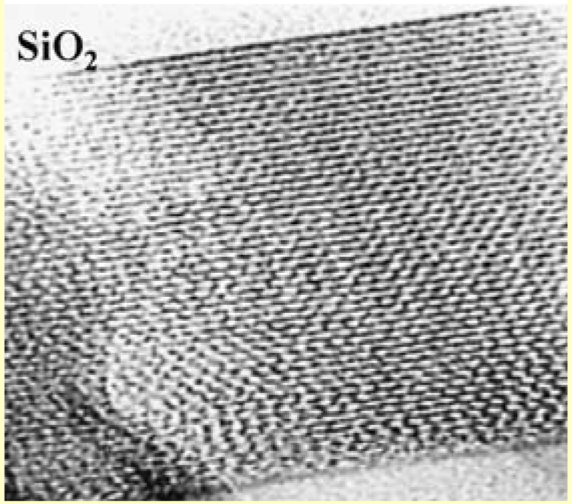


Evaporation Induced Self-Assembly (EISA)



Critical parameters of EISA process:

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



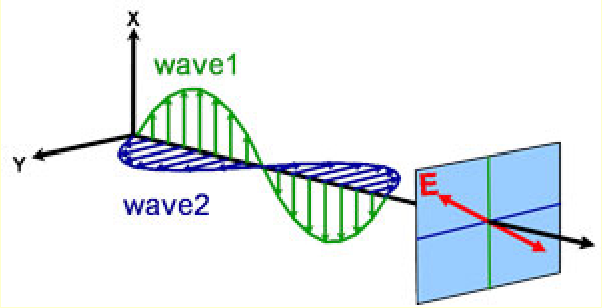
Ellipsometry

Measures the interaction between light and material:

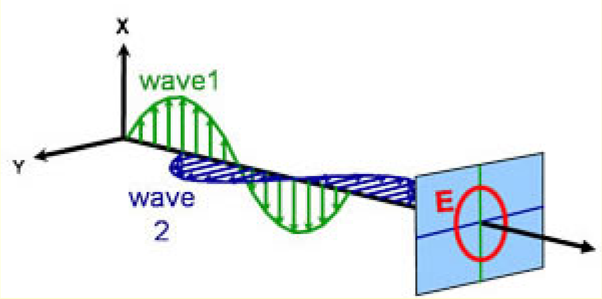
- **Layer thickness**
- **Optical constants (refractive index and extinction coefficient)**
- **Surface roughness**
- **Composition**
- **Optical anisotropy**

Light and Polarization

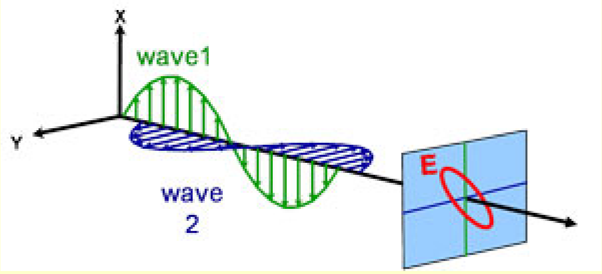
Orthogonal waves combine



(a) Linear polarization
two orthogonal light waves in-phase



(b) Circular
90° out-of-phase and equal in amplitude



(c) Elliptical
arbitrary amplitude and phase

Materials Optical Properties

The complex refractive index (*N*):
consists of the refractive index (*n*) and extinction coefficient (*k*):

$$N = n + ik$$

dielectric function *E* (complex):

$$E = N^2$$

$$E = \varepsilon_1 + i\varepsilon_2$$

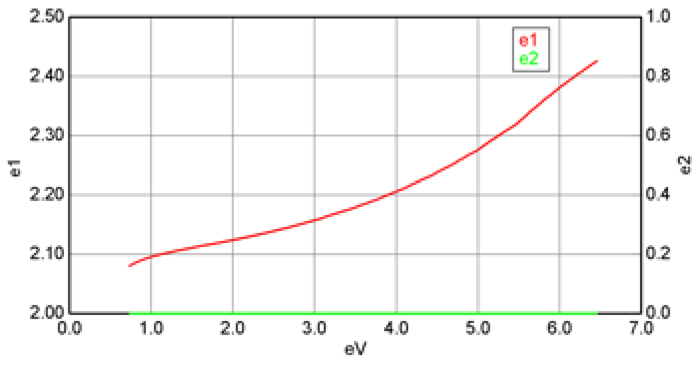
The refractive index describes the phase velocity of light as it travels in a material compared to the speed of light in vacuum, *c*:

$$\upsilon = \frac{c}{n}$$

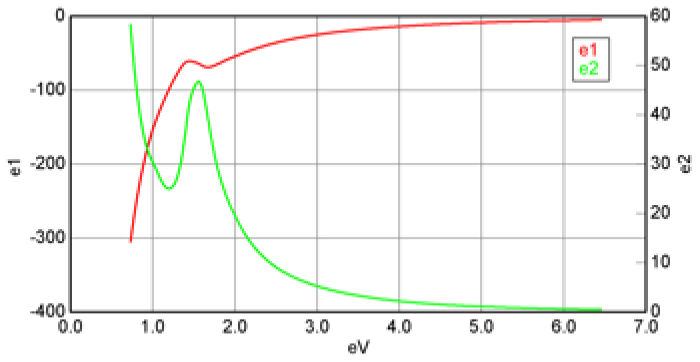
Light slows in a material with higher index, the frequency of light waves remains constant, the wavelength will shorten.

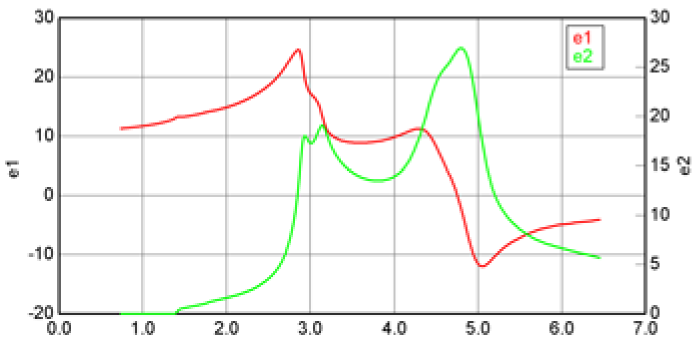
Dielectric Function of Typical Materials

SiO_2, transparent over the entire spectral region. e1 is positive, but e2=0 indicates a transparent material



Al, absorption due to free carriers over the entire spectral region, causing e2 to be nonzero over the full spectrum.



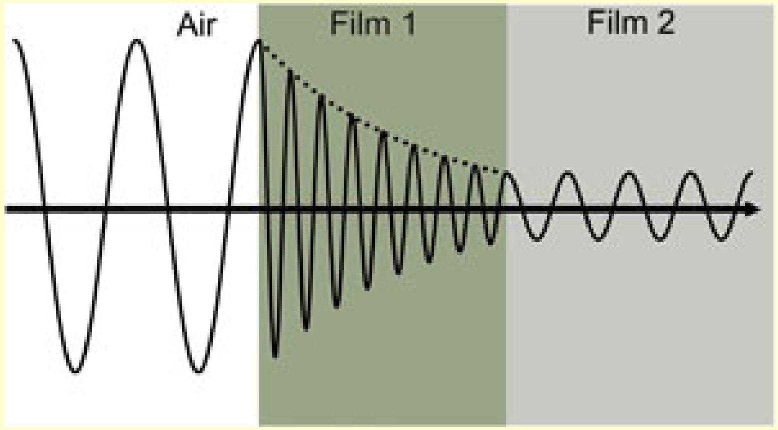


GaAs, semiconductor, bandgap near 1.42 eV, e2 is zero below the bandgap, with absorption (e2>0) above the bandgap

Extinction coefficient

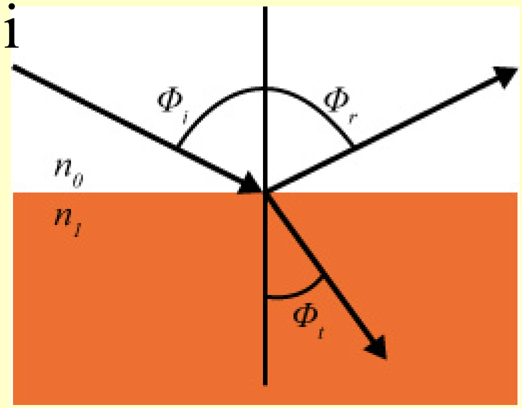
The extinction coefficient describes the loss of wave energy to the material. It is related to the absorption coefficient, α as:

$$\alpha = \frac{4\pi k}{\lambda}$$



Wave travels from air into absorbing Film 1 and then transparent Film 2. The phase velocity and wavelength change in each material depending on index of refraction (Film 1: n = 4, Film 2: n = 2).

Snell's law



Incident beam, i

Reflected beam, r

Refracted, transmitted beam, t

$$n_0 \sin \Phi_i = n_1 \sin \Phi_t$$

Frensel coefficients

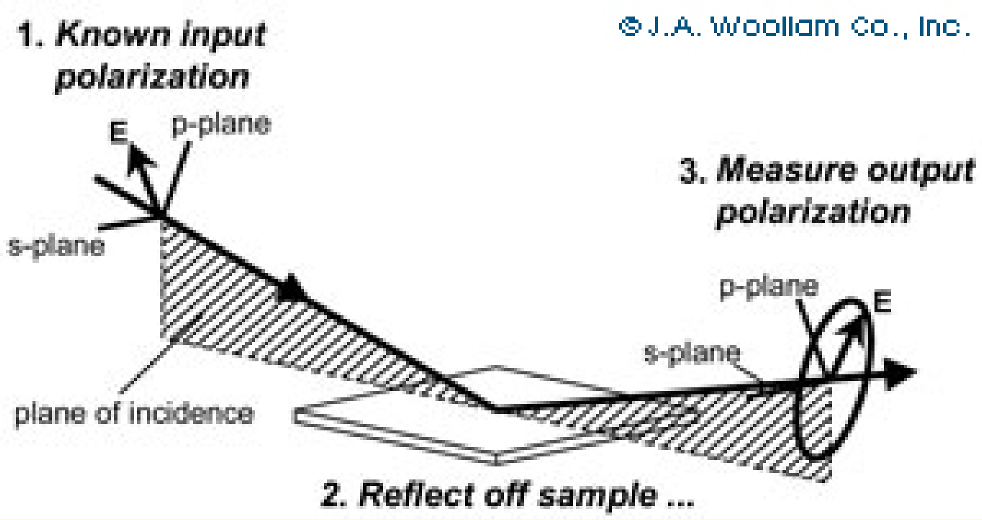
$$r_s = \left(\frac{E_{0r}}{E_{0i}}\right)_s = \frac{n_i \cos(\Phi_i) - n_t \cos(\Phi_t)}{n_i \cos(\Phi_i) + n_t \cos(\Phi_t)}$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}}\right)_p = \frac{n_t \cos(\Phi_i) - n_i \cos(\Phi_t)}{n_i \cos(\Phi_t) + n_t \cos(\Phi_i)}$$

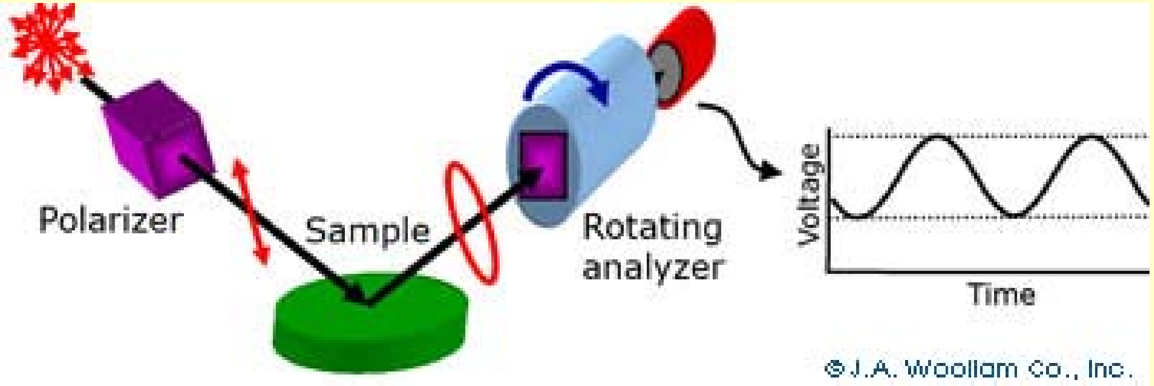
$$t_s = \left(\frac{E_{0t}}{E_{0i}}\right)_s = \frac{2 n_i \cos(\Phi_i)}{n_i \cos(\Phi_i) + n_t \cos(\Phi_t)}$$

$$t_p = \left(\frac{E_{0t}}{E_{0i}}\right)_p = \frac{2 n_i \cos(\Phi_i)}{n_i \cos(\Phi_t) + n_t \cos(\Phi_i)}$$

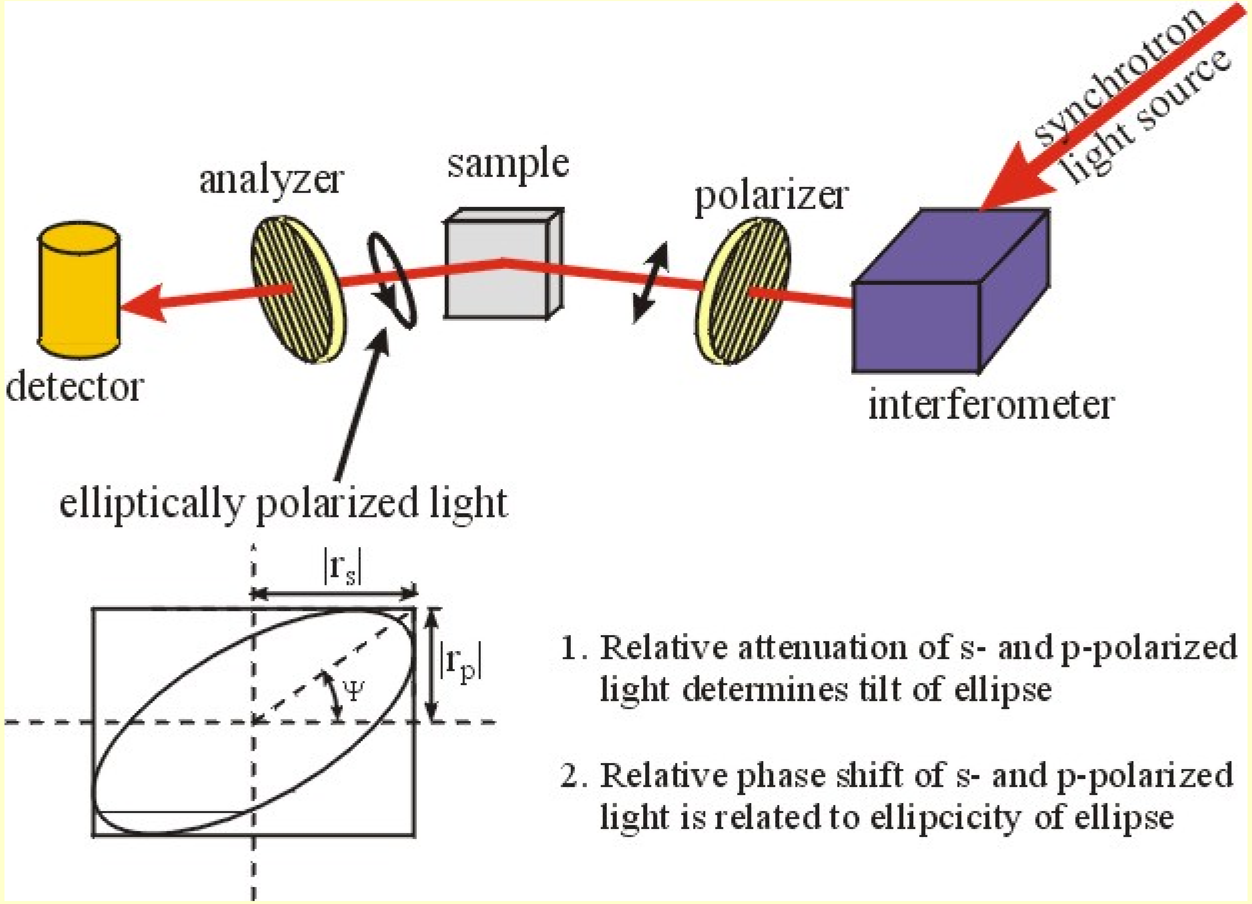
Ellipsometry Measurements



$$\tan\Psi e^{i\Delta} = \frac{r_p}{r_s} = \rho$$



Ellipsometry Measurements



1. Relative attenuation of s- and p-polarized light determines tilt of ellipse

2. Relative phase shift of s- and p-polarized light is related to ellipcicity of ellipse

Ellipsometry Measurements

A light source produces unpolarized light which is then sent through a polarizer. The polarizer allows light of a preferred electric field orientation to pass. The polarizer axis is oriented between the p- and s- planes, such that both arrive at the sample surface. The linearly polarized light reflects from the sample surface, becomes elliptically polarized, and travels through a continuously rotating polarizer (referred to as the analyzer). The amount of light allowed to pass will depend on the polarizer orientation relative to the electric field "ellipse" coming from the sample. The detector converts light to electronic signal to determine the reflected polarization. This information is compared to the known input polarization to determine the polarization change caused by the sample reflection. This is the ellipsometry measurement of Psi and Delta.

Ellipsometry Measurements

Ellipsometry measures changes in light polarization to determine the sample material's properties of interest, such as film thickness and optical constants. In the case of a bulk material, the equations derived for a single reflection can be directly inverted to provide the “pseudo” optical constants from the ellipsometry measurement

$$\langle\tilde{\varepsilon}\rangle = \sin^2(\phi)\left[1 + \tan^2(\phi)\left(\frac{1-\rho}{1+\rho}\right)\right]$$

Ellipsometry Measurements

Regression analysis is required because an exact equation cannot be written. Often the answer is over-determined with hundreds of experimental data points for a few unknowns. Regression analysis allows all of the measured data to be included when determining the solution.