# 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

$Fe(CO)_5 + O_2 \rightarrow$ 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

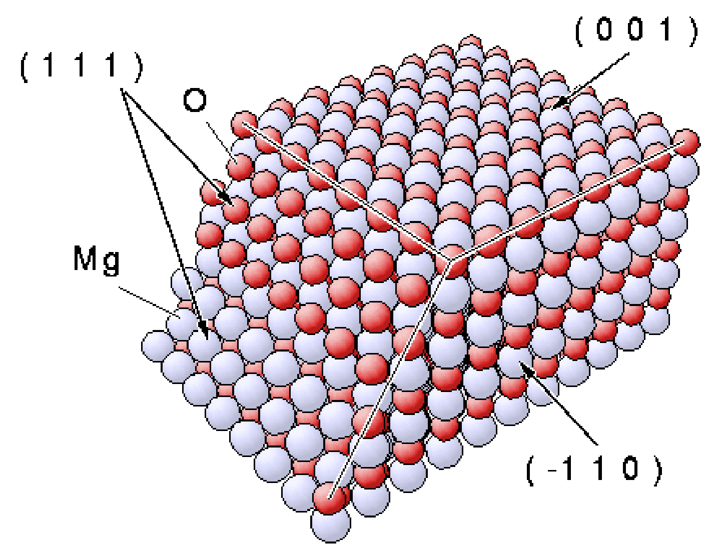
Same for liquids, different for solids

**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

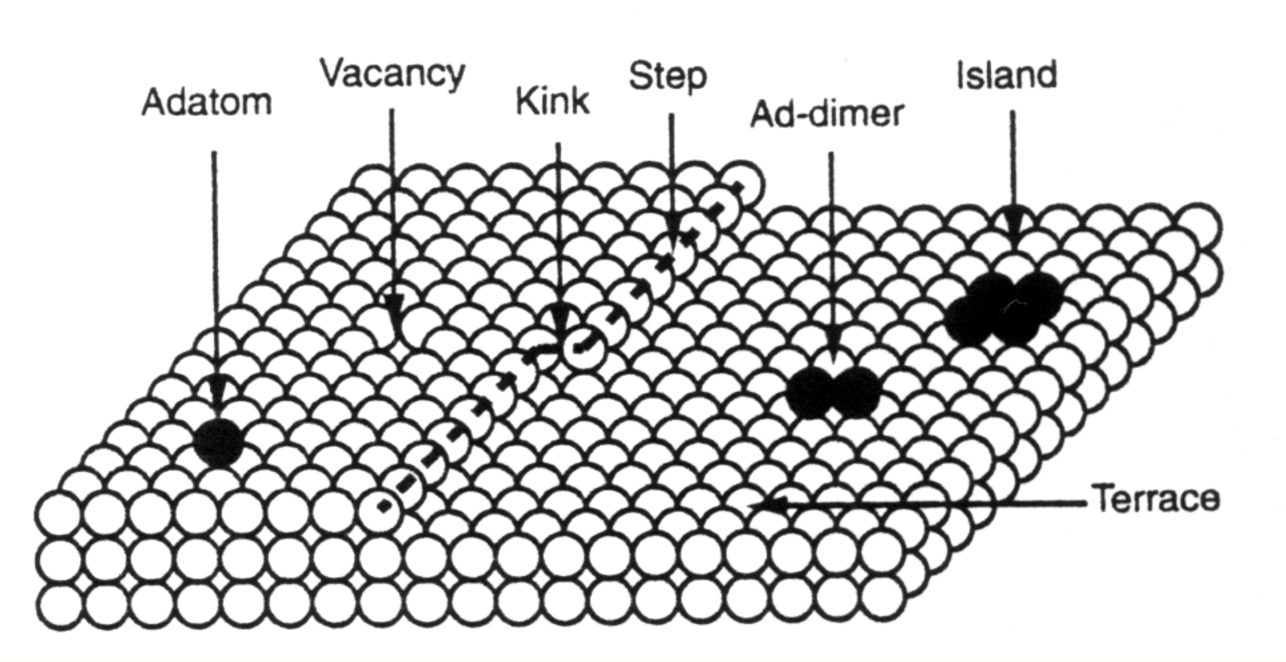


Cubic (rocksalt) MgO crystal: different netplanes

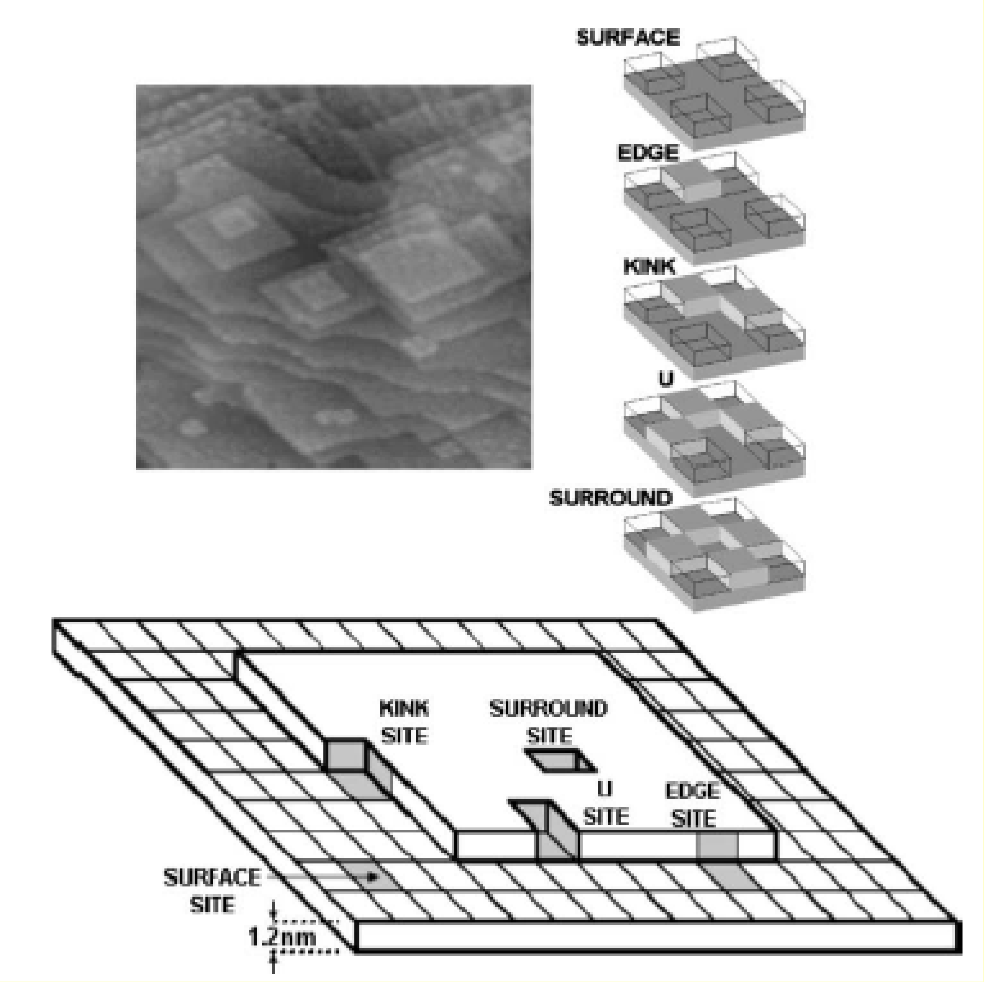
# Surfaces

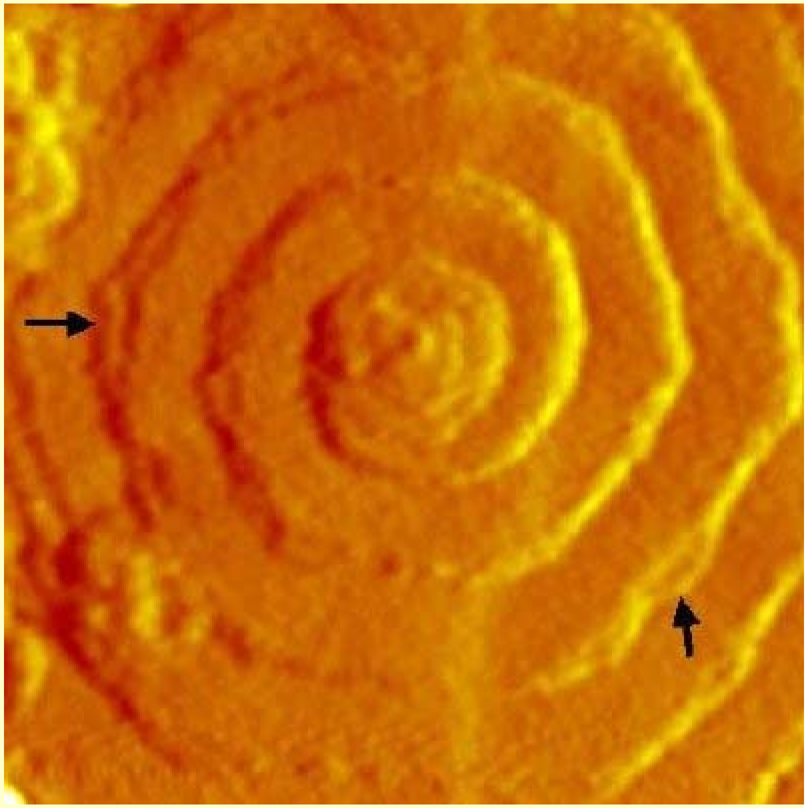
## The TSK (TLK) Model of a Surface (Kossel/Stranski)

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



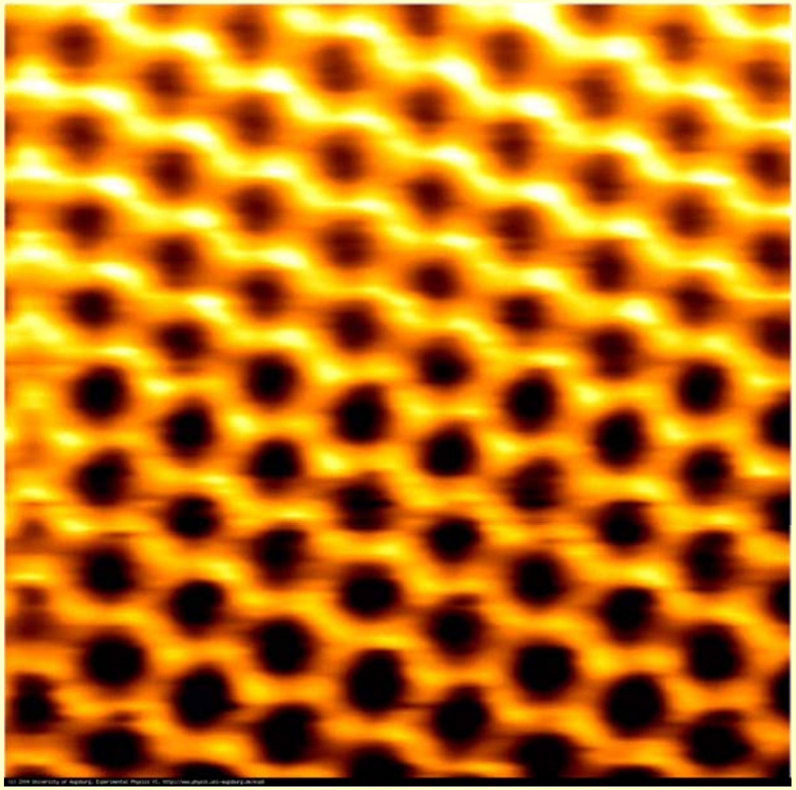
# Surfaces





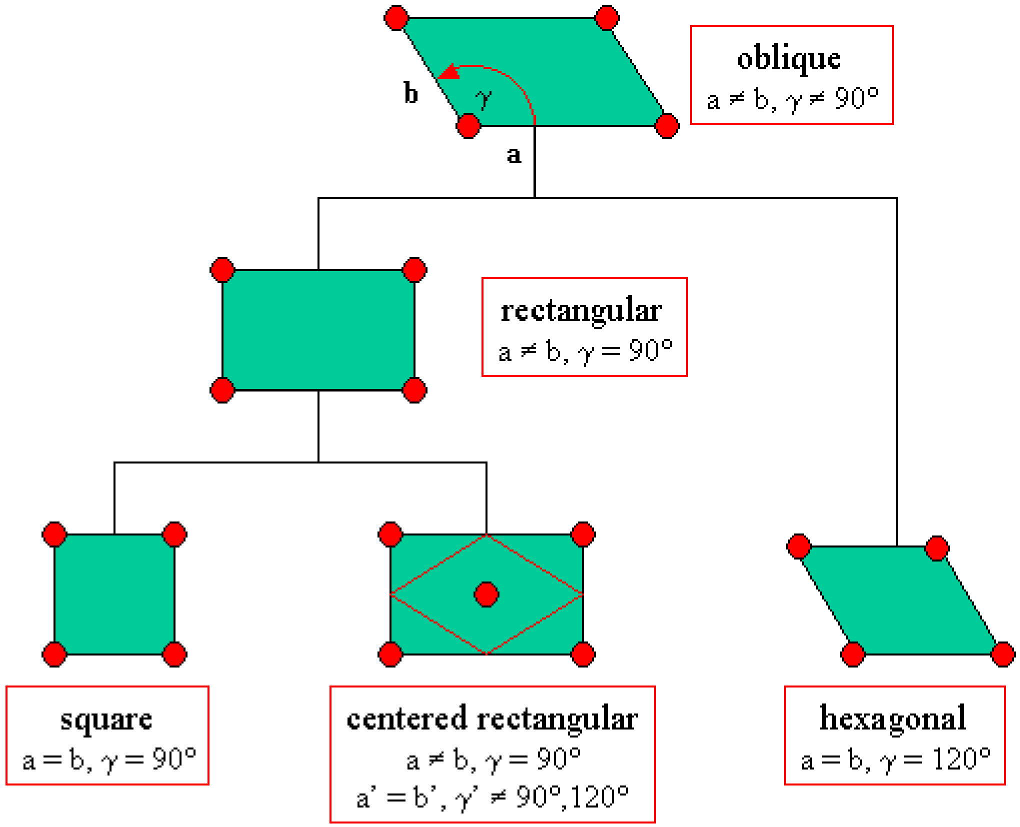
**Screw dislocation on graphite**
**Spiral growth**

# Surfaces



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

# Surface Bravais Lattices



**oblique**
$a \neq b,\ \gamma \neq 90^\circ$

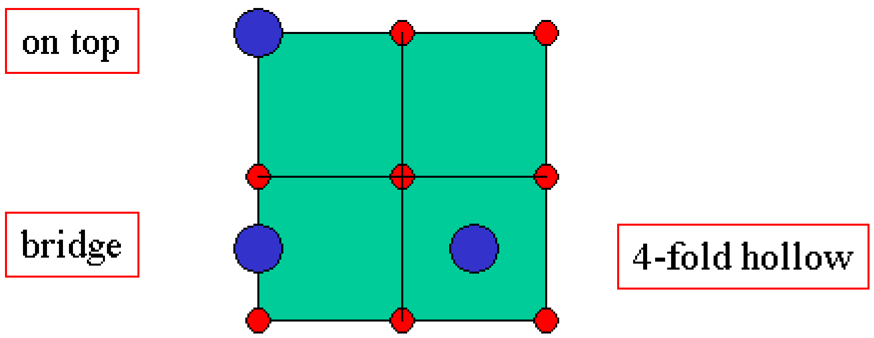
**rectangular**
$a \neq b,\ \gamma = 90^\circ$

**square**
$a = b,\ \gamma = 90^\circ$

**centered rectangular**
$a \neq b,\ \gamma = 90^\circ$
$a' = b',\ \gamma' \neq 90^\circ, 120^\circ$

**hexagonal**
$a = b,\ \gamma = 120^\circ$

# Absorption Sites



# Surface Diffusion

**Surface diffusion coefficient D**

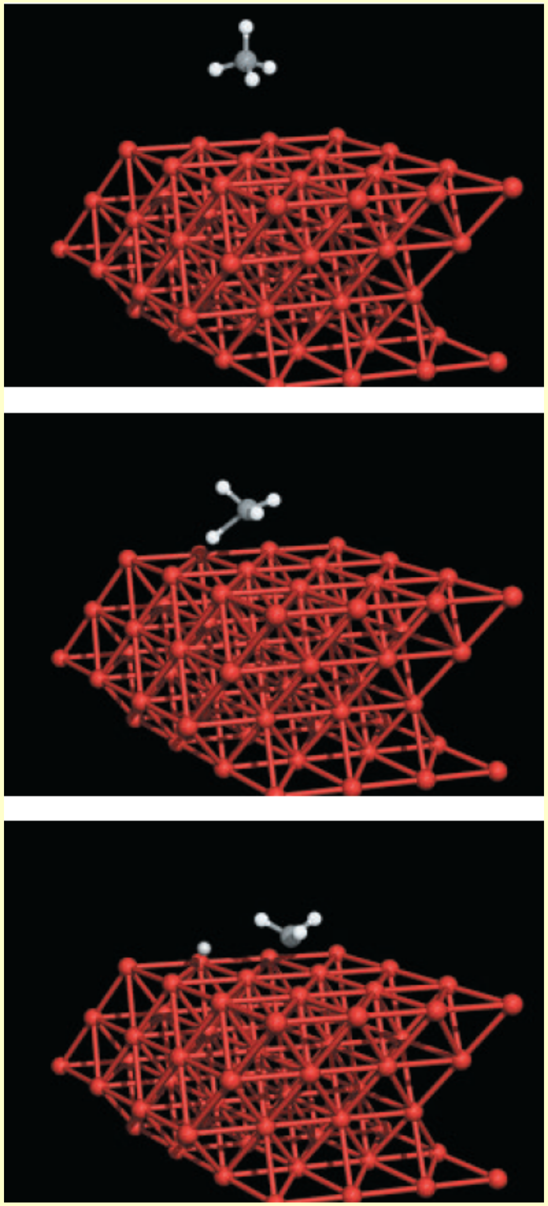
**$D = a^2 k_s$ a … effective hopping distance between sites**

**$k_s$ … 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**

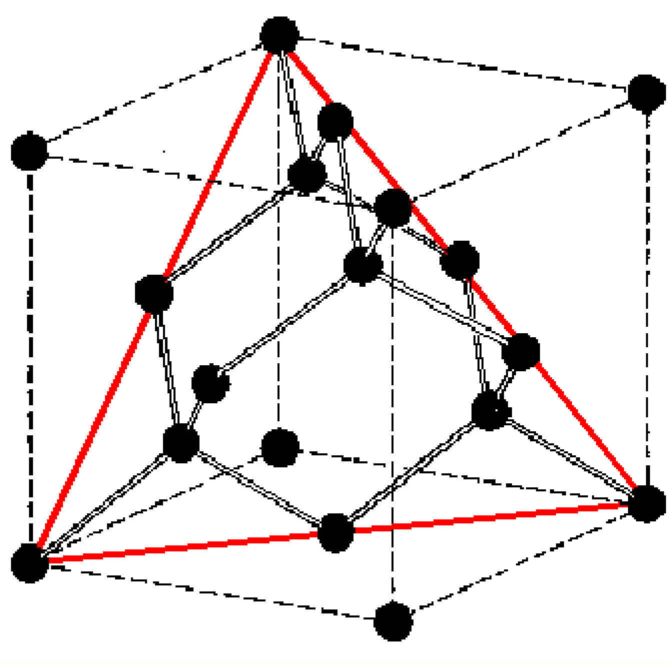
**T … substrate temperature**

## 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

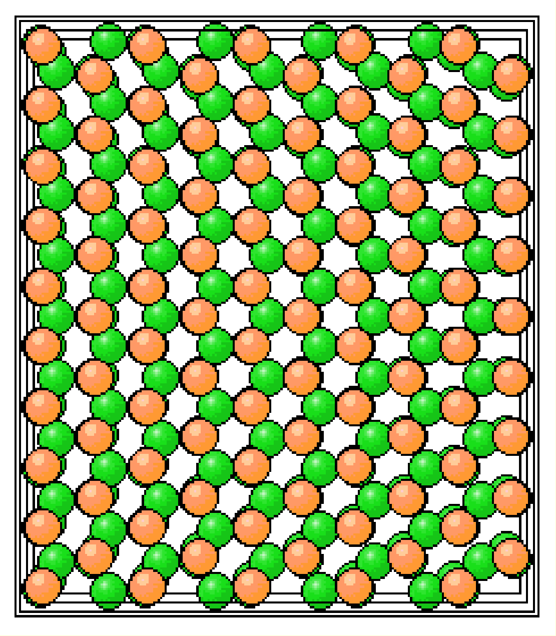
**Si(111) = a set of atomic planes**

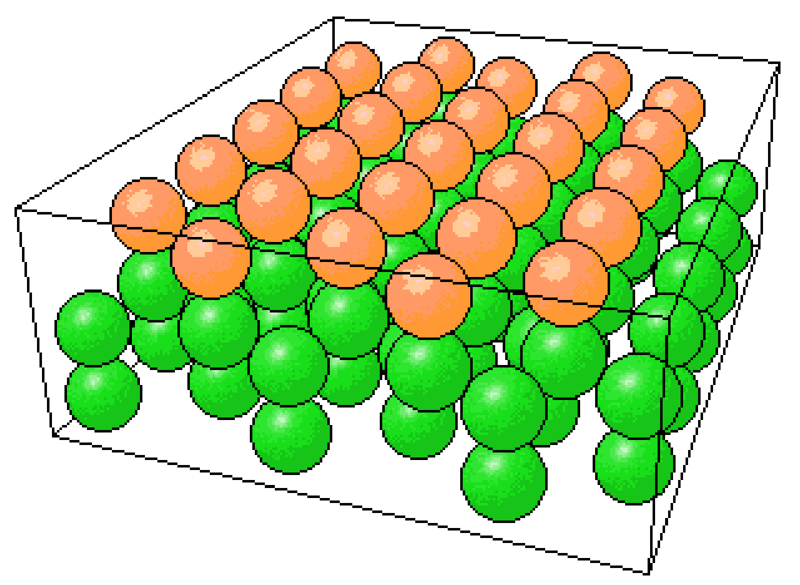
**One plane outlined with red**

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

# Si(111) Surface

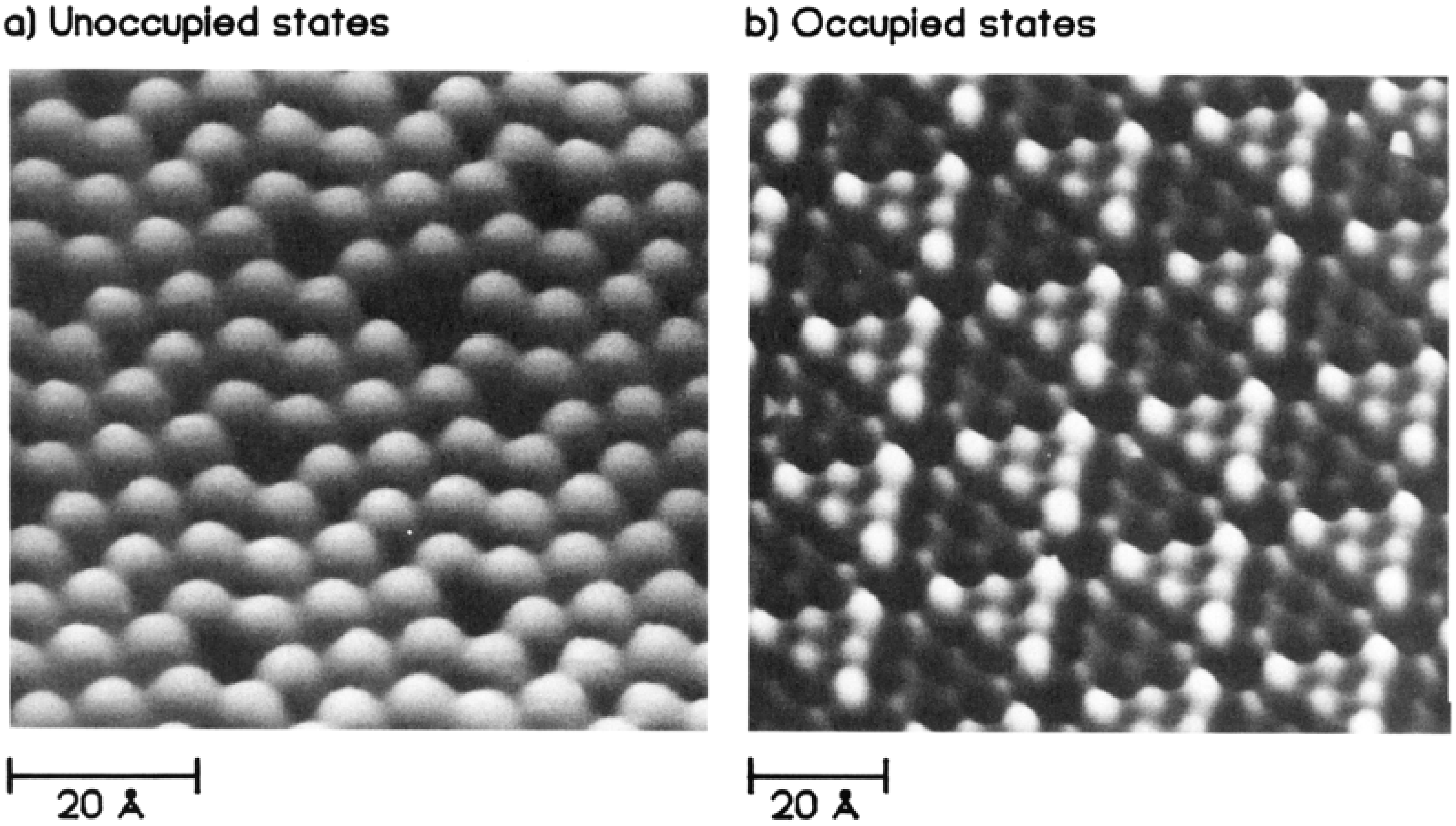
**A top view of the atomic arrangement for the (111) plane**





**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

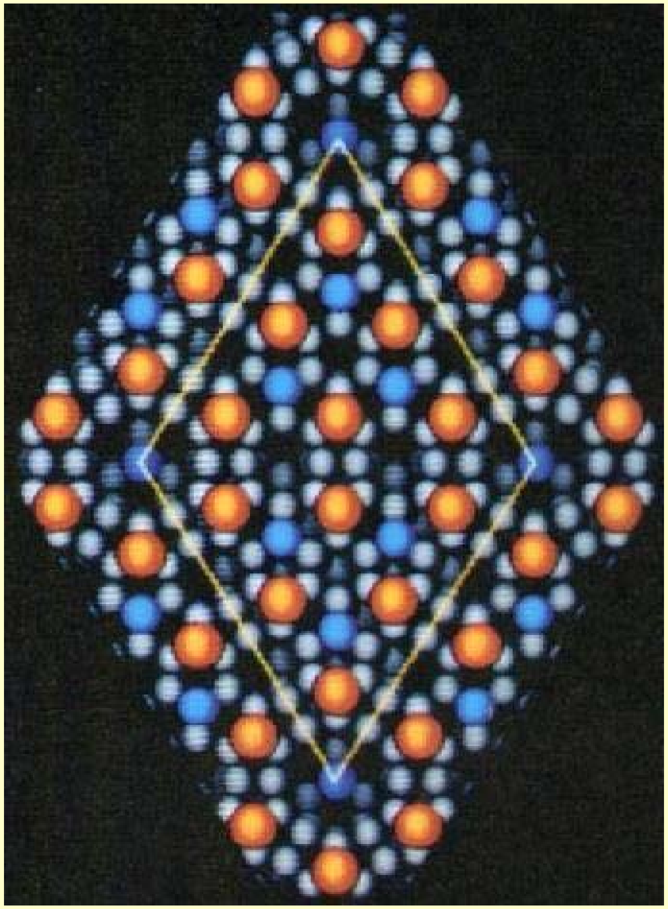
**Relaxation** = energy lowering, no chnge in symmetry

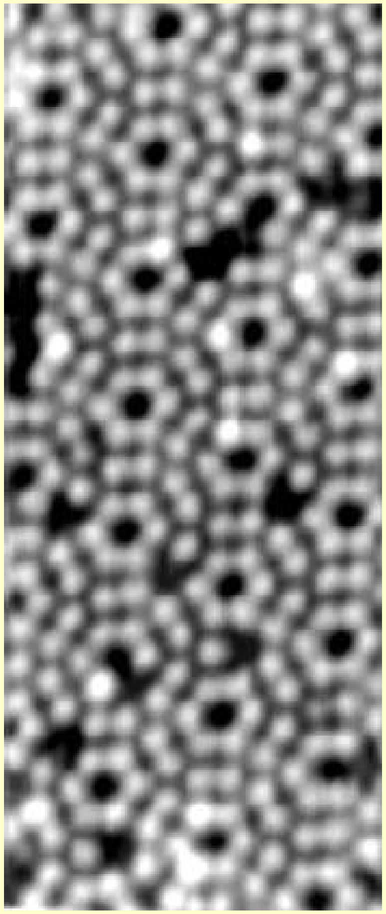
**Reconstruction** = the surface atoms rearrange to a more energetically stable configuration.

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

# 7x7 Reconstruction

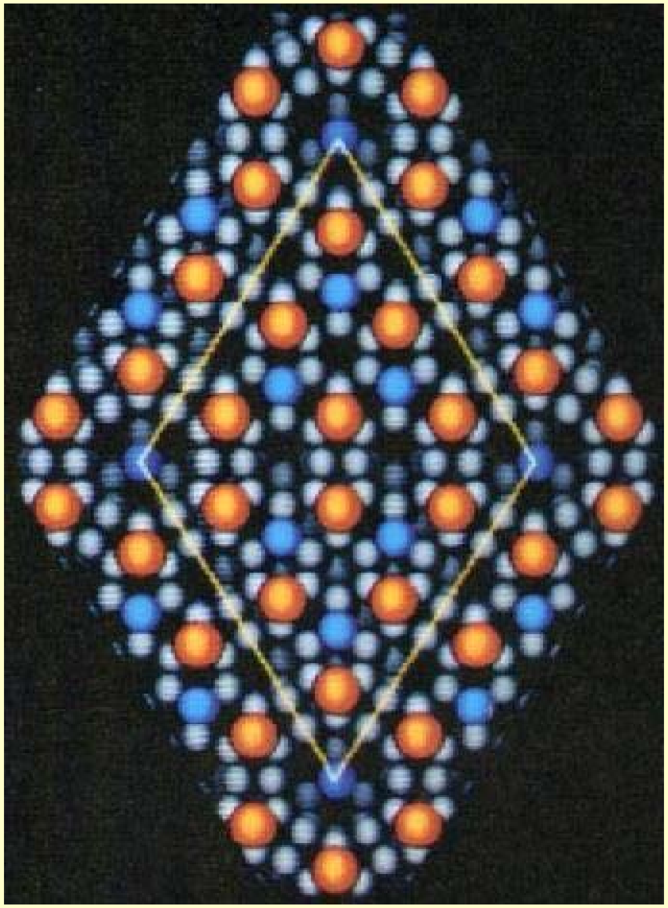
**When (111) surface of Si is heated to high temperatures under the Ultra-High Vacuum conditions the surface atoms rearrange to a more energetically stable configuration called 7x7 reconstruction.**

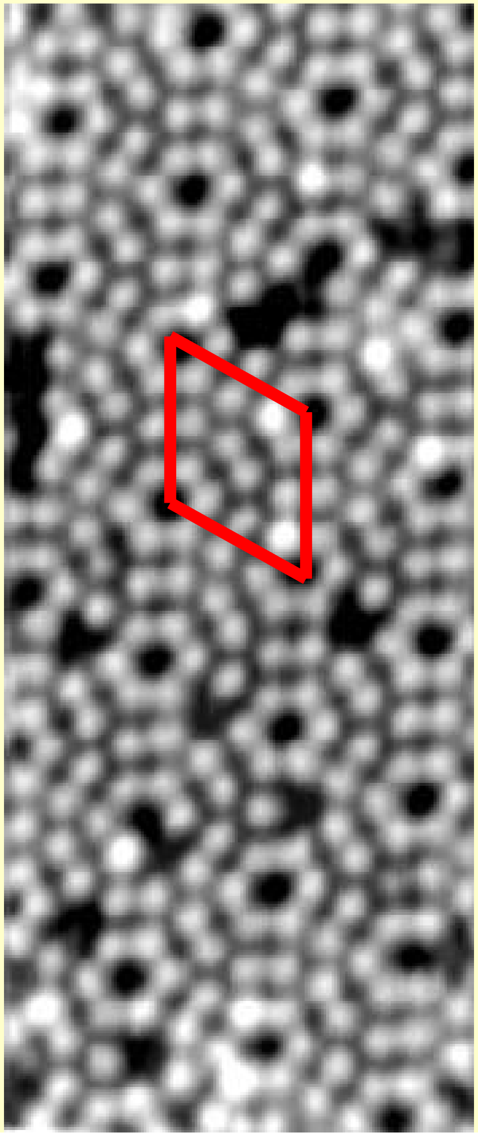




**STM image of Si(111) surface**

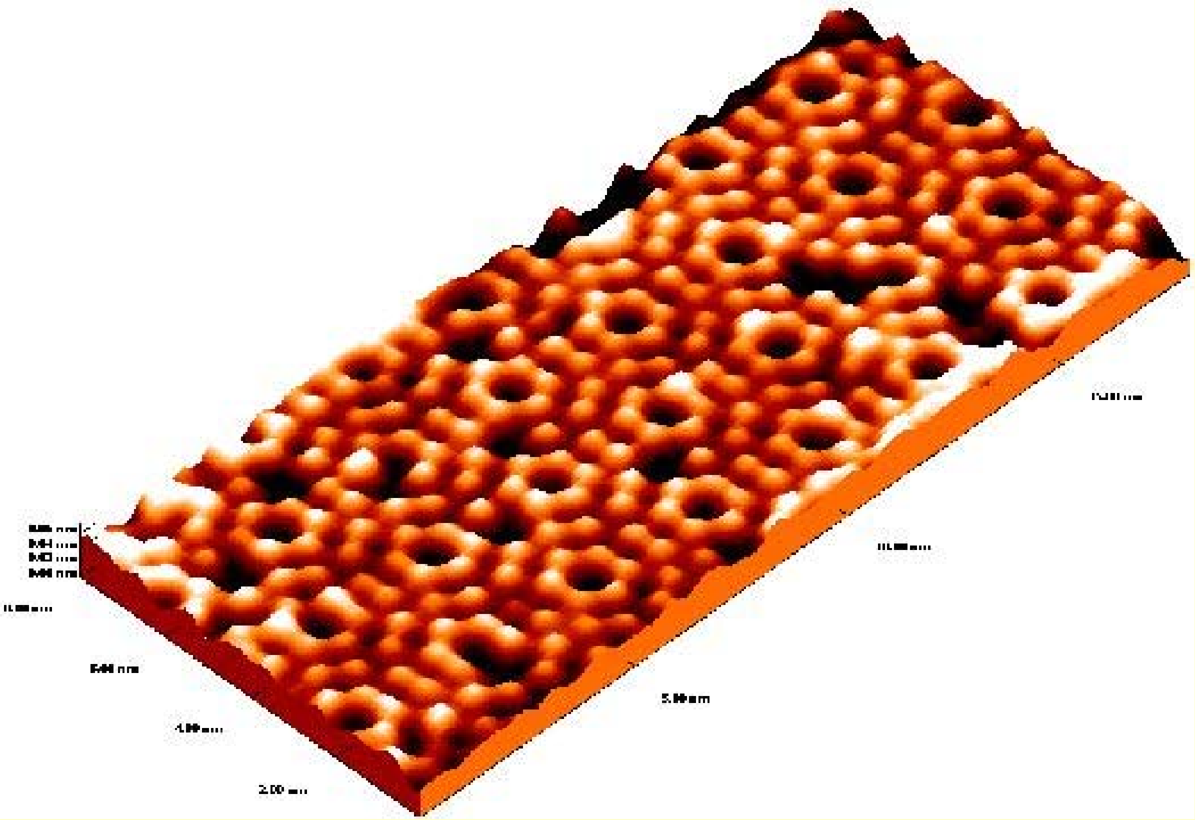
# 7x7 Reconstruction



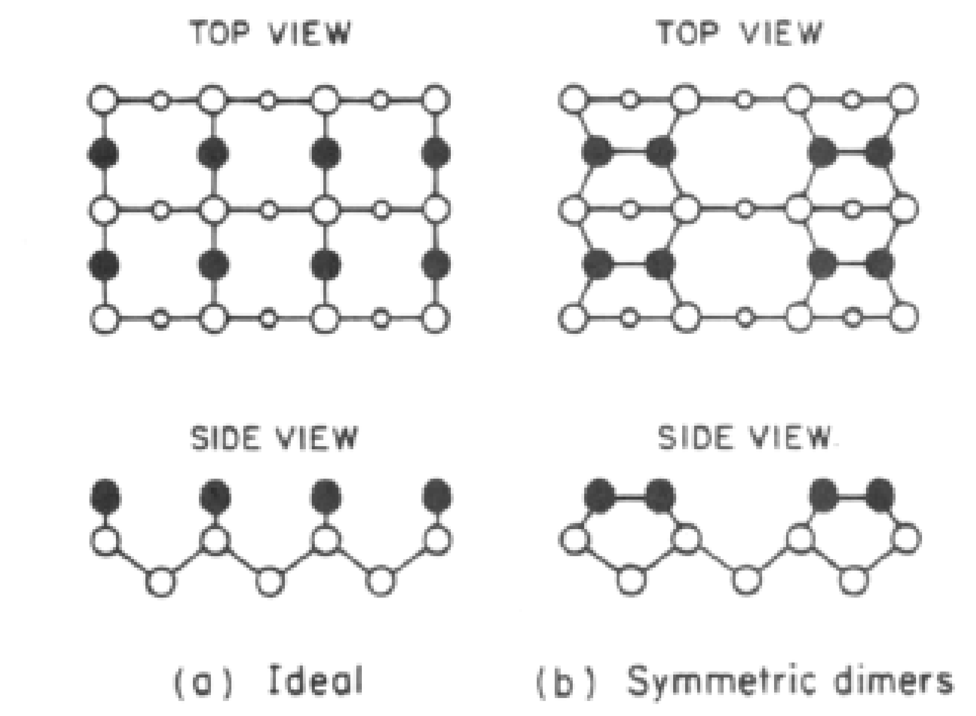


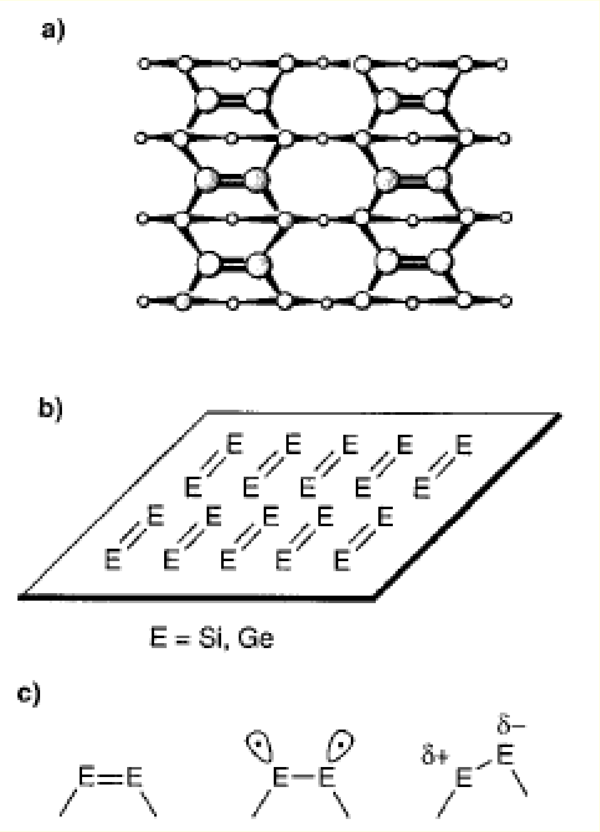
# 7x7 Reconstruction

**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





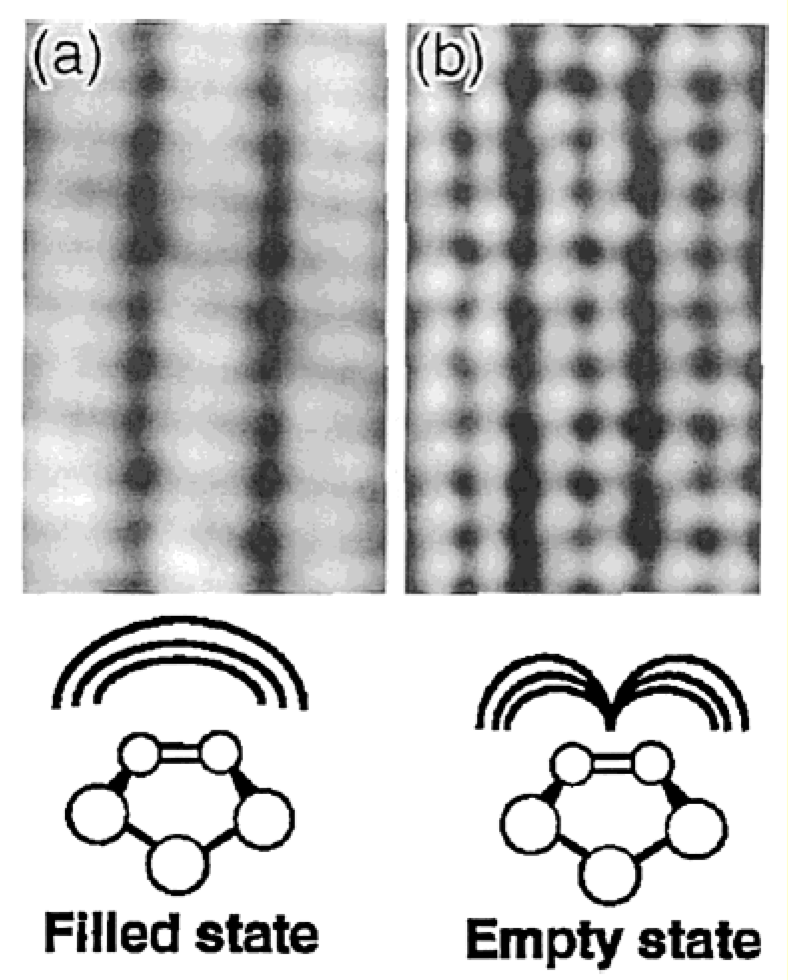
ideal reconstructed

**STM images of the silicon-silicon dimers imaged with**

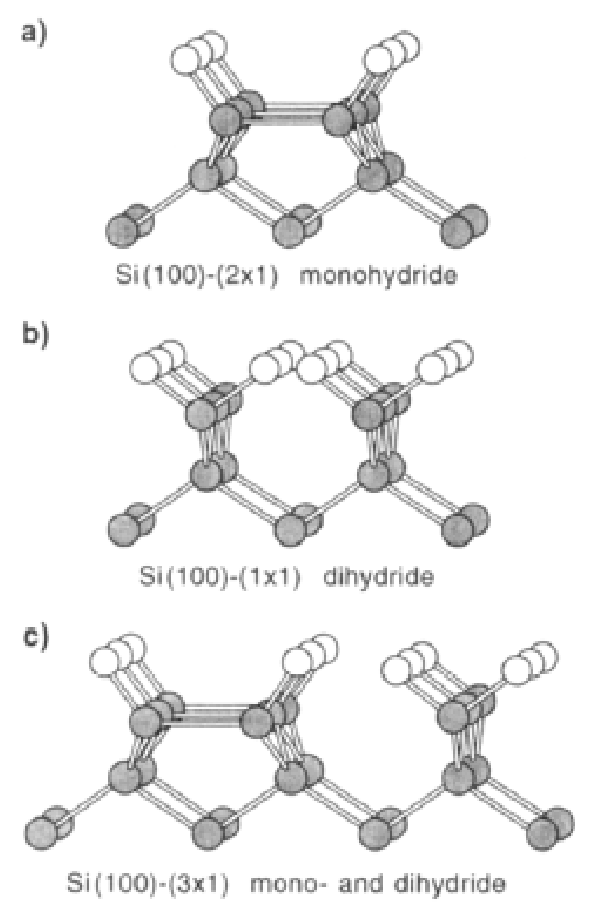
**(a) $V_{\text{sample}}$ = -2.0 V**
**(b) $V_{\text{sample}}$ = 2.3 V**

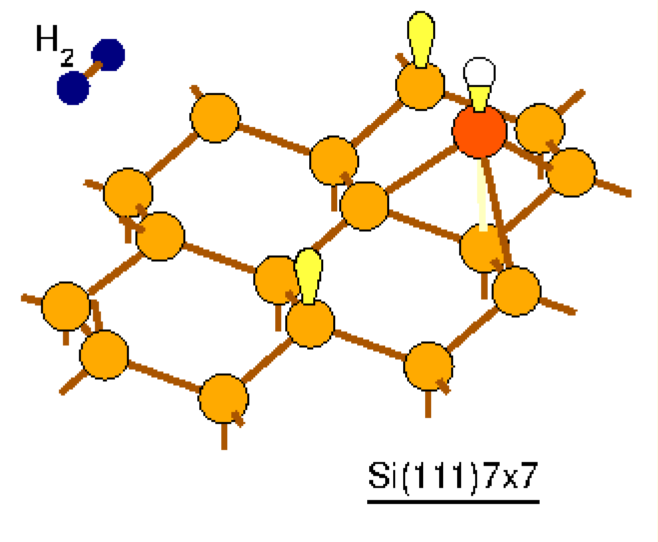
**The filled and empty states of these highly ordered dimers can be probed by biasing the surface in the opposite directions**

**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**

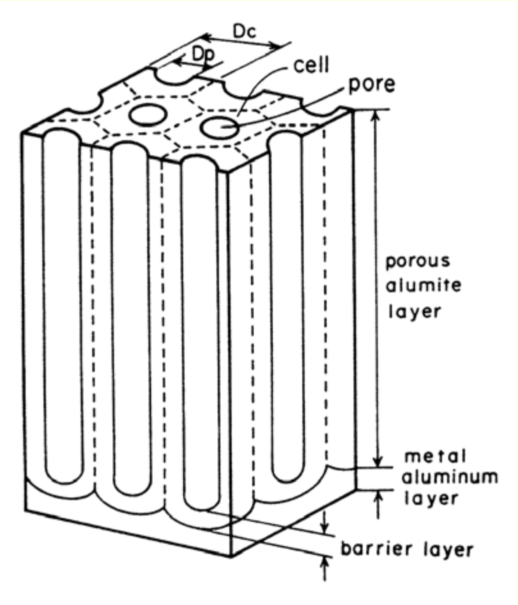
**$PO_4^{3-} + 2e^- \rightarrow PO_3^{3-} + O^{2-}$ cathode**

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

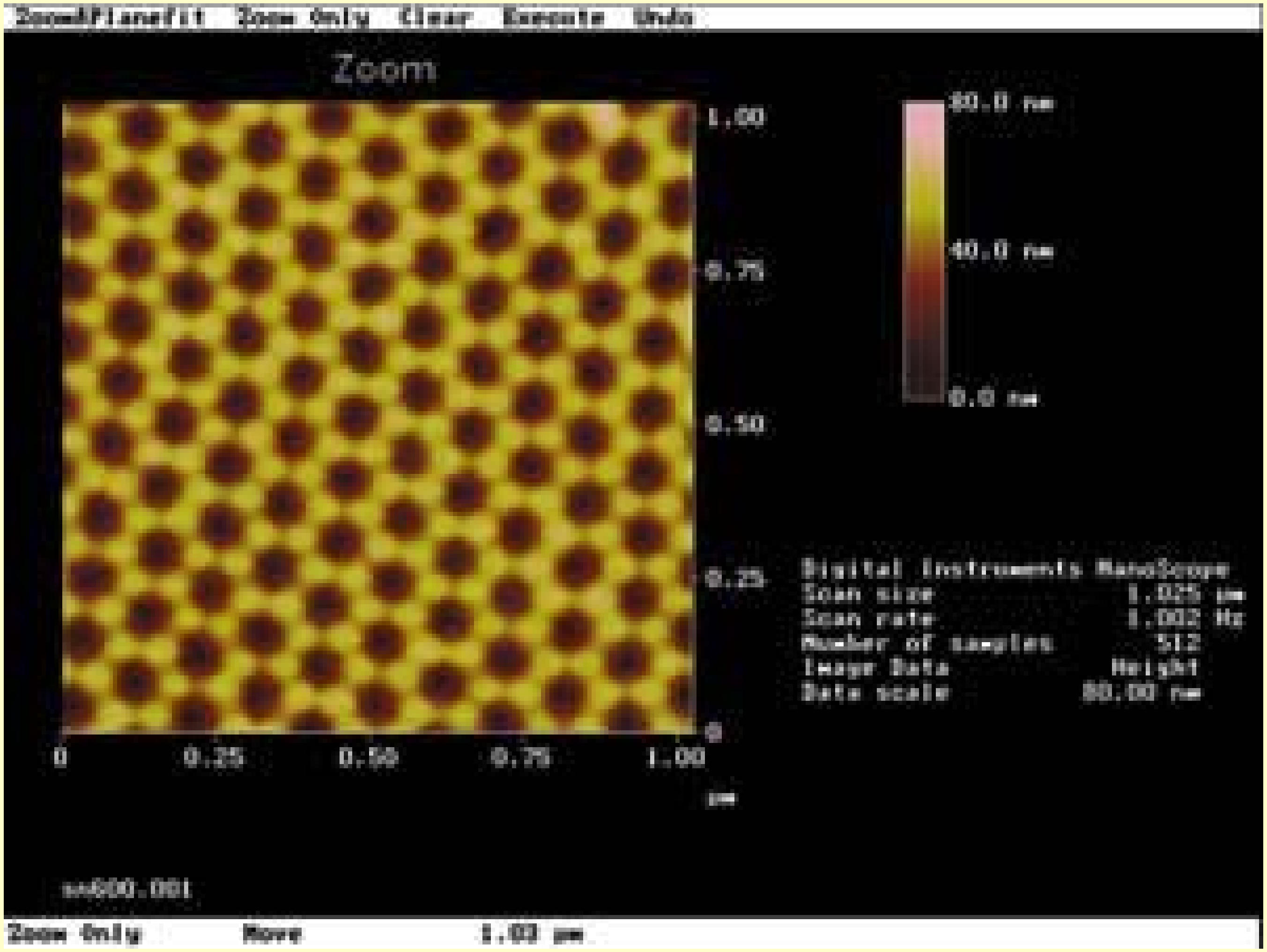
# Porous Alumina Films



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

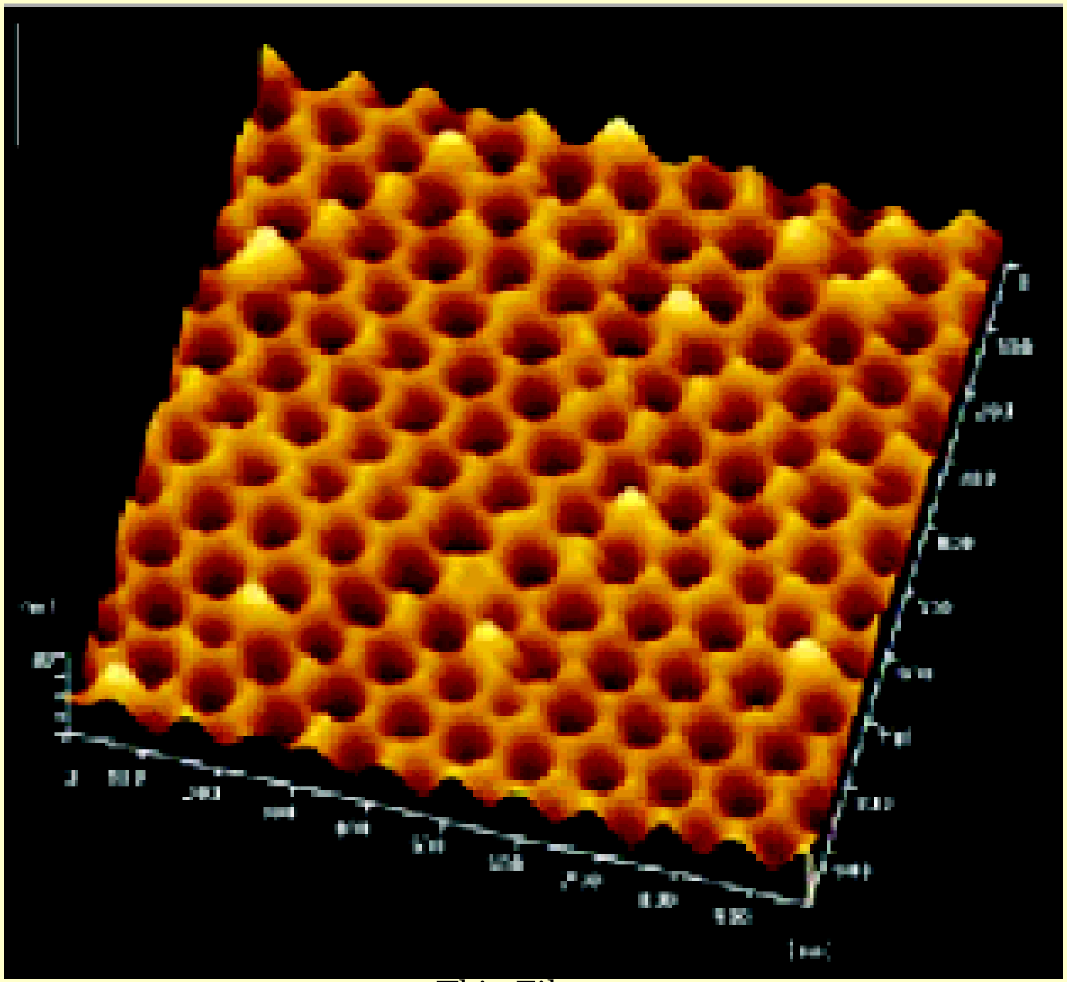
**Exceptionally useful process for creating controlled porosity membranes, photonic gap materials, template for synthesizing semiconductor nanostructures, host for synthesizing and organizing aligned carbon nanotubes for high intensity electron emission displays, and last but not least, fuel cell electrode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

# AFM picture of porous alumina film

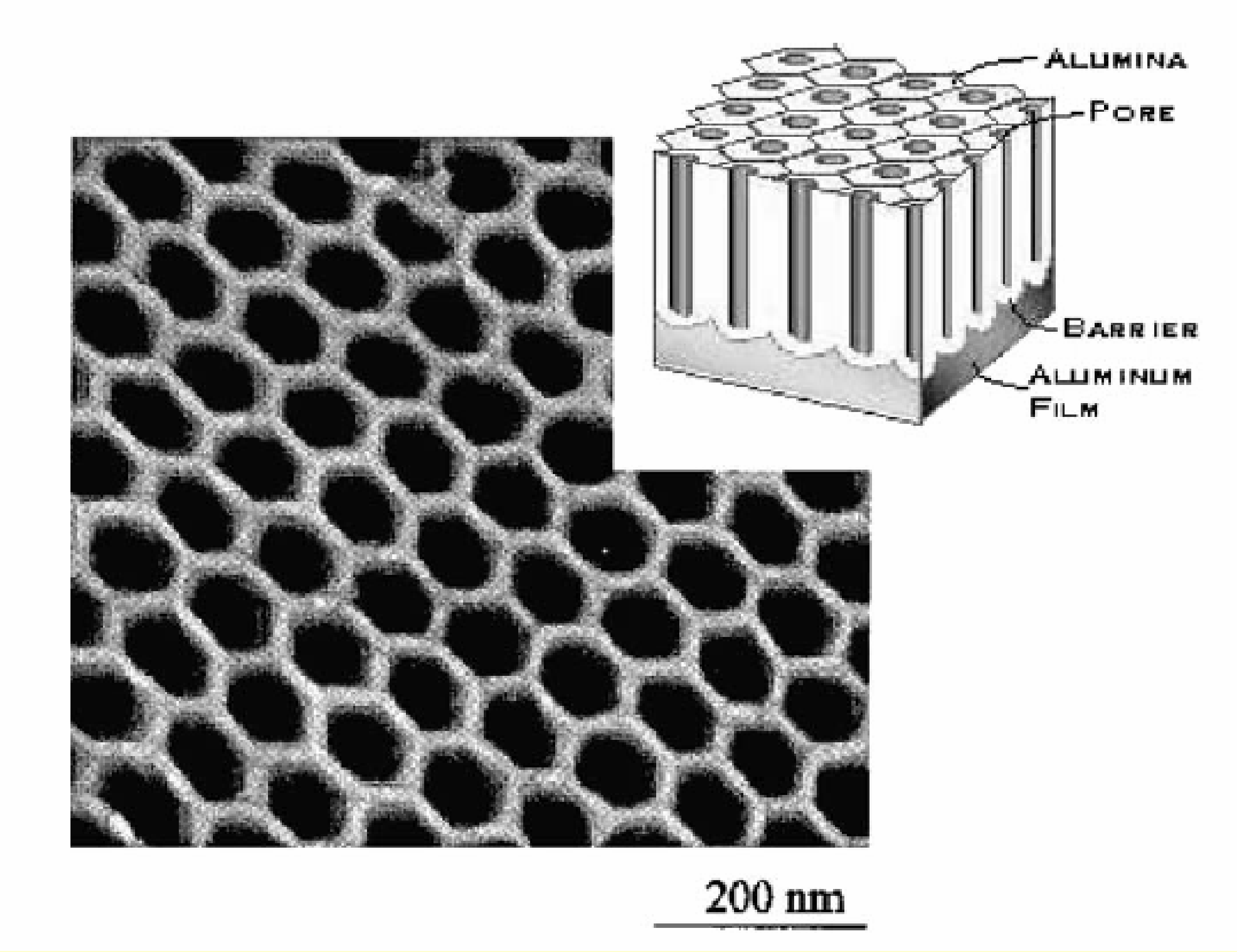


Digital Instruments NanoScope
Scan size 1.025 µm
Scan rate 1.002 Hz
Number of samples 512
Image Data Height
Data scale 80.00 nm

# AFM picture 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**

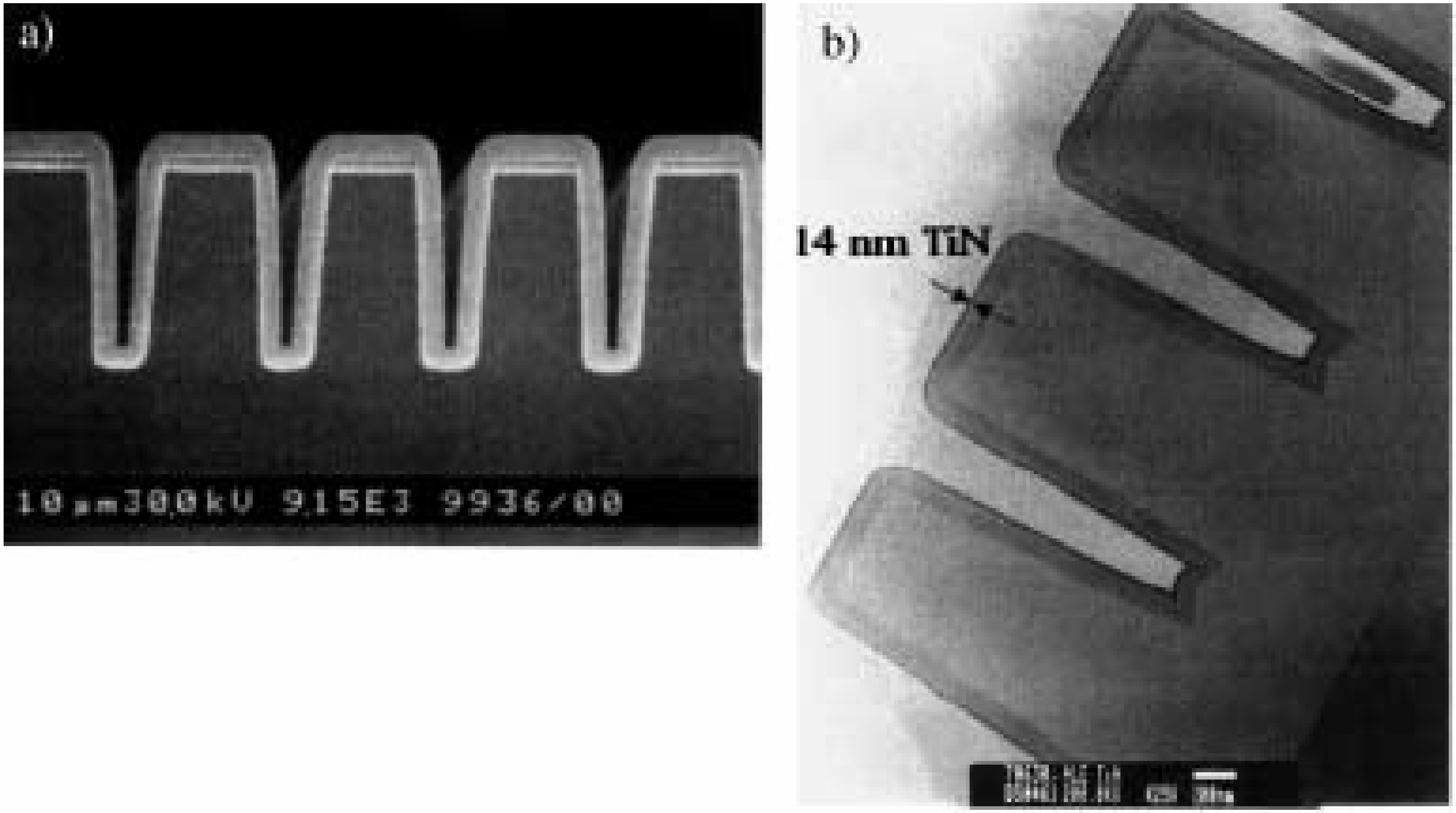
$CH_4 + H_2$ **(RF, MW) → C, diamond films**

$Et_4Si$ **(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 300kV 915E3 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**

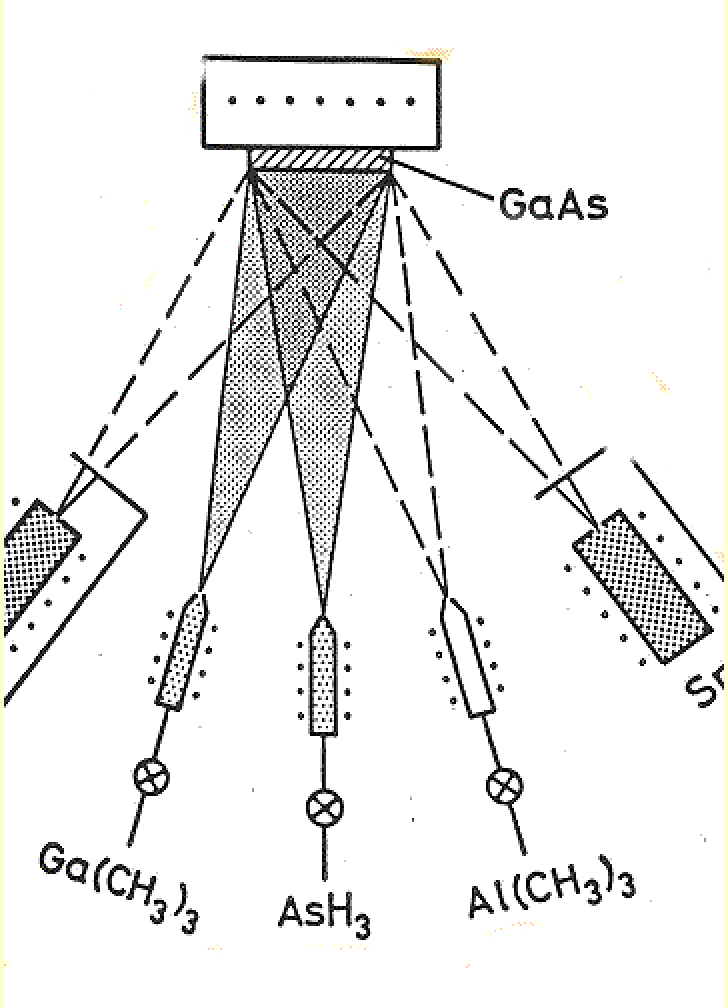
**Homoepitaxy – same compound/orientation in substrate and film**
**Heteroepitaxy – different compounds in the substrate and film**

# 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**

# 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**

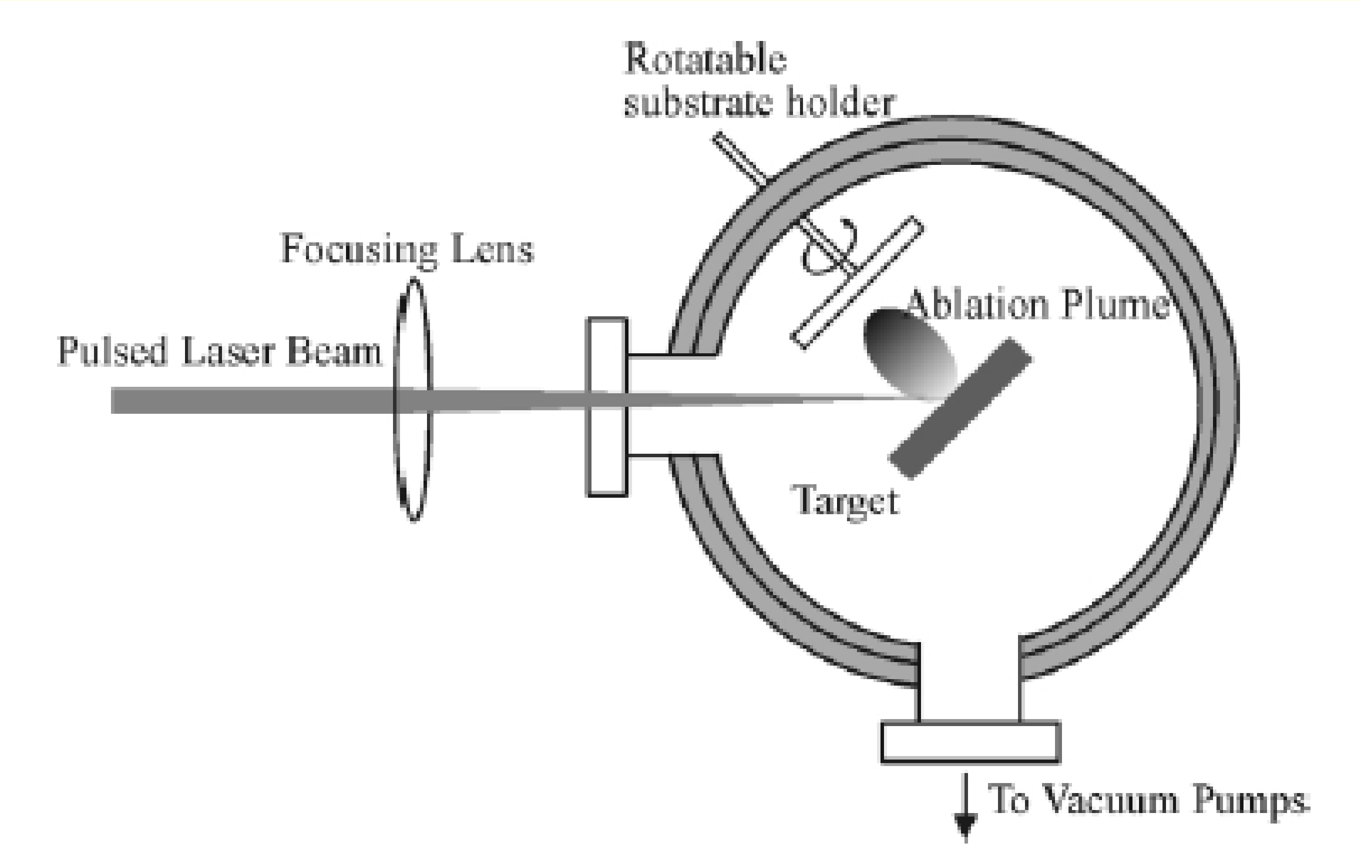
$CH_3Br(g)\ (h\nu\ ) \rightarrow CH_3(g) + Br(g)$

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

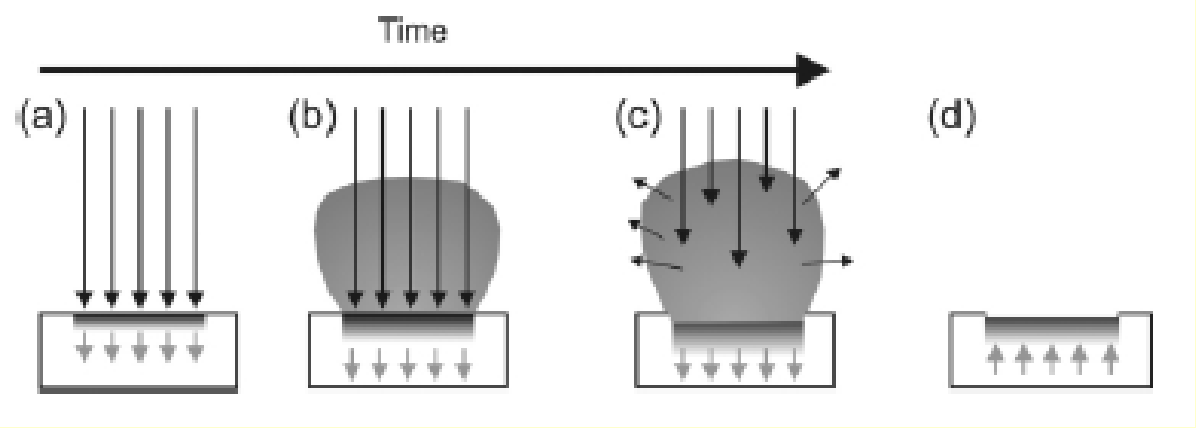
$GaAs\ldots Br_n(ad) \rightarrow GaBr_n(g) + AsBr_n(g)$

**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



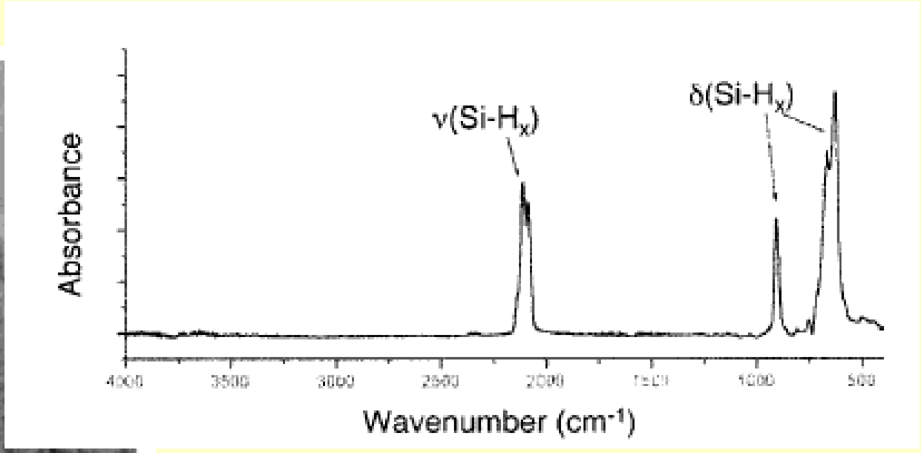
**(a) Initial absorption of laser radiation (indicated by long arrows), melting and vaporization begin (shaded area indicates melted material, short arrows indicate motion of solid–liquid interface)**

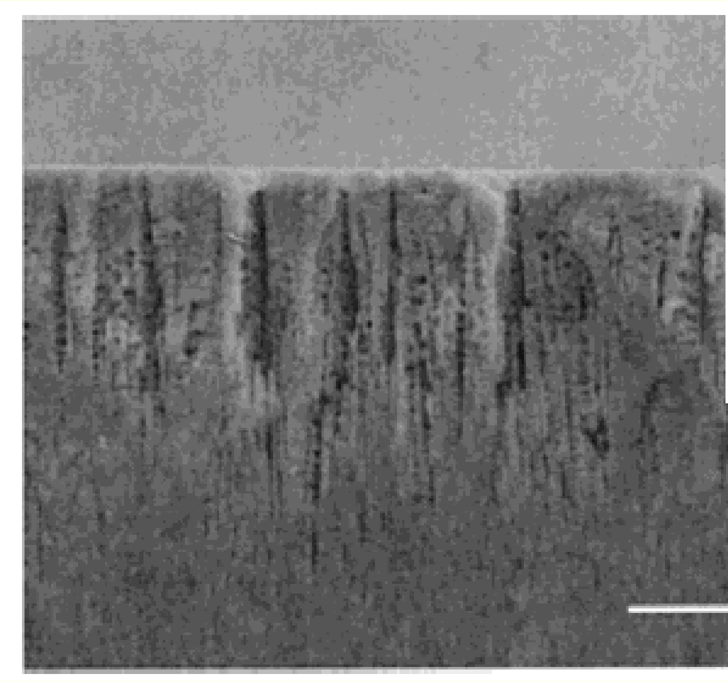
**(b) Melt front propagates into the solid, vaporization continues and laser-plume interactions start to become important**

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

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

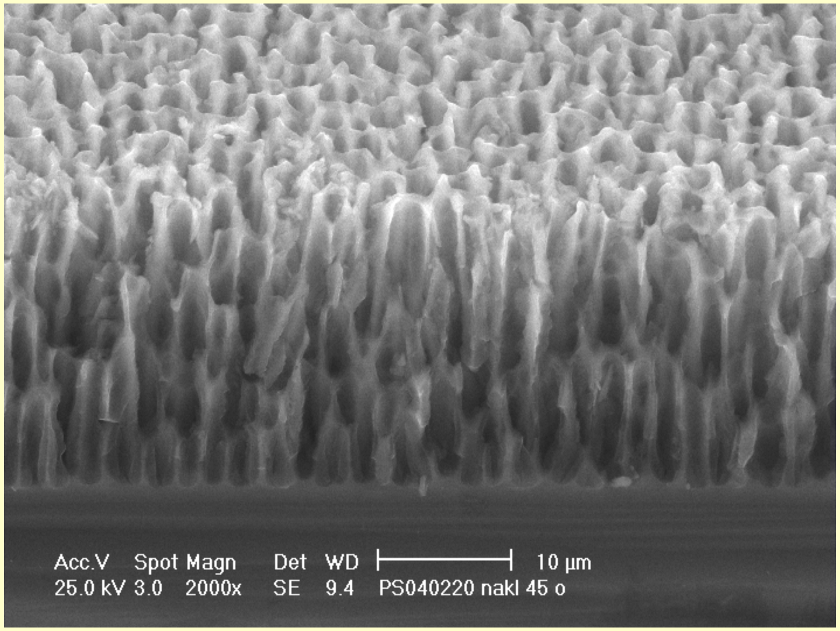
# Porous Si

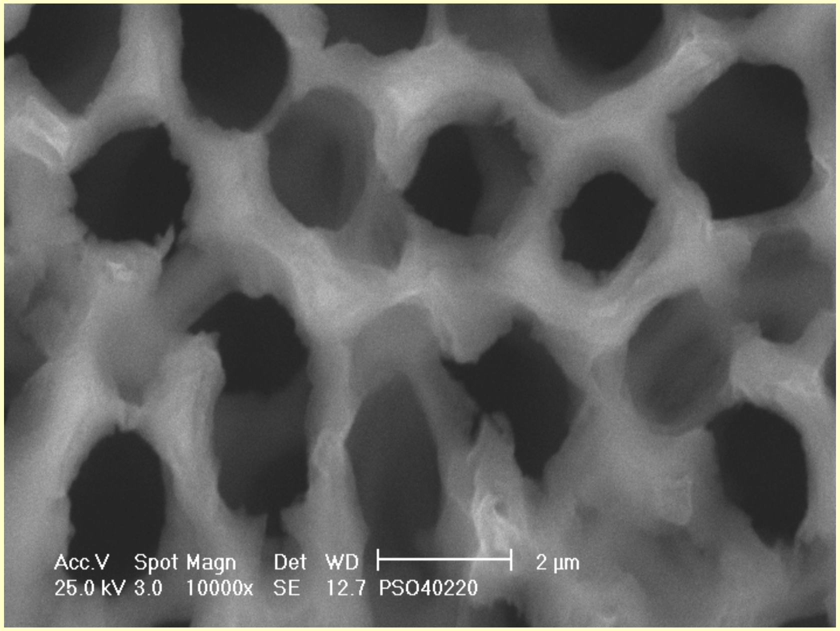




**SEM of a porous silicon, the pores extending from the surface of the Si(100) wafer down into the bulk, etched from n-type Si(100) (P-doped, 0.75-0.95 ø,cm) at 77.2 mA cm$^{-2}$ for 1 min with a 1:1 solution of 49% HF(aq)/ EtOH. Scale bar is 10 $\mu$m.**

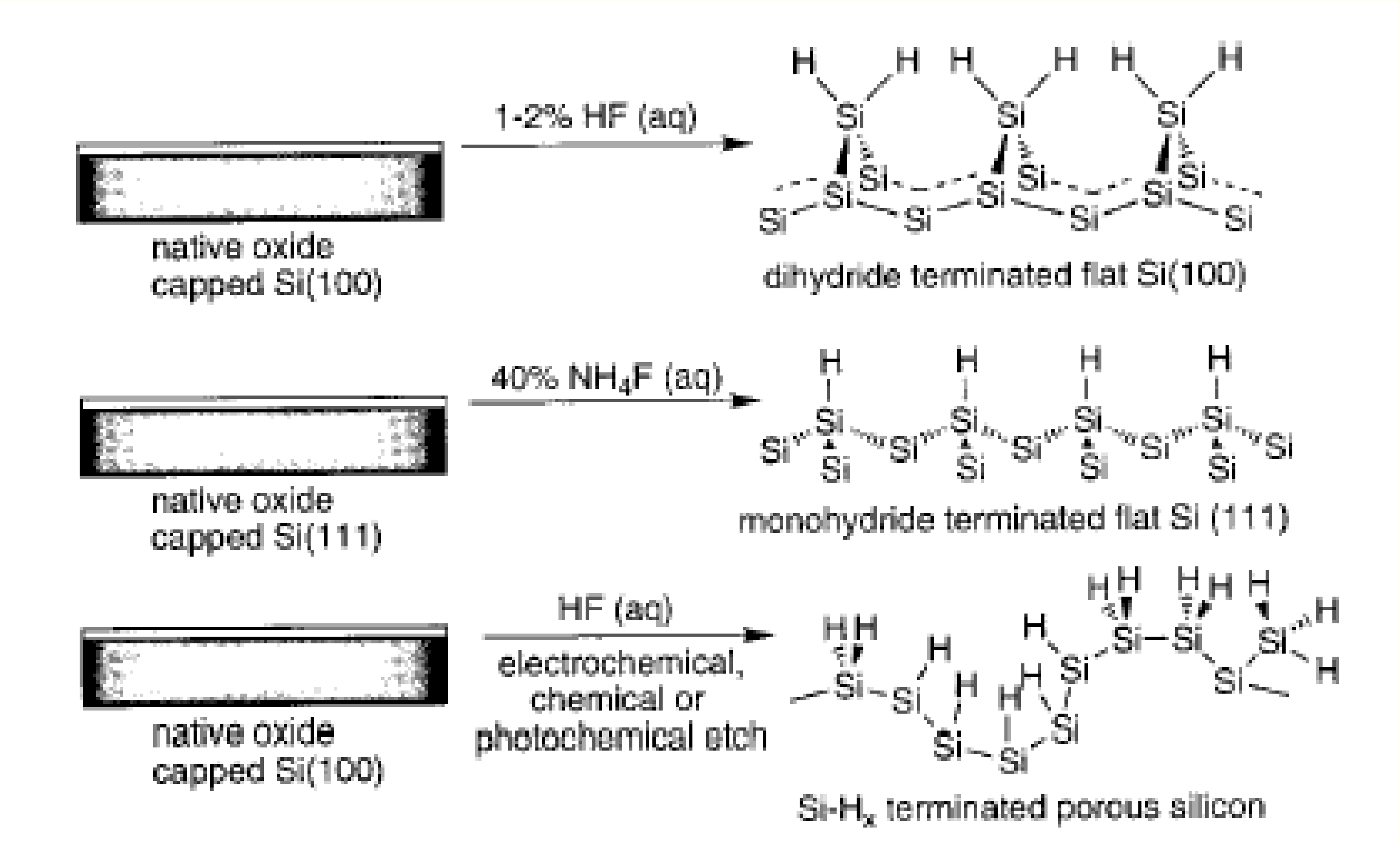
# Porous Si





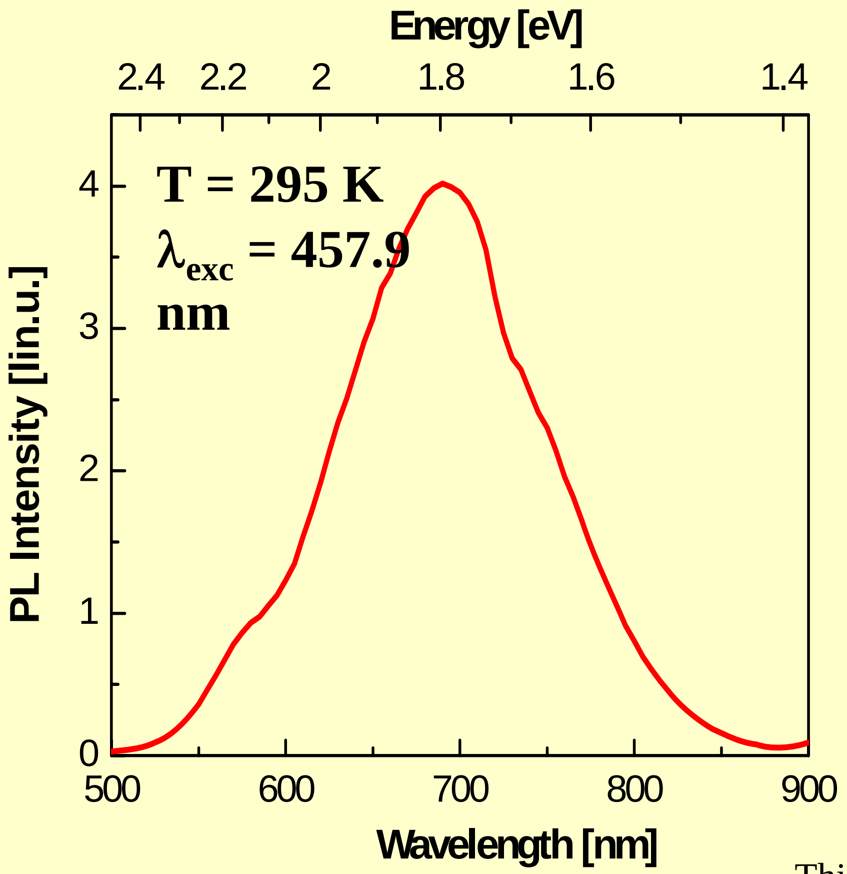
HF:EtOH = 1:2.5
$j = 10$ mA/cm$^2$
$t = 30$ min

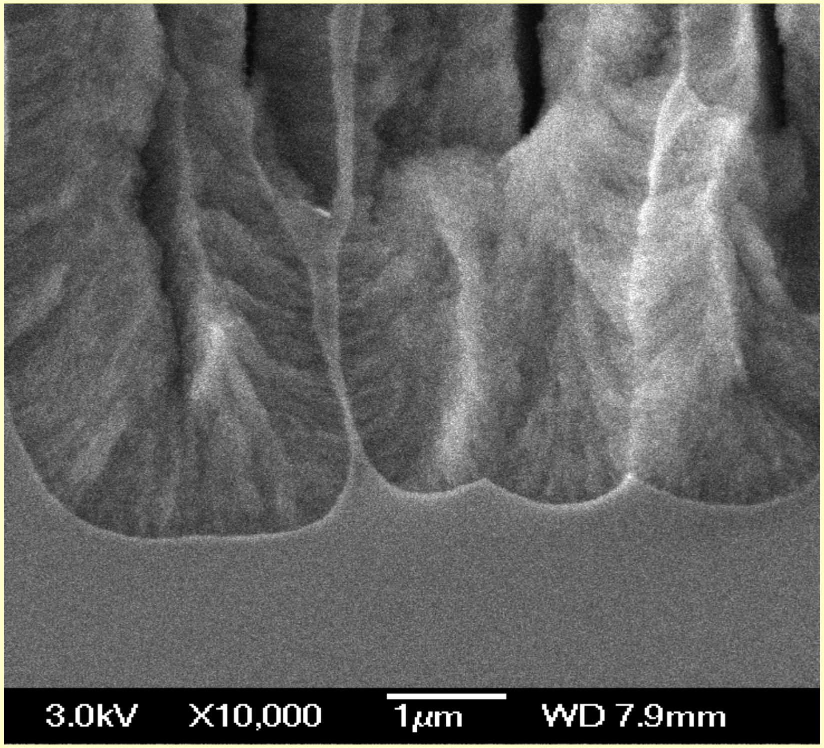
# Chemistry on Si Surface



# Porous Si

Luminiscence of p-Si





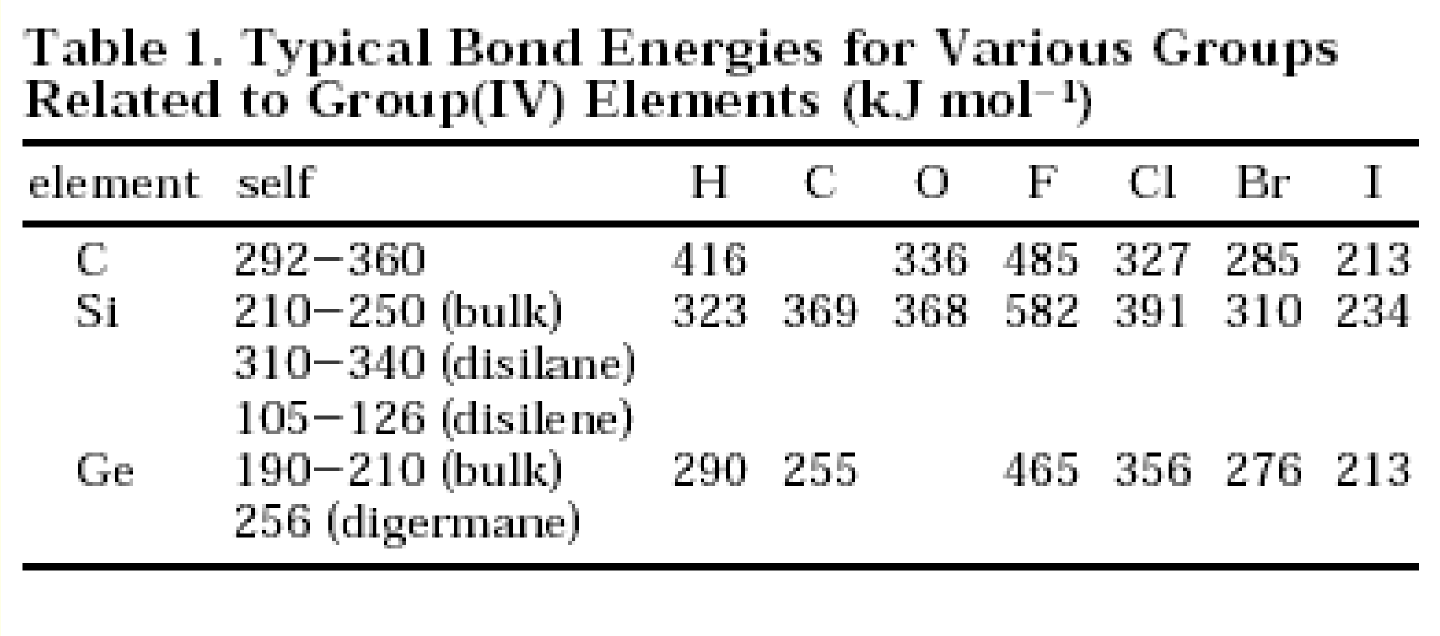
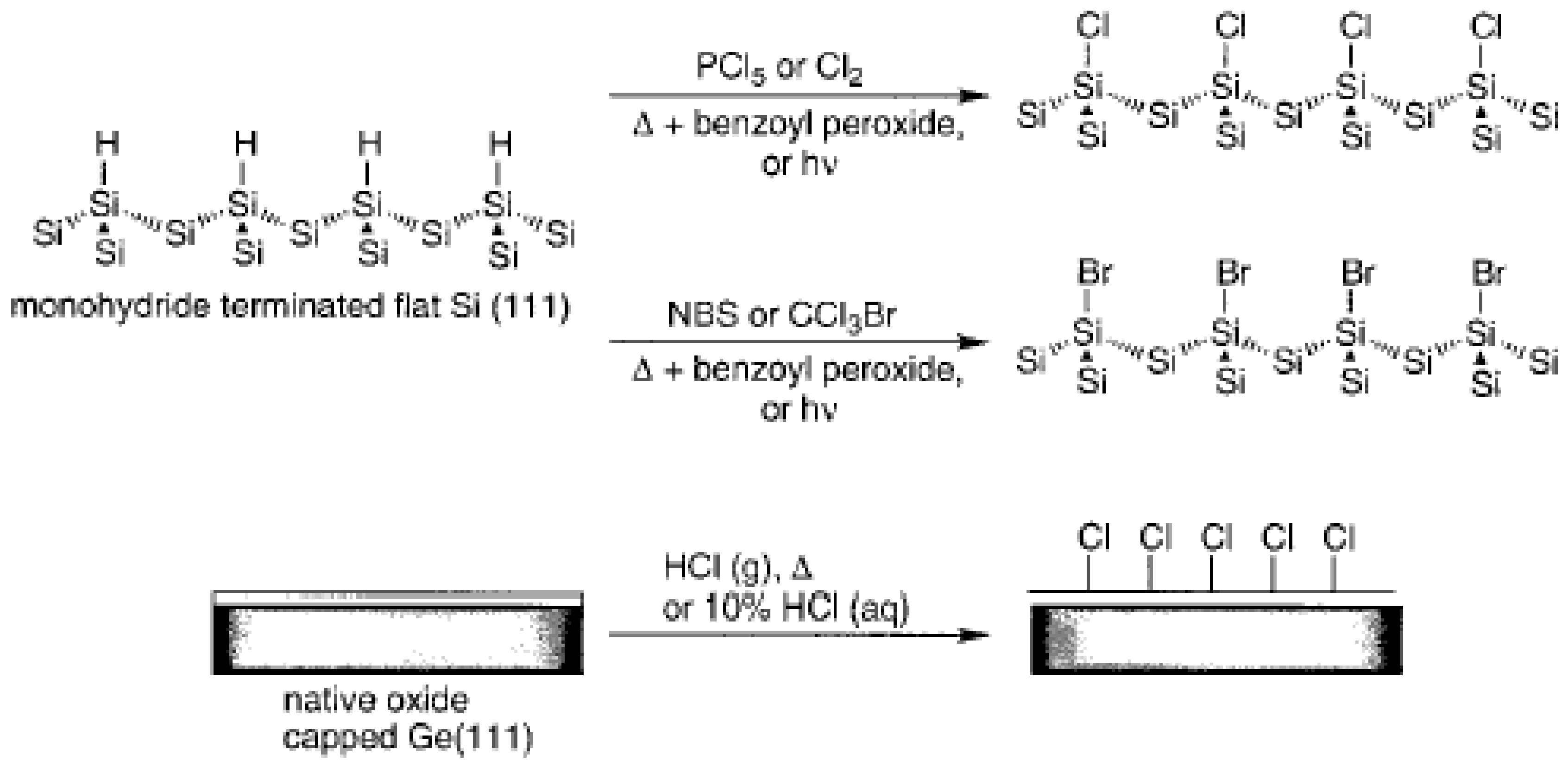


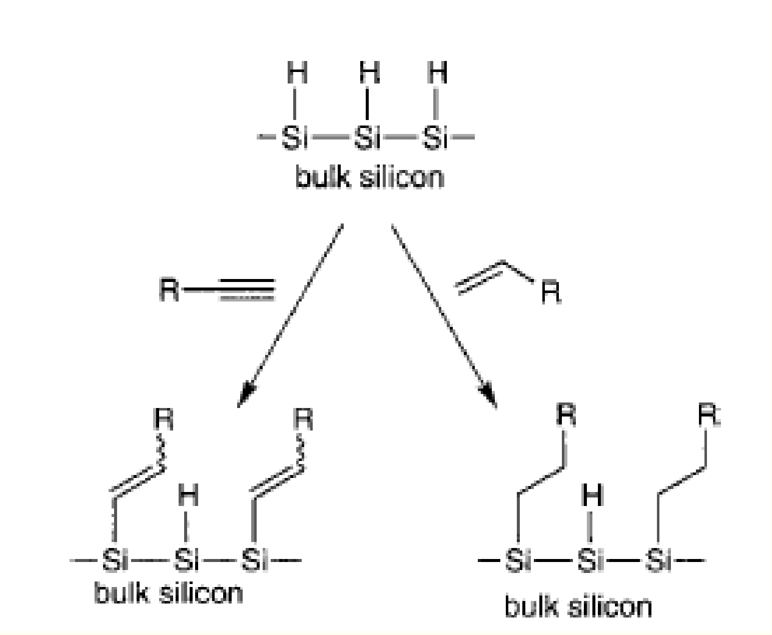
**Table 1. Typical Bond Energies for Various Groups Related to Group(IV) Elements (kJ mol$^{-1}$)**

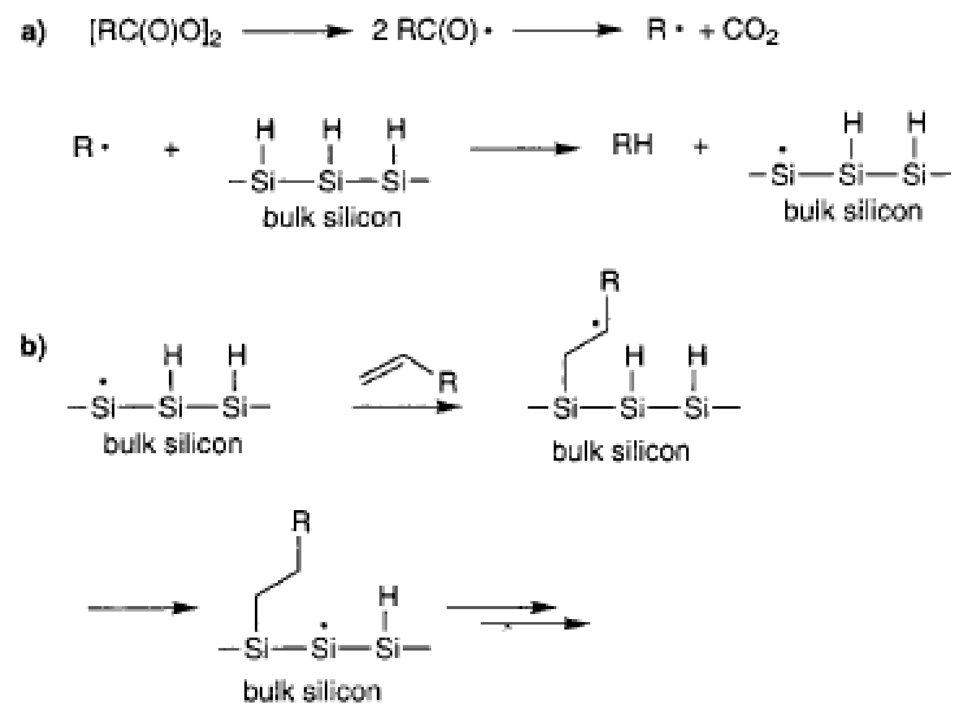
| element | self | H | C | O | F | Cl | Br | I |
|---|---|---|---|---|---|---|---|---|
| C | 292−360 | 416 | | 336 | 485 | 327 | 285 | 213 |
| Si | 210−250 (bulk)<br>310−340 (disilane)<br>105−126 (disilene) | 323 | 369 | 368 | 582 | 391 | 310 | 234 |
| Ge | 190−210 (bulk)<br>256 (digermane) | 290 | 255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

# Chemistry on Si Surface

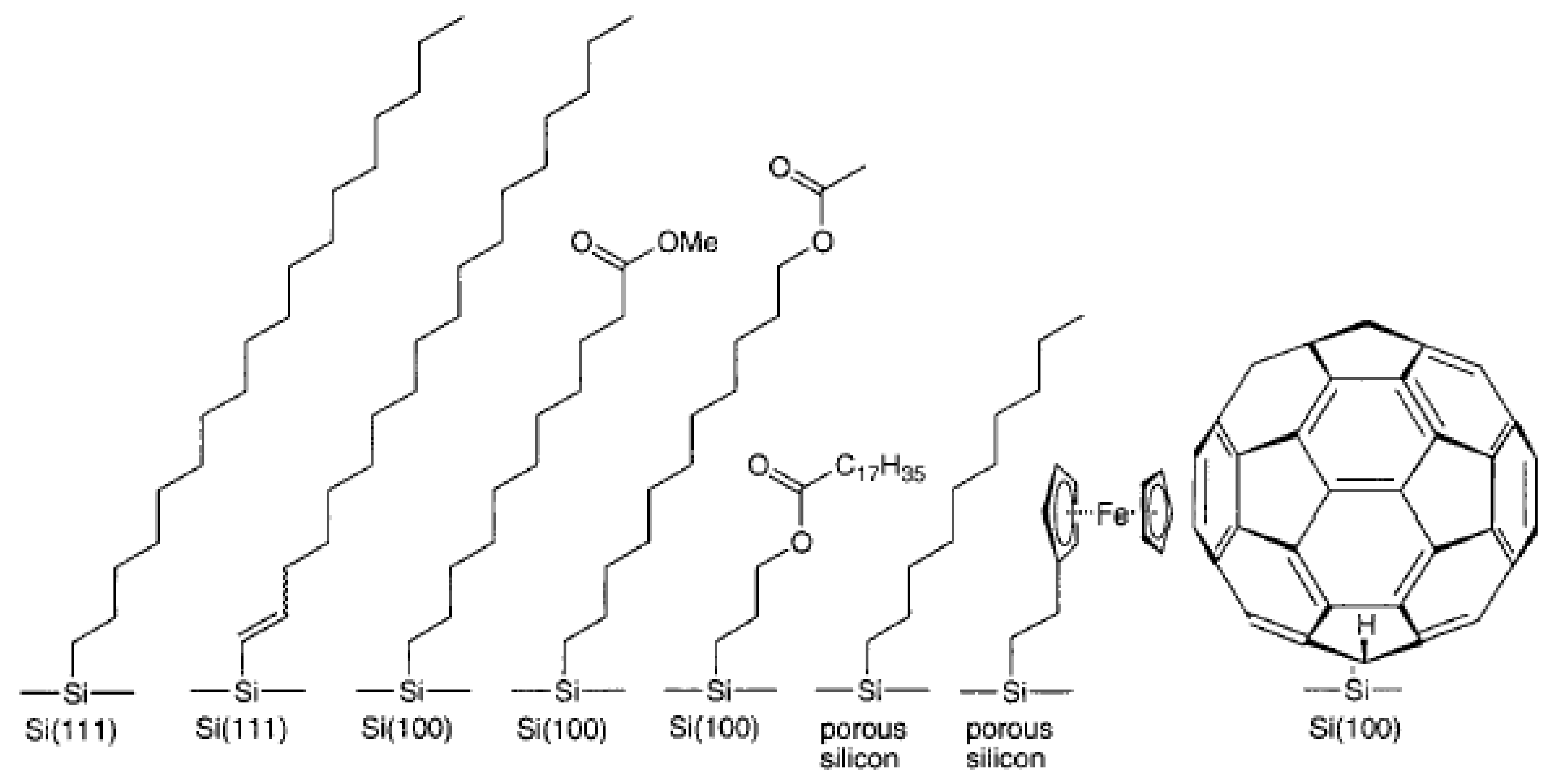


# Hydrosilylation

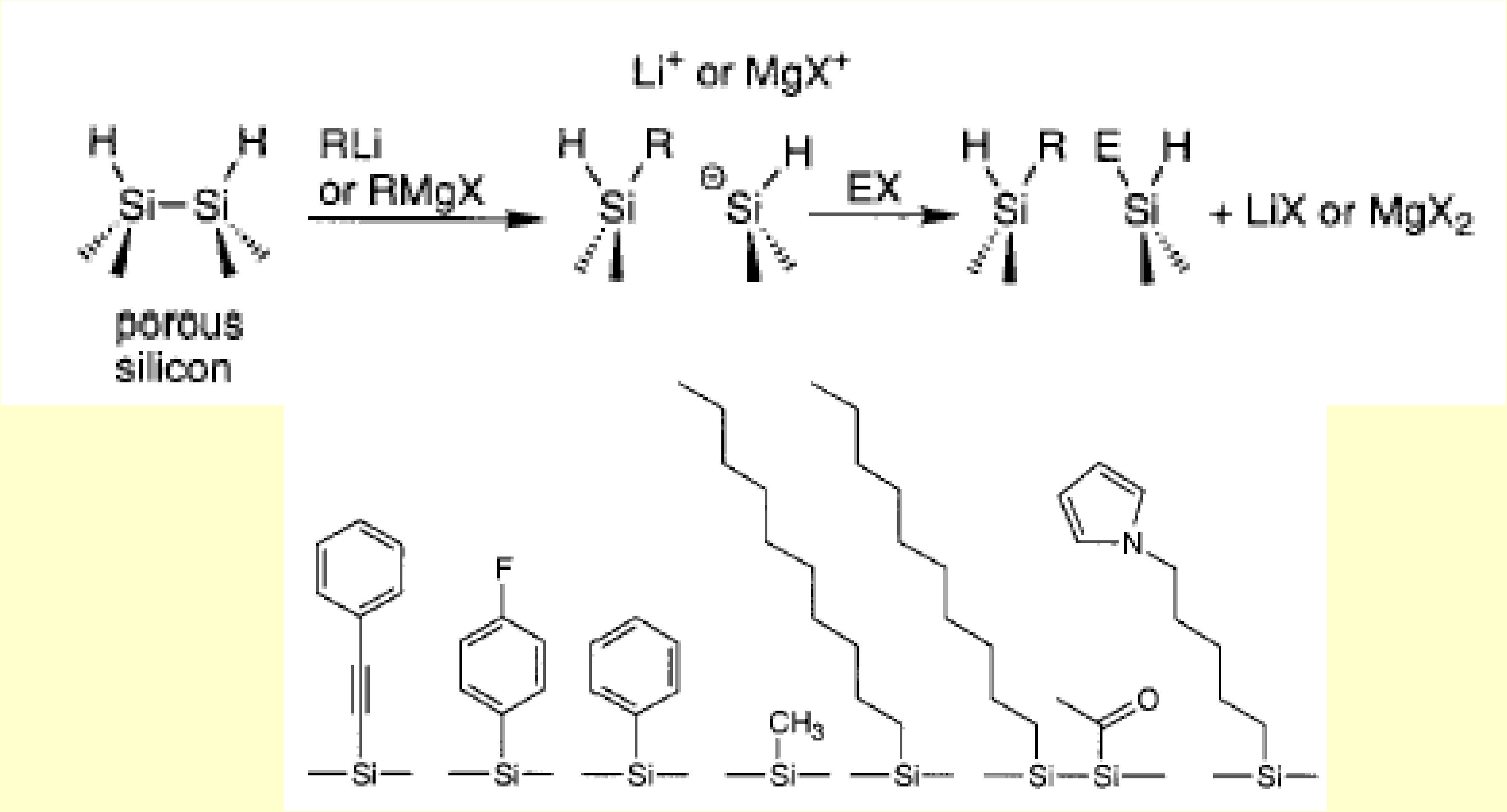


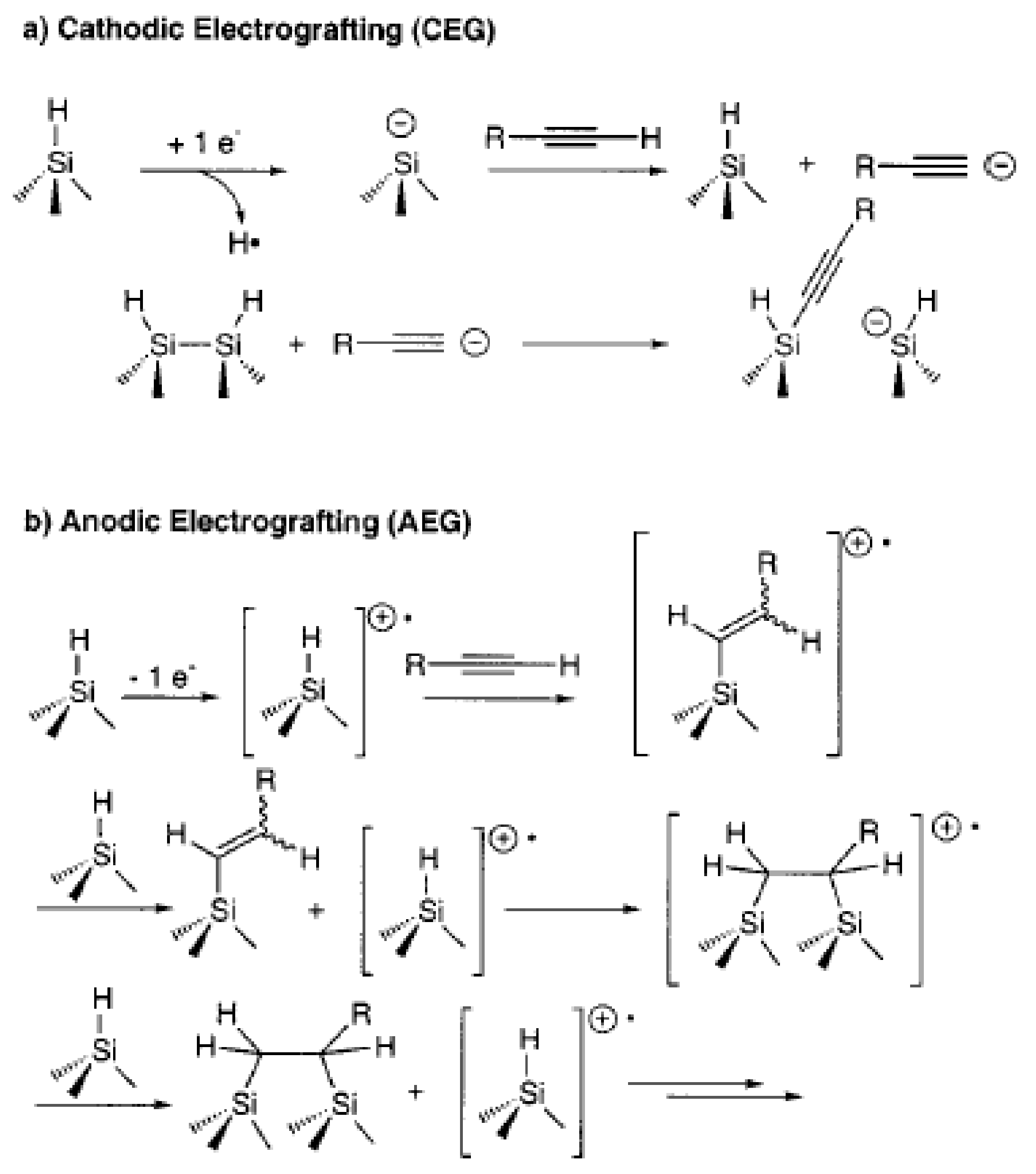


# Chemistry on Si Surface



# Carbaanion LiR, RMgX

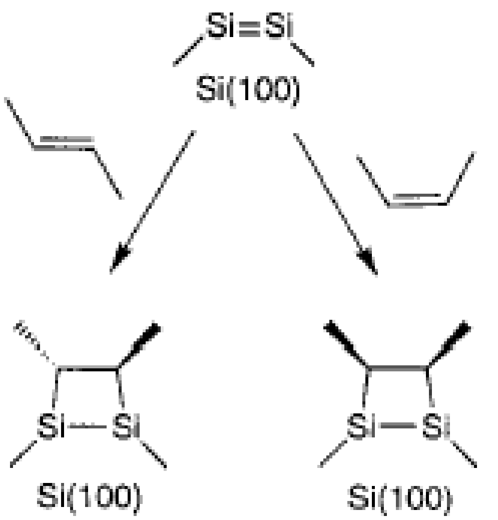


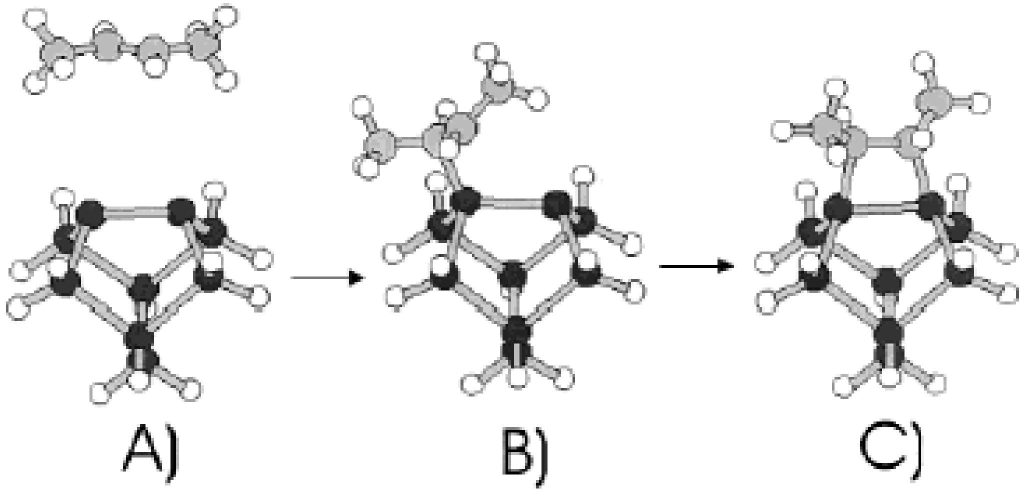


a) Cathodic Electrografting (CEG)

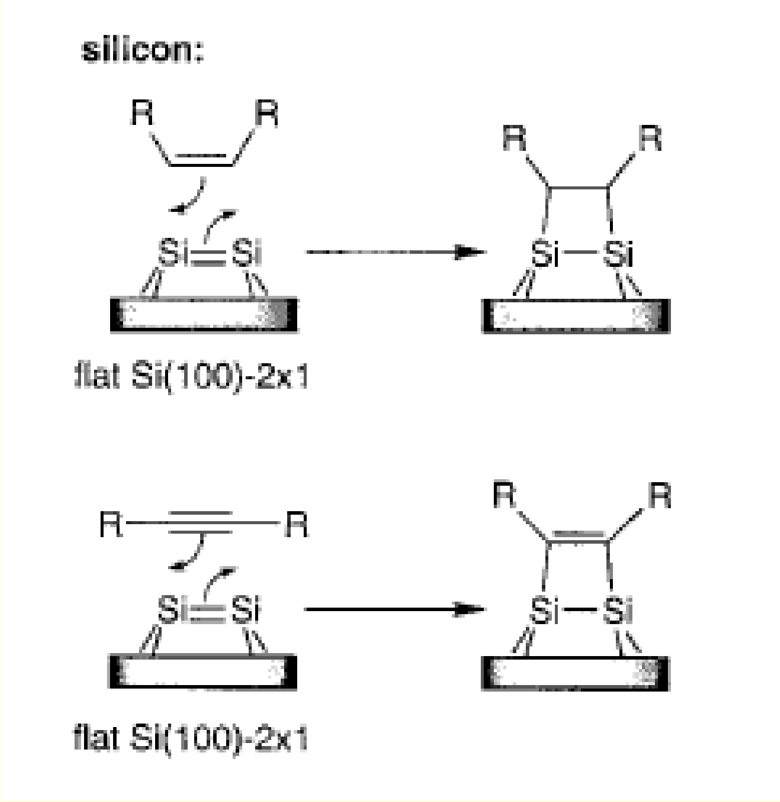
b) Anodic Electrografting (AEG)

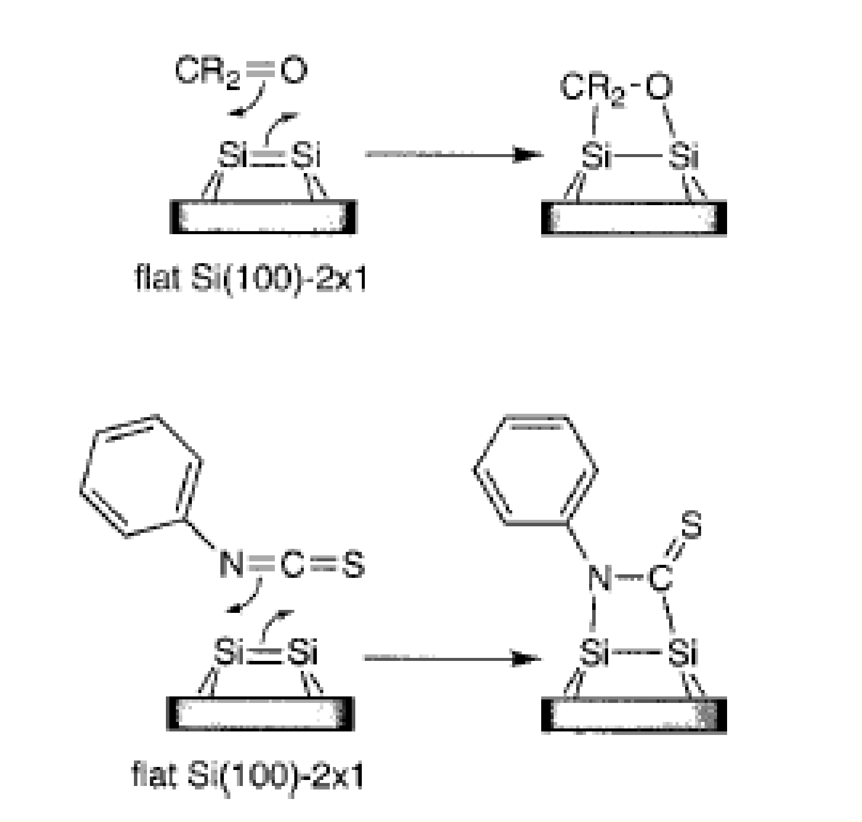
# 2+2 Cycloaddition



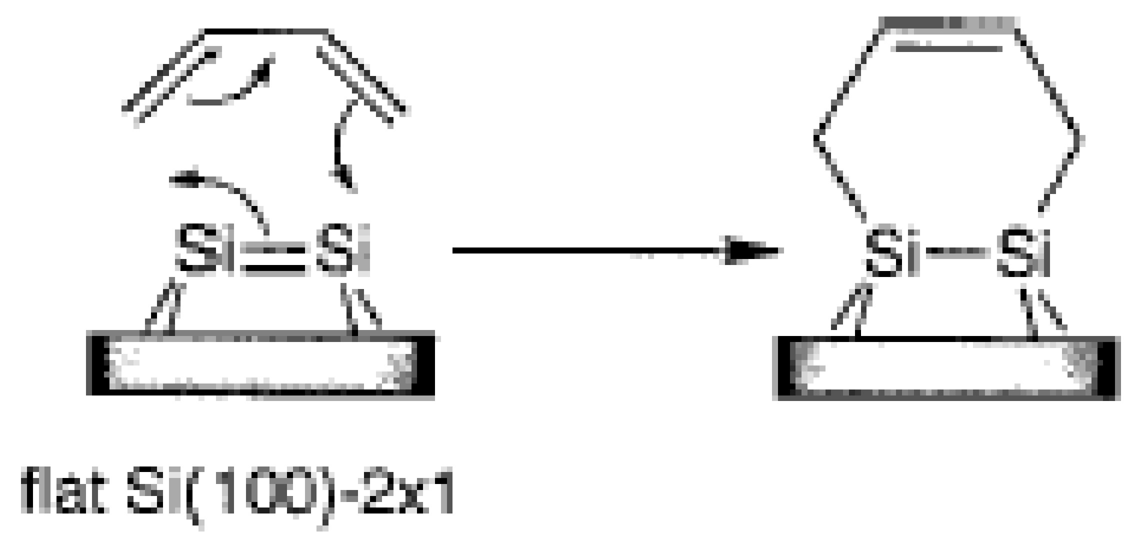


# 2+2 Cycloaddition

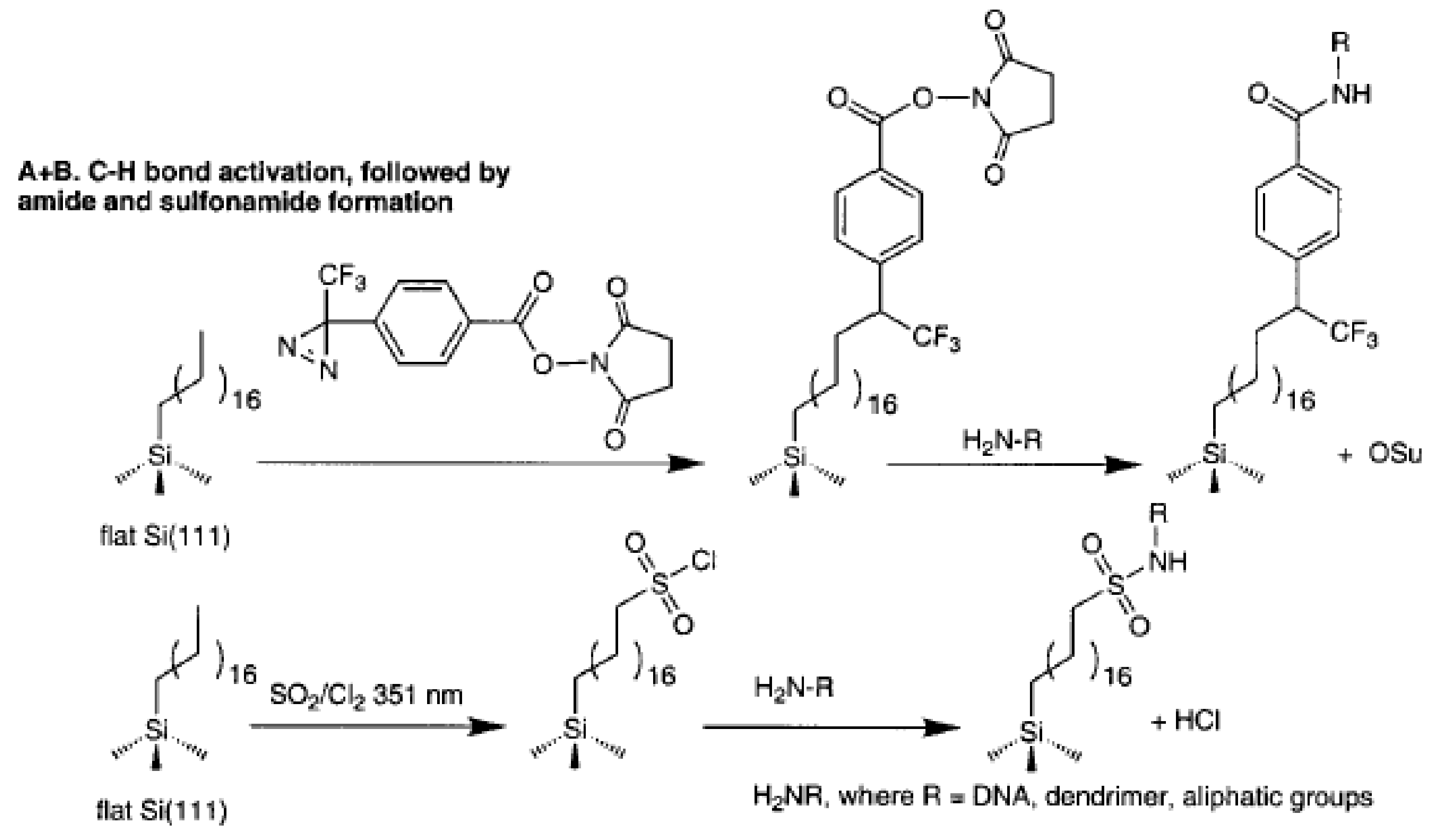




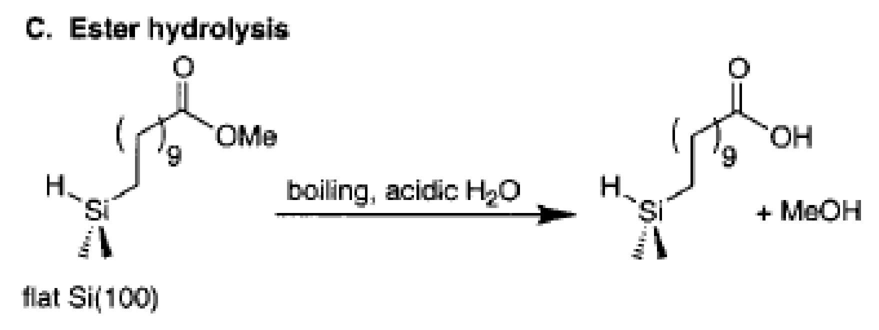
# DA 4+2



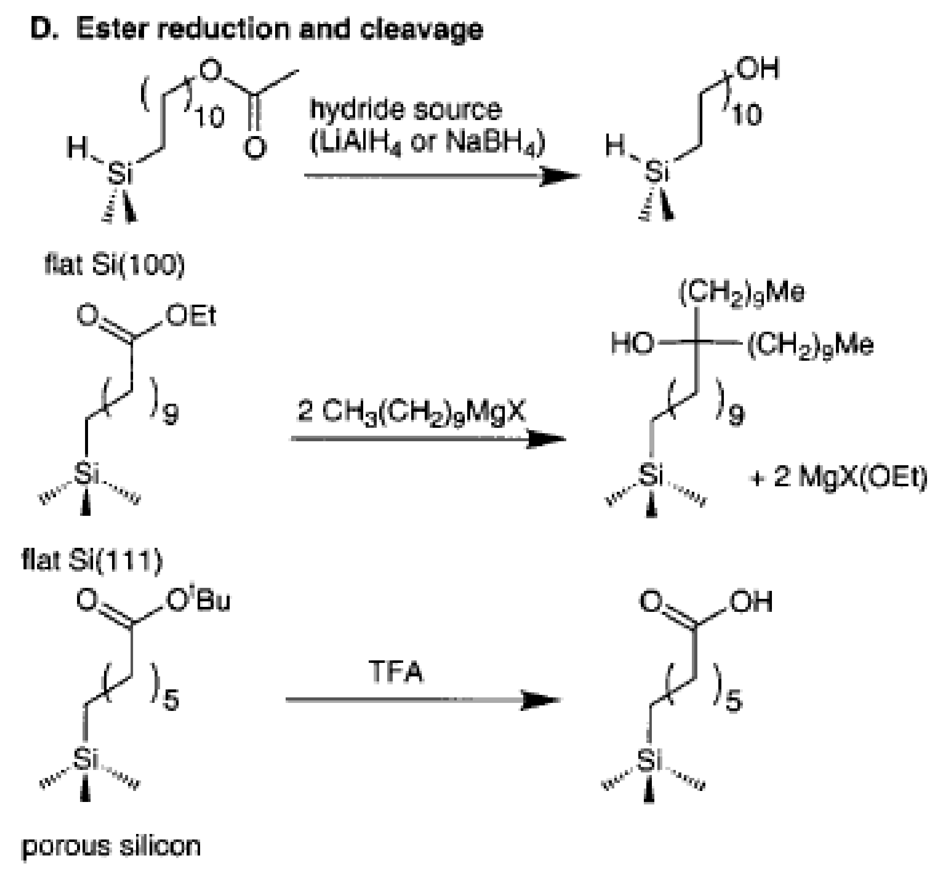
# Secondary Chemistry



# Secondary Chemistry

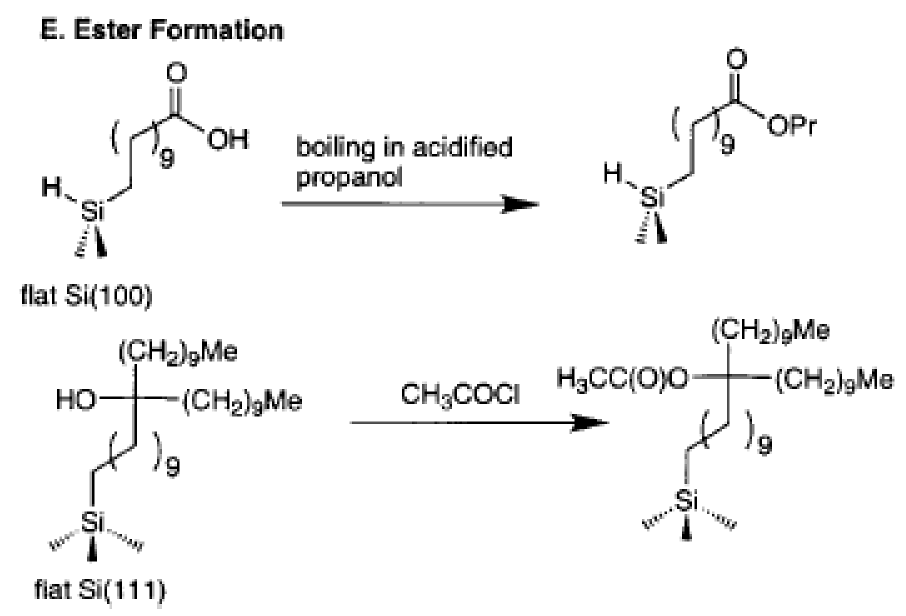


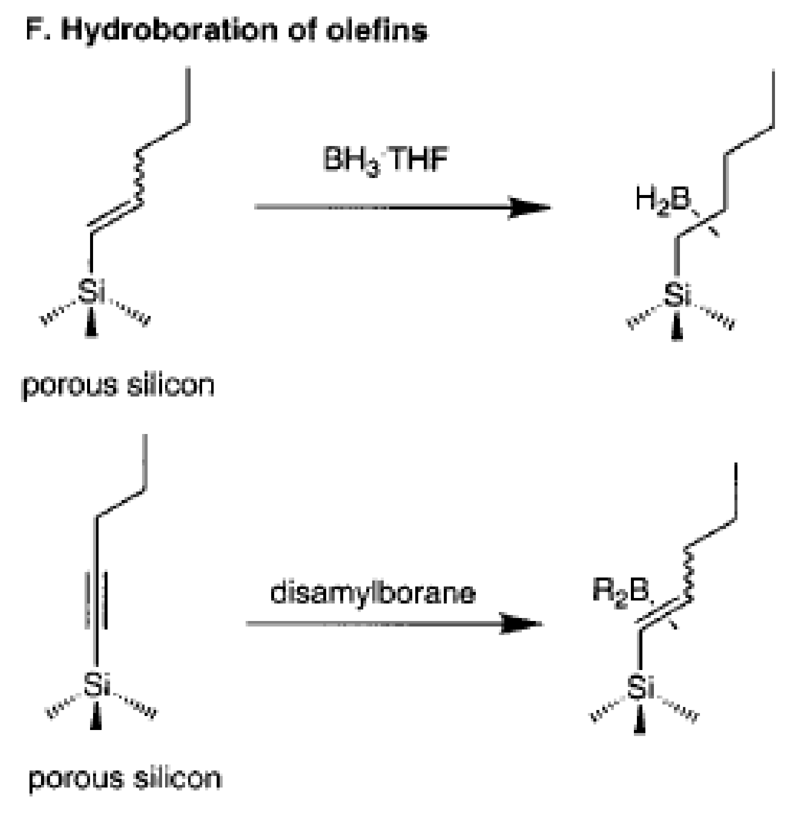
C. Ester hydrolysis



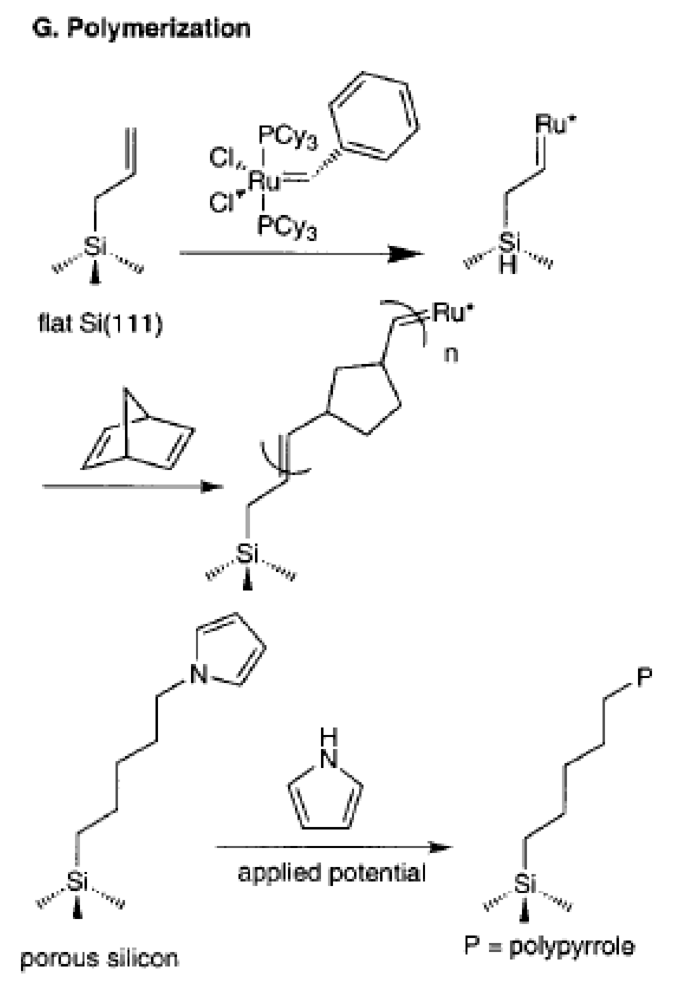
D. Ester reduction and cleavage

# Secondary Chemistry





# Secondary Chemistry



# SELF-ASSEMBLED MONOLAYERS

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

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

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

# SELF-ASSEMBLED MONOLAYERS

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

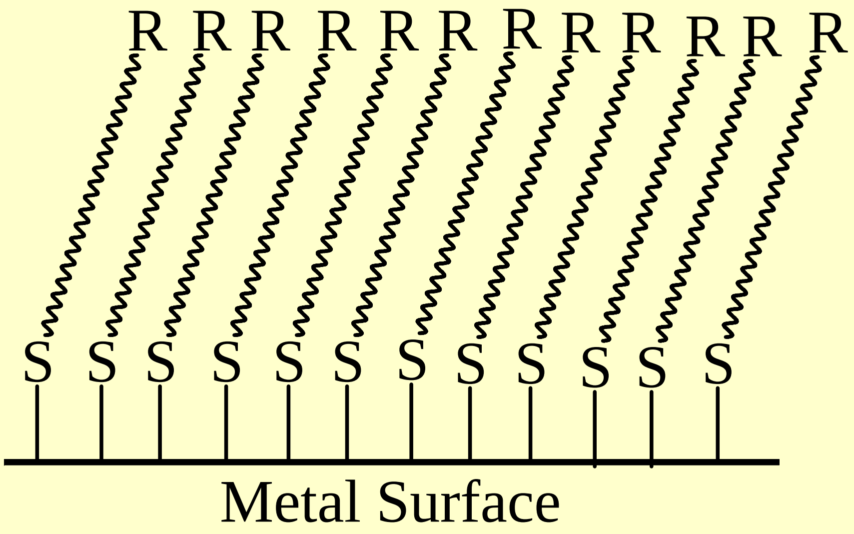
| | | |
|---|---|---|
| **Thiols** | $M + RSH \longrightarrow M\text{-}S\text{-}R + 1/2\ H_2$ | |
| **Disulfides** | $2\ M + RSSR \longrightarrow 2\ M\text{-}S\text{-}R$ | |
| **Sulfides** | $M + RSR \longrightarrow M\text{-}S\text{-}R$ | |

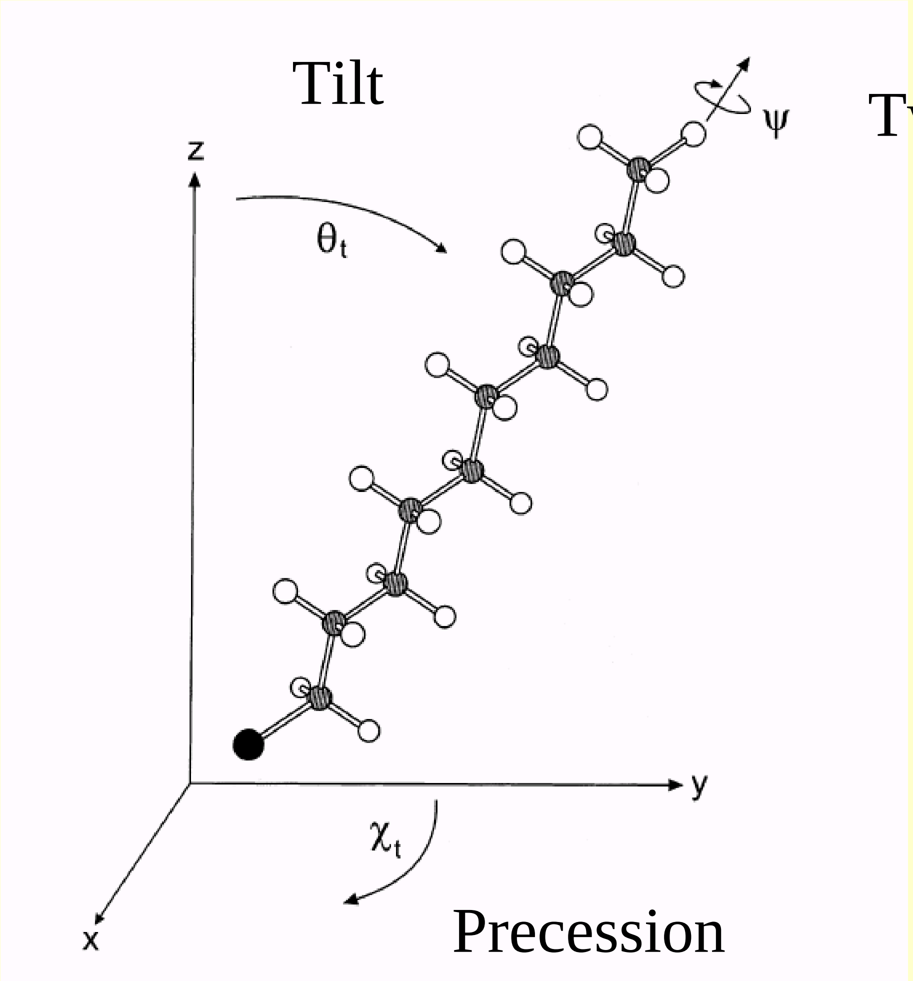
**Same products formed in all three reactions: thiolates. RSH are more soluble and react $10^3$ faster with Au than RSSR.**

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

**Thickness 5-300 nm, sputtering, evaporation**

**Atomically flat**

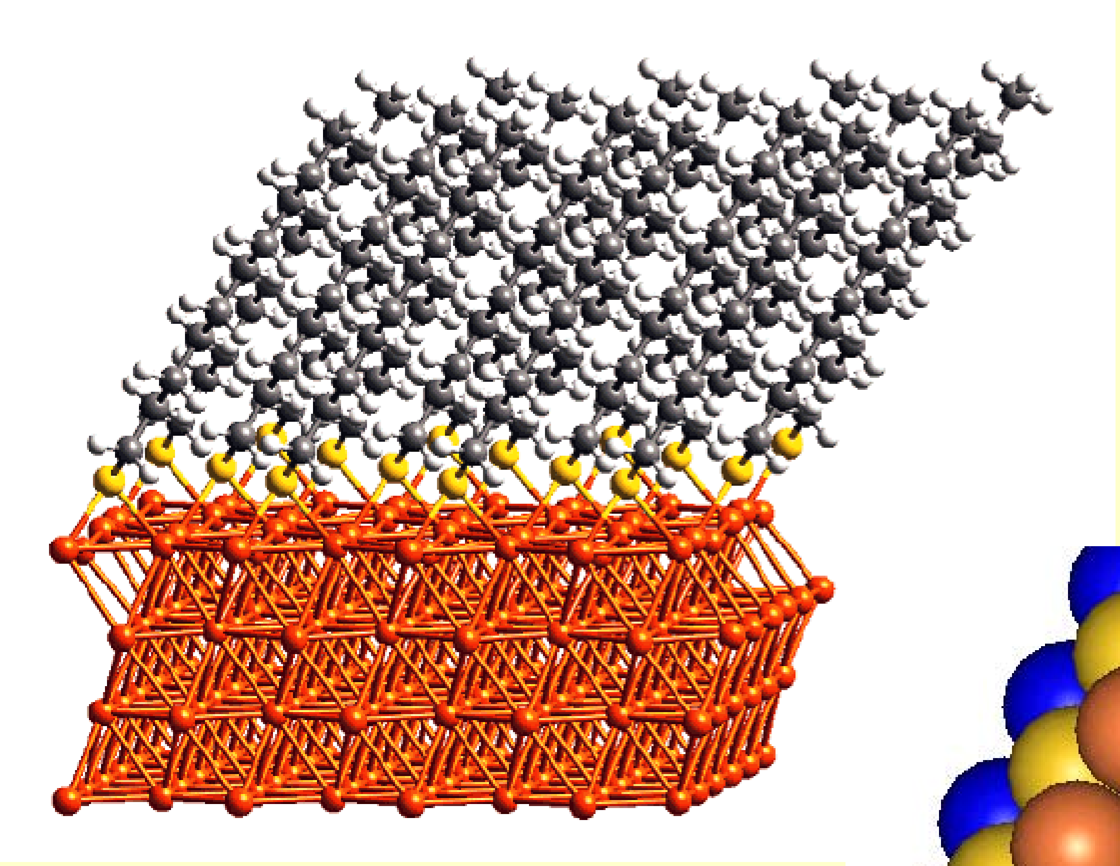


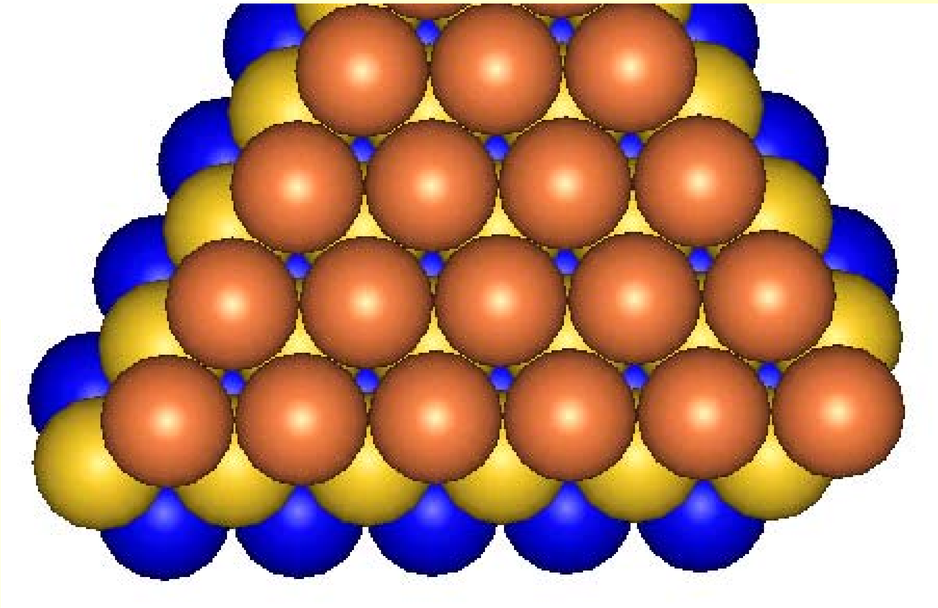


Tilt

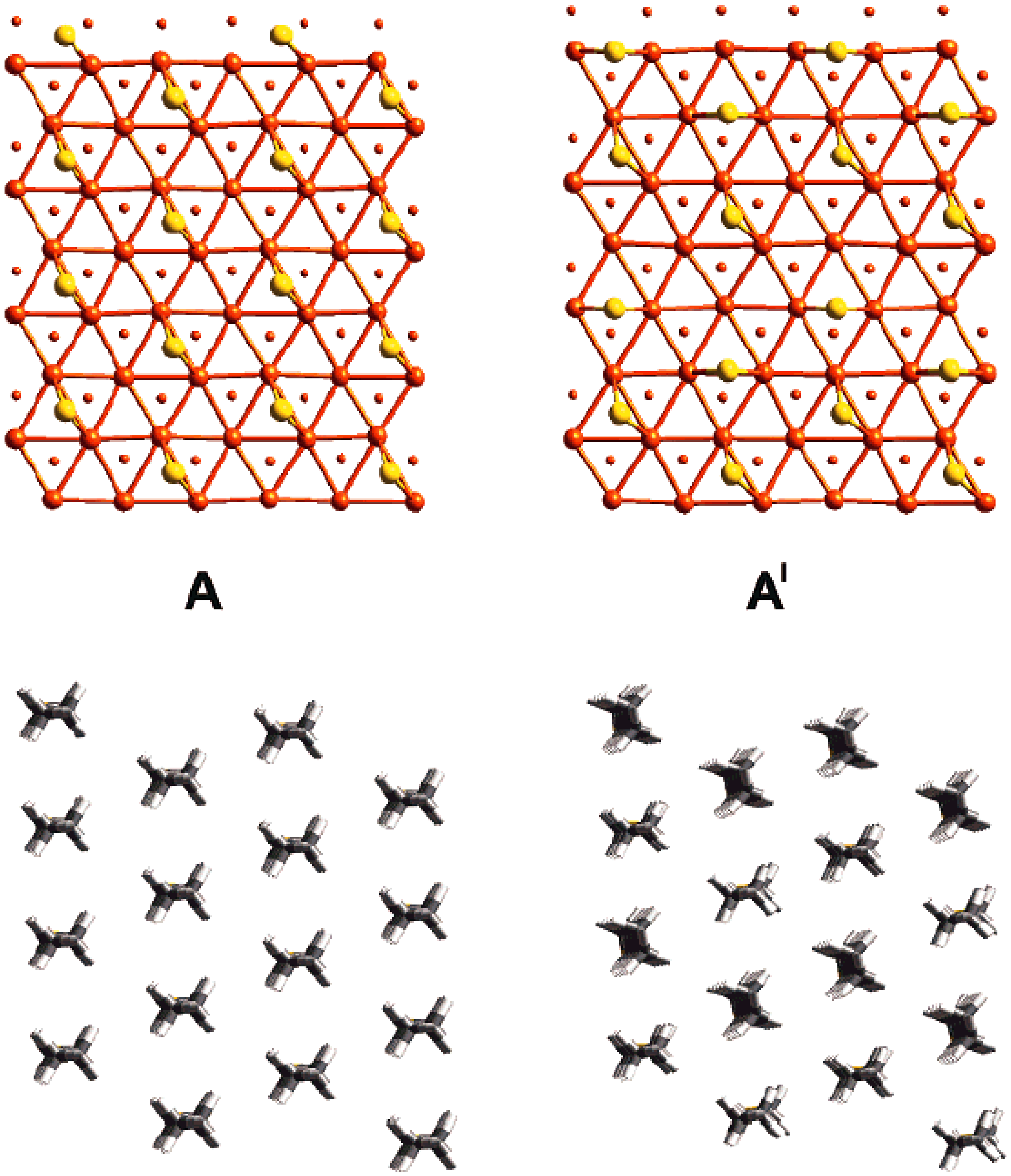
Twist

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.**

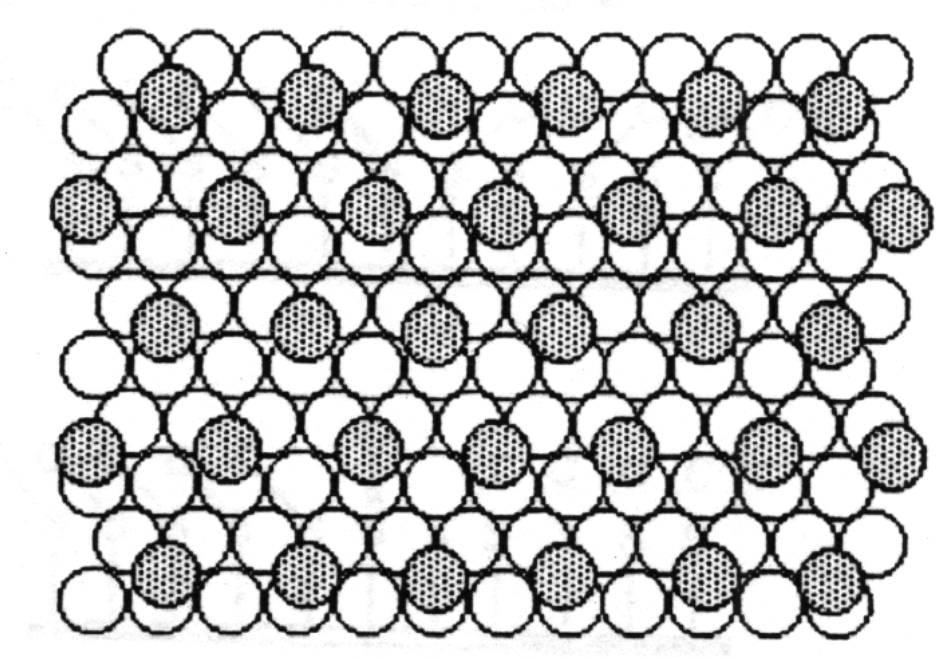
**Surface coverage $10^{14}$ molecules per $cm^2$**
**$C_{16}$ chain length ~2.2 nm, 32-40° tilted, all-trans**

**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**

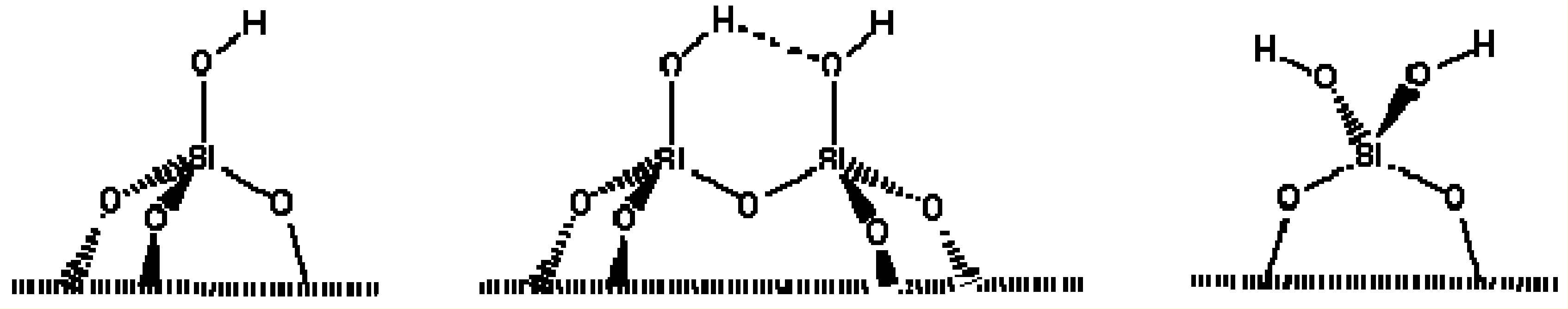
**♠ Self-assembly, at thermodynamic minima, rejects defects, high degree of perfection.**
**♠ Dimension in the range 1 nm to 1000 μm, too large for chemical synthesis, too small for microlithography.**
**♠ High efficiency, spontaneous.**

# $SiO_2$ 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.**

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

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

# $SiO_2$ Surfaces

**2. Chlorination/Displacement Method**
**The first step is the replacement of the Si-OH groups by more reactive Si-Cl bonds by chlorination.**

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

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

**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.**

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

# $SiO_2$ 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).**

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

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

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

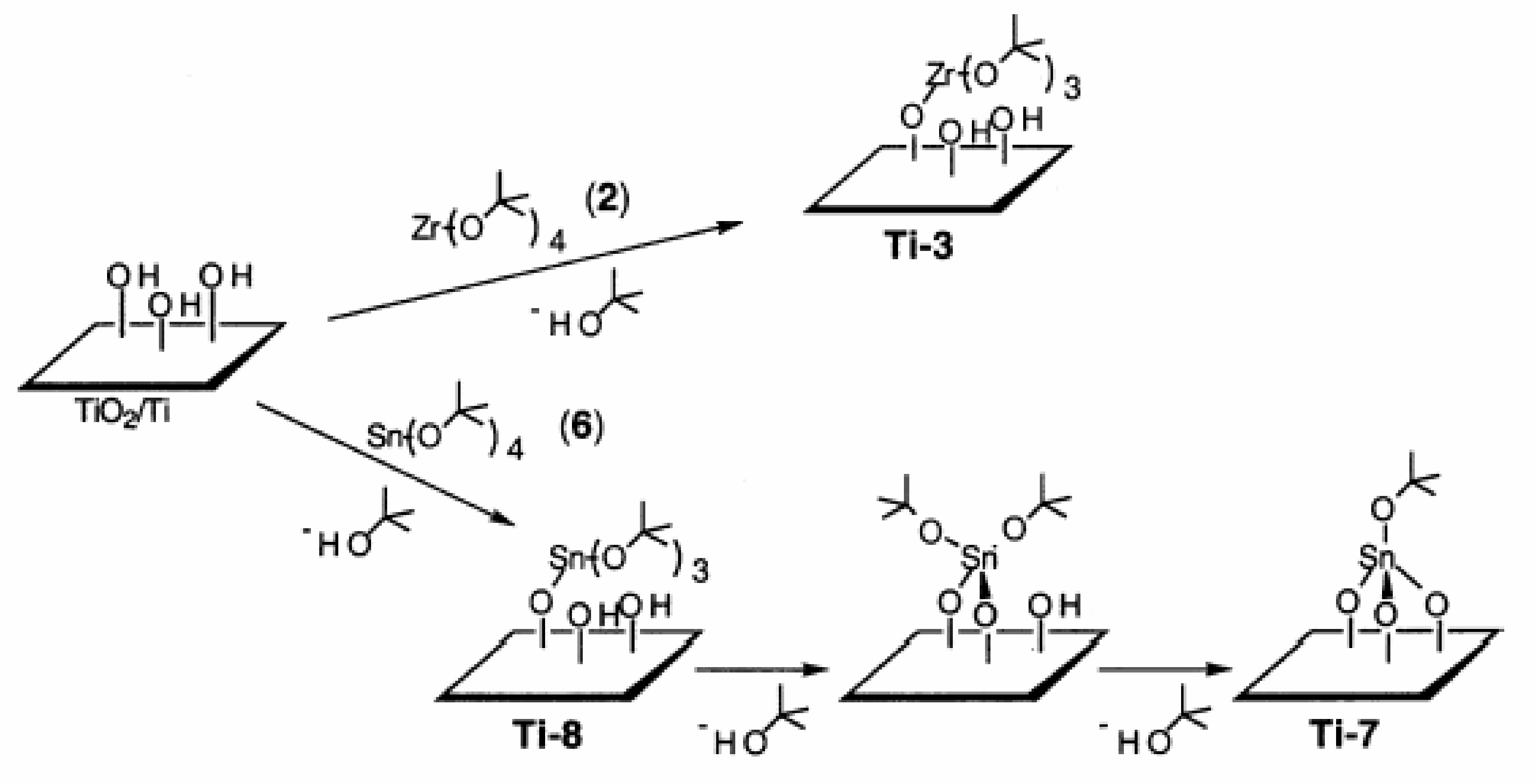
$$[O_3Si]\text{—}OH + R''O\text{–}ML_n \longrightarrow R''OH + [O_3Si]\text{—}O\text{–}ML_n$$

# $SiO_2$ Surfaces

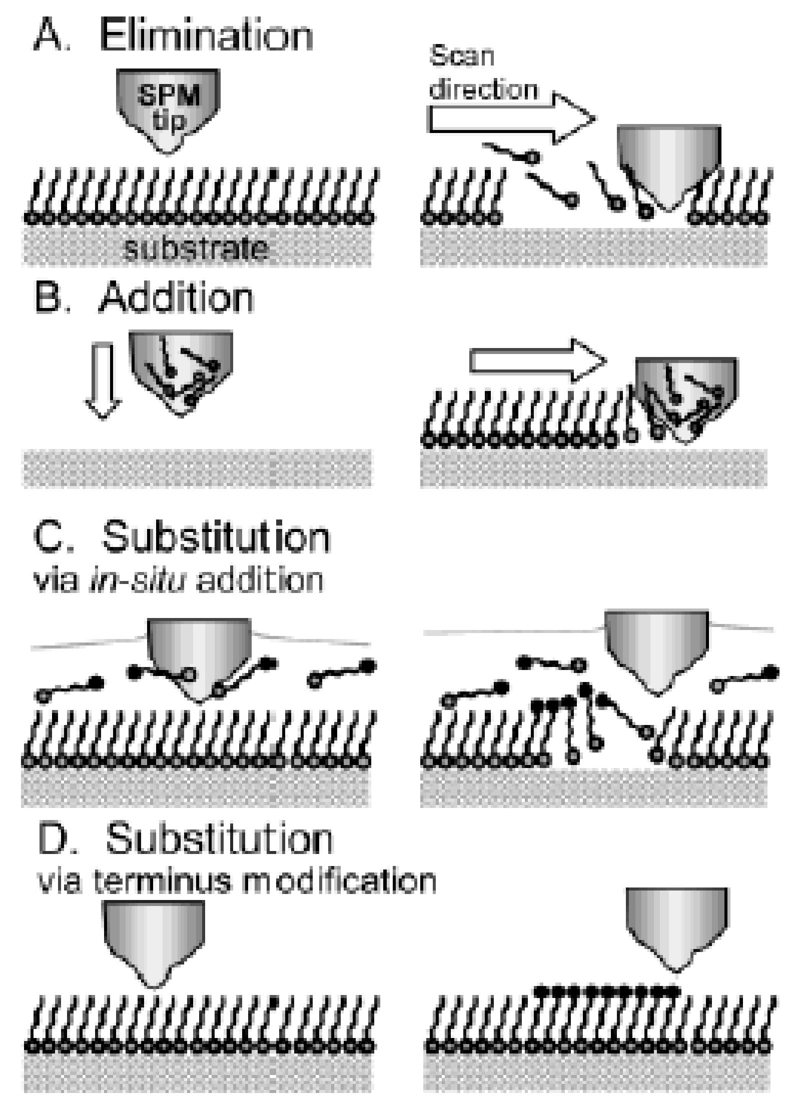
**These organometallic moieties can serve as attachment points for further modification with long chain alcohols, thiols, carboxylic acids, phosphates, and diketonates.**

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

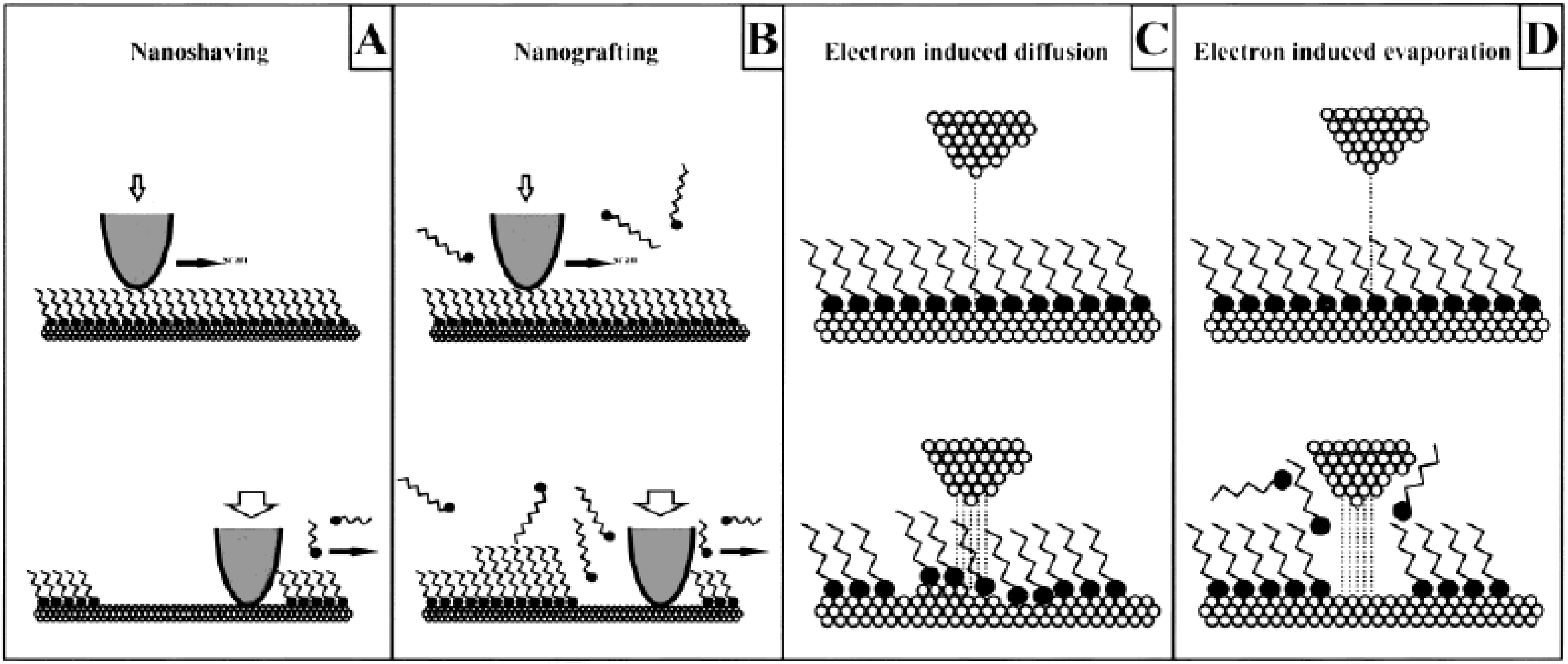
$$[O_3Si]\text{—}O\text{–}ML_n + HOOCR \longrightarrow [O_3Si]\text{—}O\text{–}ML_{n-1}\text{–}OOCR + HL$$


TiO2/Ti
Zr(O-tBu)4 (2)
- HO-tBu
Ti-3
Sn(O-tBu)4 (6)
- HO-tBu
Ti-8
- HO-tBu
- HO-tBu
Ti-7

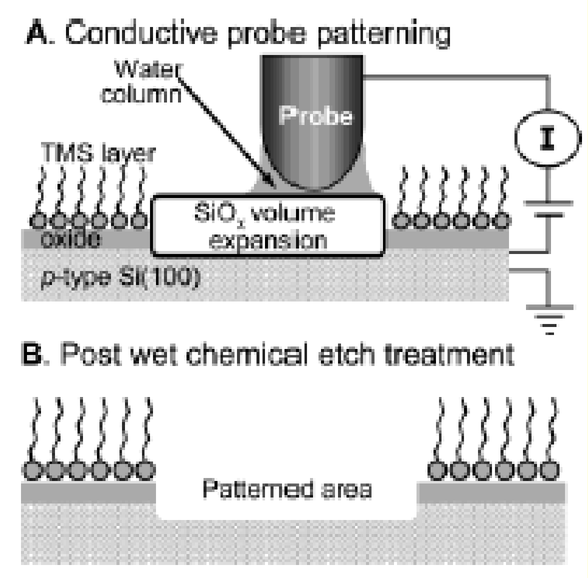
# Manipulations with SAM

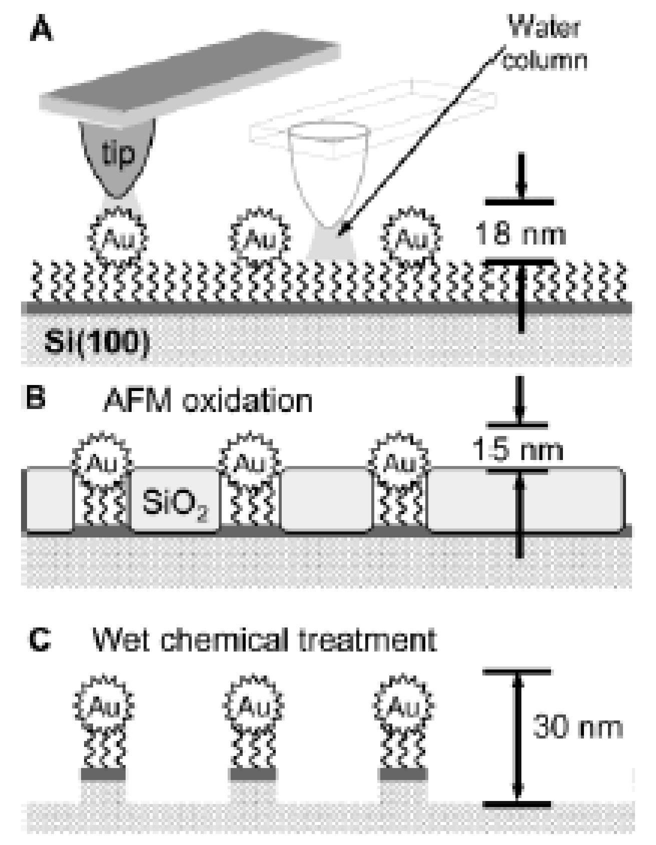


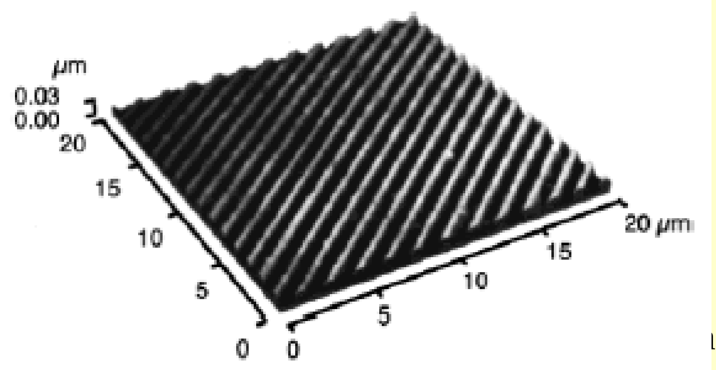
# Manipulations with SAM



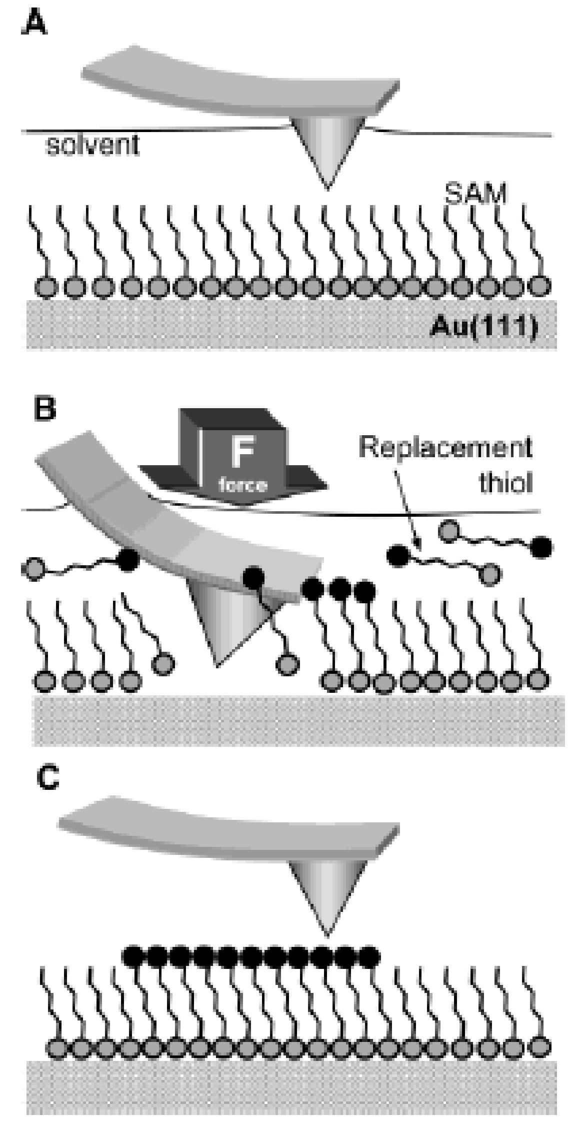
# Manipulations with SAM







# Manipulations with SAM



# Manipulations with SAM