Surface chemistry

Sami Franssila,

With material from Mikko Ritala,

University of Helsinki

Surface energy

- change in Gibbs free energy upon a change in surface area at constant pressure and temperature

    $$dG_{T,P} = \gamma \, dA$$

    where γ = surface energy and A = surface area
- for stable systems γ must be positive, otherwise the surface area would spontaneously expand
- at equilibrium surface area tends to minimum
    - if γ is independent of orientation (e.g. liquids), the equilibrium shape is a sphere
    - there is always a driving force for processes that decrease the total surface area (sintering)

Seong et al: Dominant mechanisms of the sintering of copper nano-powders, 2016
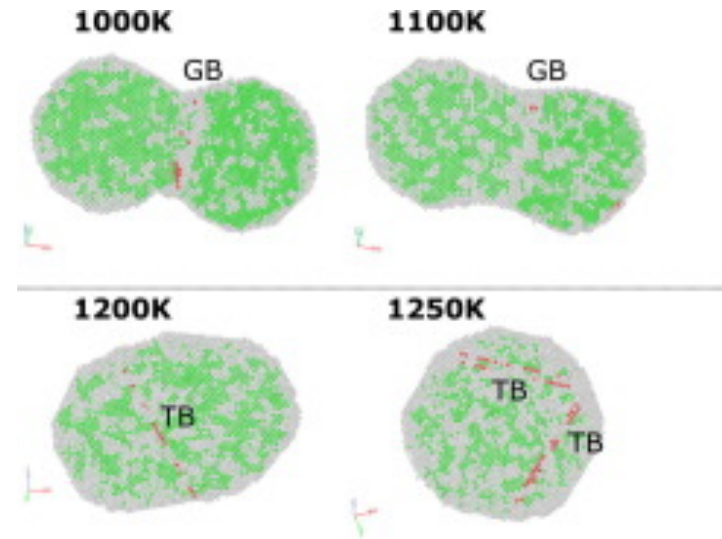
Surface tension

- surface tension is force per unit length acting on an imaginary line drawn on the surface $\gamma = F / \delta x$
- for liquids creation and stretching of the surface are equivalent processes: $\gamma = surface\ tension$
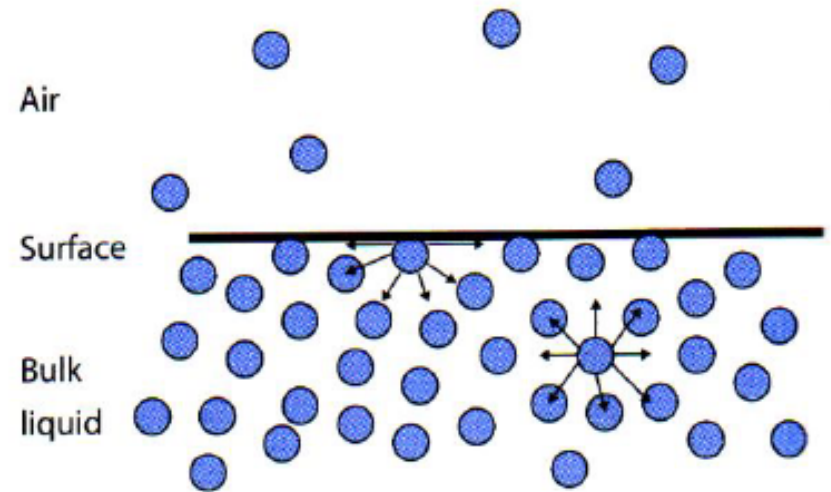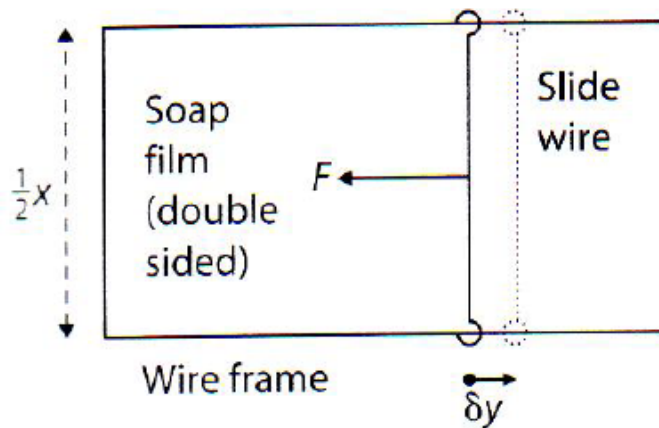- a *double sided* soap film on the slide with a length of $2(\frac{1}{2}x) = x$ exerts a force $F = \gamma x$

Table 6.1 Selected values of surface tension or surface energy. Source: Adamson and Gast [1]

	$T(^{\circ}C)$	$\gamma(mN\ m^{-1})$
Liquid–vapour interface		
Perfluoropentane	20	9.89
Heptane	20	20.14
Ethanol	20	22.39
Methanol	20	22.50
Benzene	30	27.56
	20	28.88
Water	25	72.13
	20	72.94
Mercury	25	485.5
	20	486.5
Silver	1100	878.5
Copper	1083[a] (T_f)	1300
Platinum	1772[a]	1880

Note: T, temperature; γ, surface tension or surface energy
[a]At temperature of fusion.

Surface energy of solids

- for a solid creation and stretching of the surface are not equivalent because surface area can be increased both by *adding atoms from bulk* but also by *increasing the distance between surface atoms*
- surface energy of a solid: $\gamma(\mathbf{m})$
  ($\mathbf{m}$ = unit vector in the direction of surface normal)
  - the energy required to create a unit of the surface area; depends on the crystallographic orientation: *anisotropic*
  - difficult to measure but may be estimated based on bonds broken in creation of the surface

Estimating surface energy

- surface energies of solids are very difficult to measure
- one way for estimating surface energy is the nearest neighbour broken bond model:
  - surface is thought to be formed by splitting a crystal
    - two surfaces formed!
  - surface geometry shows
    - how many bonds are broken per atom when the surface is created (n_{bonds}) – smallest possible
    - atom density per m^2 (N_S)
- bond energy E_b, if not available, is estimated e.g. from sublimation enthalpy
- $\gamma = n_{bonds}\, E_b\, N_S\, / \, 2$

Silicon surface energy

Silicon atom surface density, ca. 10^{15} cm^{-2},
and hydrogen bond energies, 25-40 kJ/mol,
which translate to ca. 200-350 mJ/m^2.
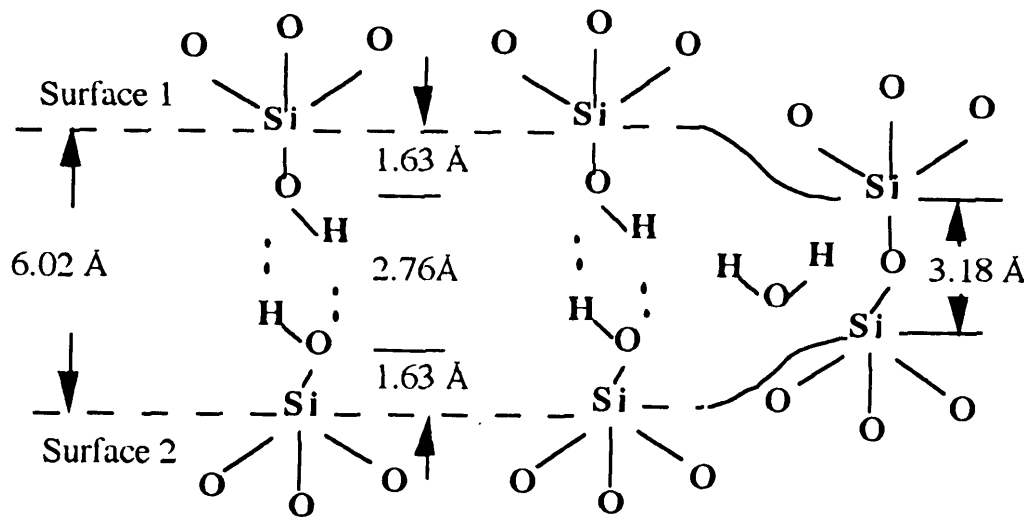
Tong, Q.-Y. & U. Gösele: *Semiconductor Wafer Bonding,* John Wiley & Sons, 1999

Surface energies calculated from Si – O bond energies (4.5 eV/bond or 430 kJ/mol) translate to ca. 3000 mJ/m^2.

Surface energy of metals

- in the fcc bulk each metal atom has 12 nearest neighbours
- it is assumed that only nearest neighbour interaction is important
- when two (111) surfaces are made by splitting bulk, number of bonds breaken is $3 N_s$ and surface energy $\gamma = 3 N_S E_b / 2$
- in sublimation 6 bonds are broken per each atom:
  - binding energy $E_b = \Delta H_V / 6L$
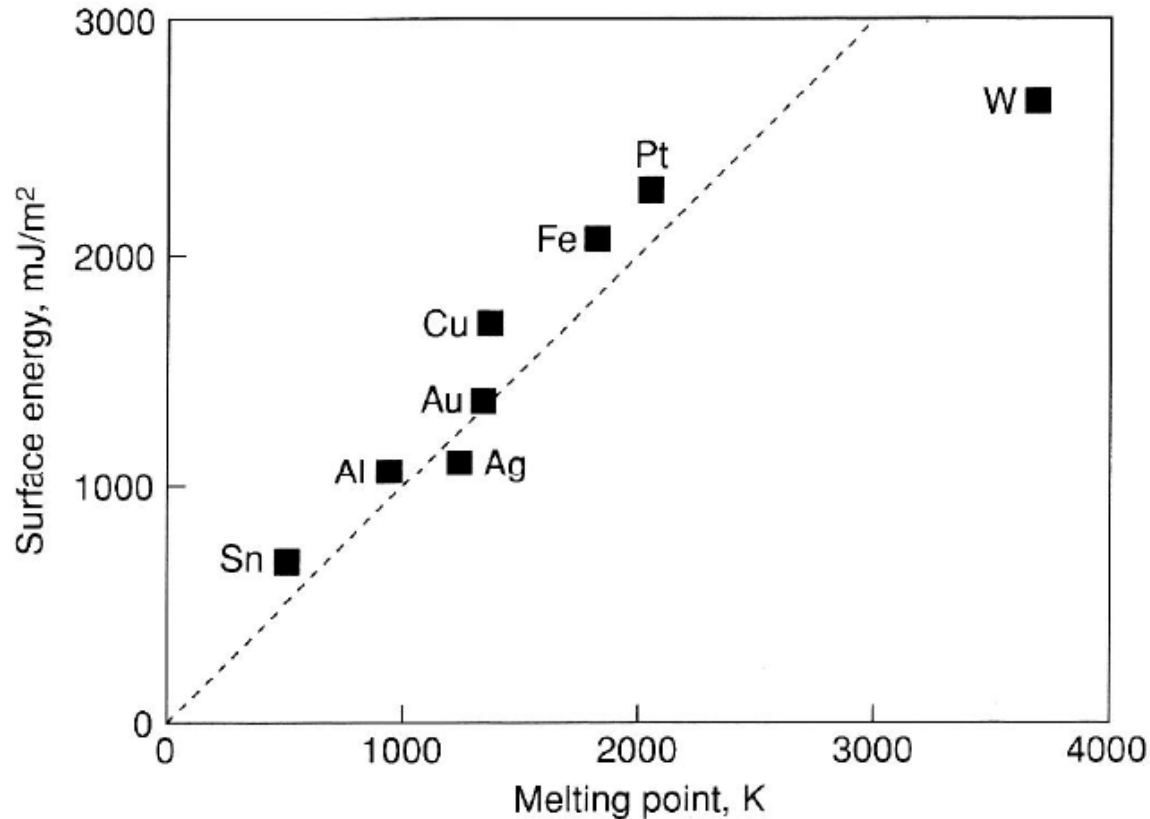
    ΔH_V = sublimation enthalpy

    L = Avogrado's number

Surface energy of metals (2)

- $\gamma_{(111)} = 3\,(4/3^{1/2}a^2)\,E_b\,/\,2 = 3.5\,E_b\,/\,a^2$
- $\gamma_{(110)} = 6\,(2/2^{1/2}a^2)\,E_b\,/\,2 = 4.2\,E_b\,/\,a^2$
- $\gamma_{(100)} = 4\,(2/a^2)\,E_b\,/\,2 = 4\,E_b\,/\,a^2$
- $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)} < \gamma_{(stepped\ surfaces)}$

Rule of thumb:
-stabilty comes from high surface atom density and high coordination number.

(001) (110) (111)

a $\sqrt{2}a$ $\sqrt{2}a$

a a $\sqrt{(3/2)}\,a$
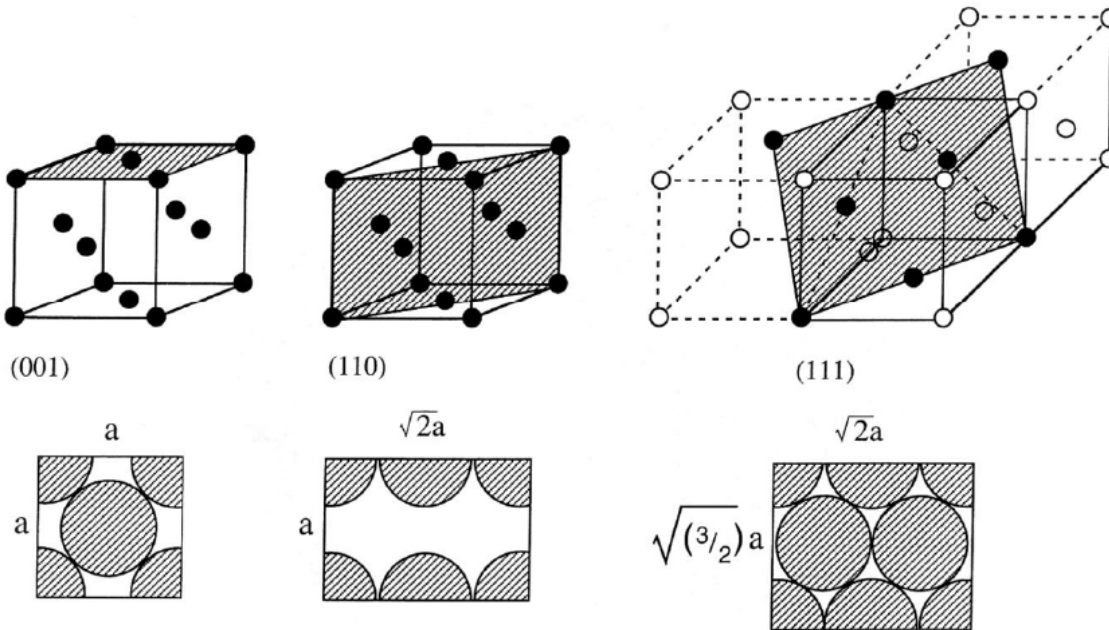
# Surface energy vs. melting point

Bond strength determines both.

12.2. Correlation of surface energy with melting point. From W. F. Hosford, *Physical Metallurgy.* (Boca Raton, FL: CRC Press, 2004), p. 77, figure 4.8.

Silicon surface termination

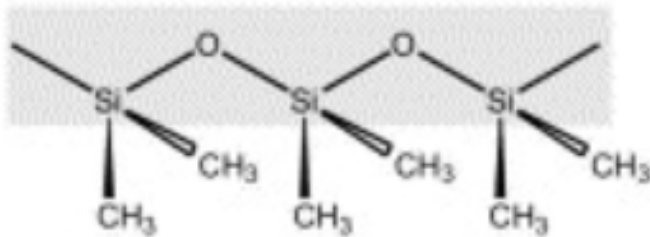a) Negatively charged oxygen attracts positively charged H+
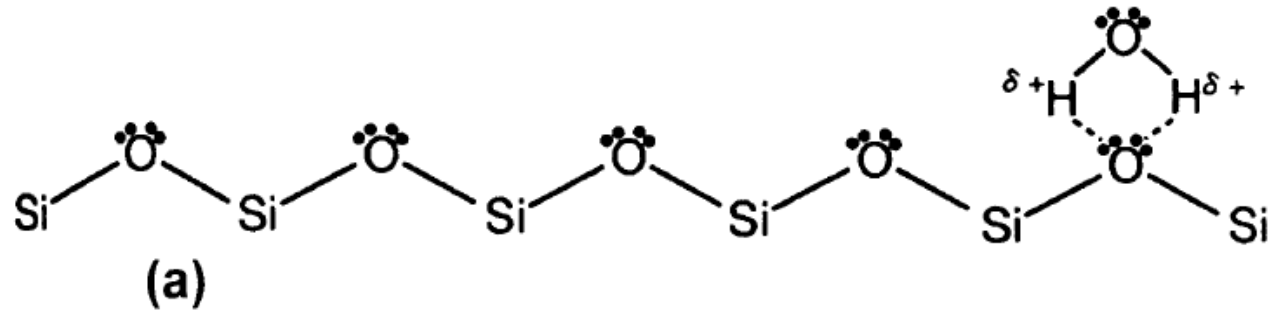
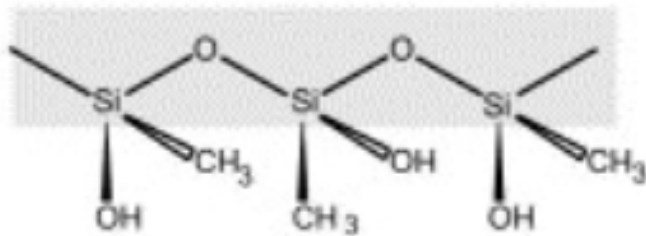b) Negatively charge H+ repels negatively charged oxygen

Hattori, T. (ed.): *Ultraclean surface processing of silicon wafers,*
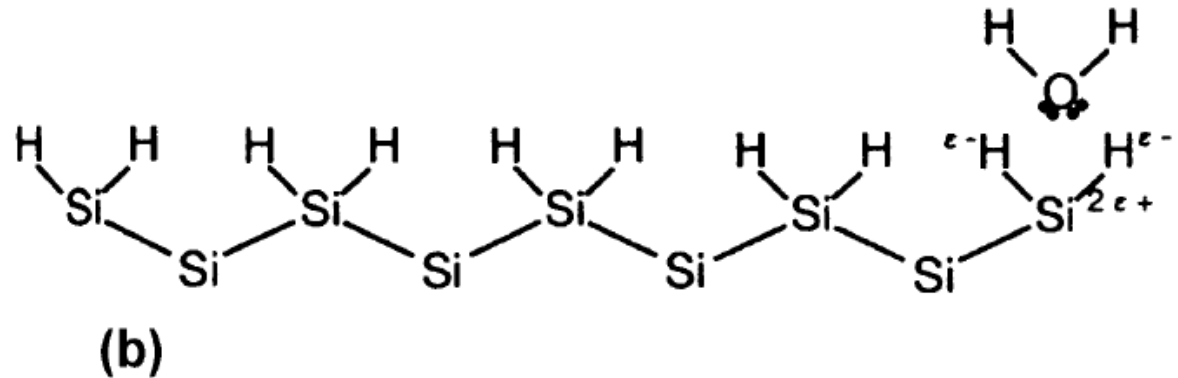
Modifying surface chemistry

Methyl-terminated, $-CH_3$
➔ Hydrophobic
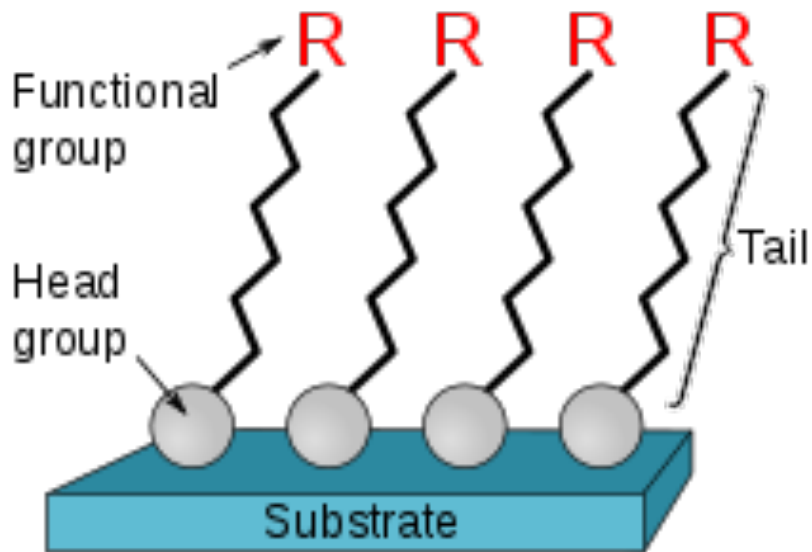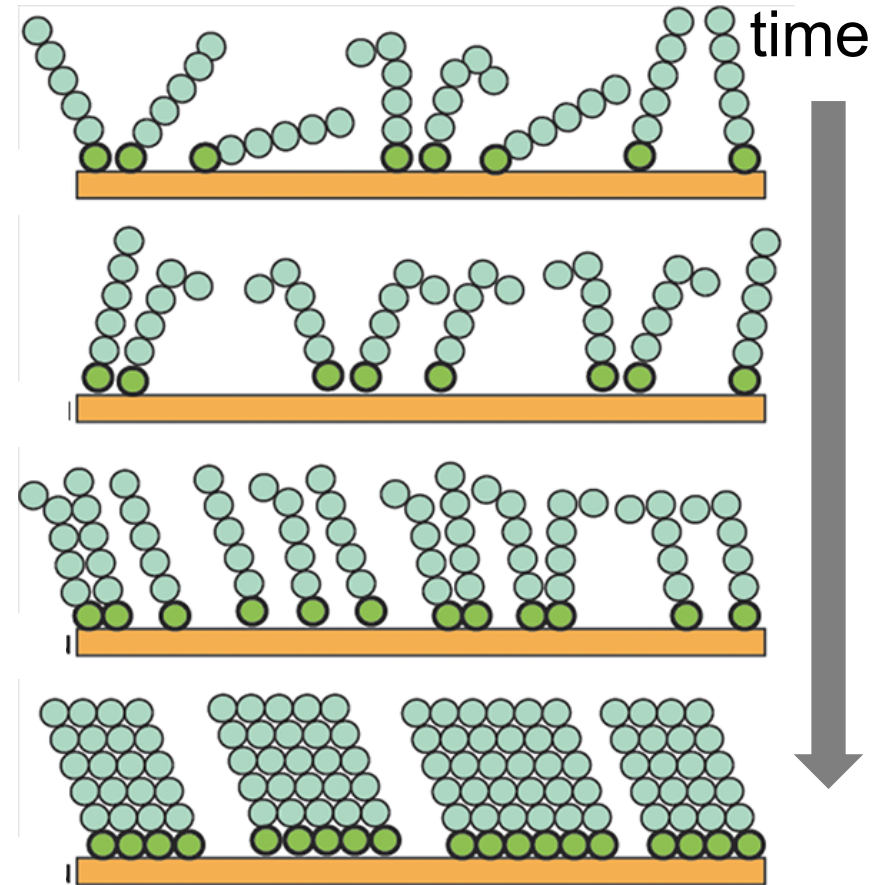
Oxygen plasma treatment turns some methyl groups to hydroxyl OH-, groups
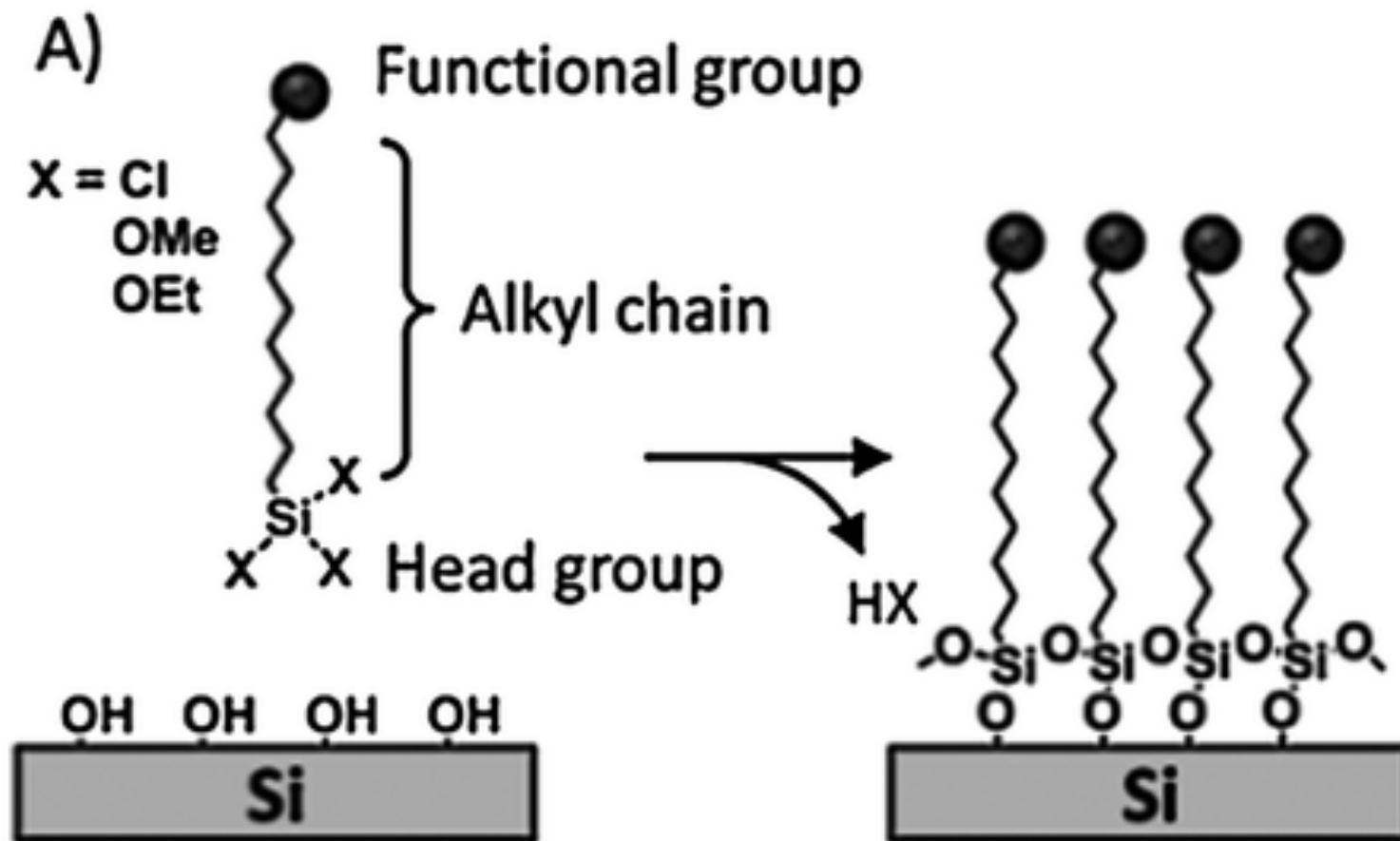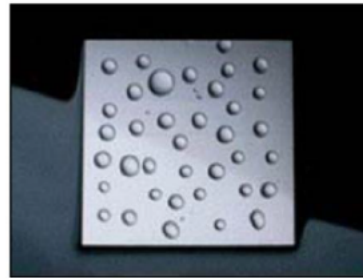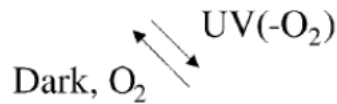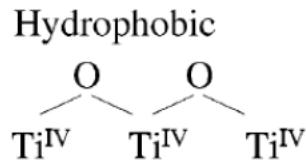➔ hydrophilic

SAMs
(Self-assembled monolayers)
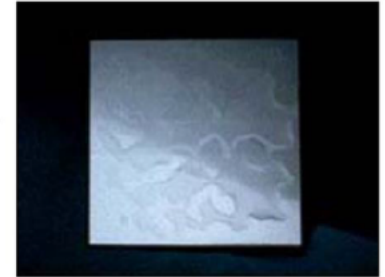

Either in liquid phase or gas phase deposition.

Silane-SAM

Self-cleaning mirrors/windows
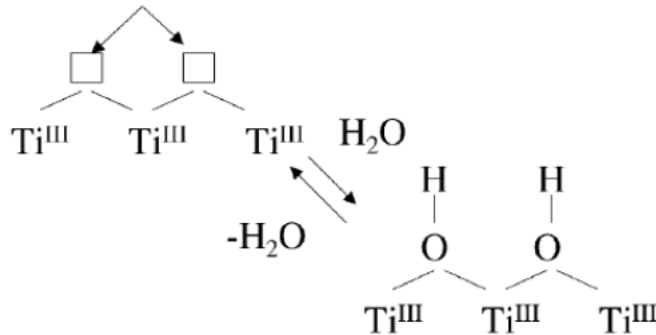
From *TiO₂ Photocatalysis; Fundamentals and Applications*,
A. Fujishima, K. Hashimoto and T. Watanabe, BKC Inc., Tokyo, 1999

37

Adsorption

- materials that are soluble in one or both phases may find it energetically favourable to concentrate at the interface, for example
  - gases adsorb onto solids
  - solutes adsorb onto solids
  - surfactants: one part of the molecule favours one phase, the other part the other phase

Hydrophobic or oleophilic part

(usually composed of carbon and hydrogen)

Hydrophilic part (ionic or polar group)

Hydrophobic 'tails'

Hydrophilic 'heads'
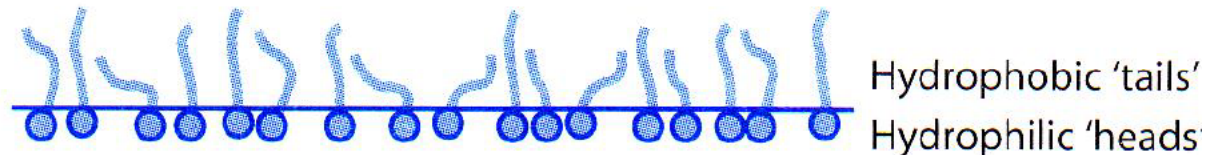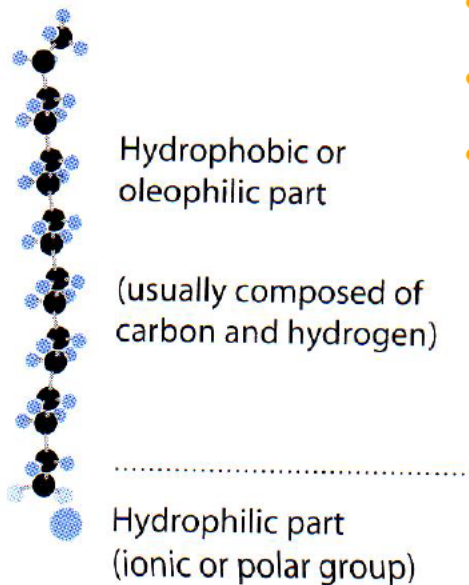
G. T. Barnes and I. R. Gentle, Interfacial Science

Atoms hitting the surface may:

1. Bounce back
-elastic scattering without energy loss
-inelastic scattering with energy loss

2. Stay on surface
-by weak interaction: physisorption
-by strong interaction: chemisorption

3. Act on surface:
-surface diffusion
-surface reactions
-desorption

Adsorption concepts

- *adsorption* - the process in which a molecule becomes adsorbed onto a surface of another phase
  - note: *a<u>b</u>sorption* – uptake *into the bulk* of a solid or liquid phase
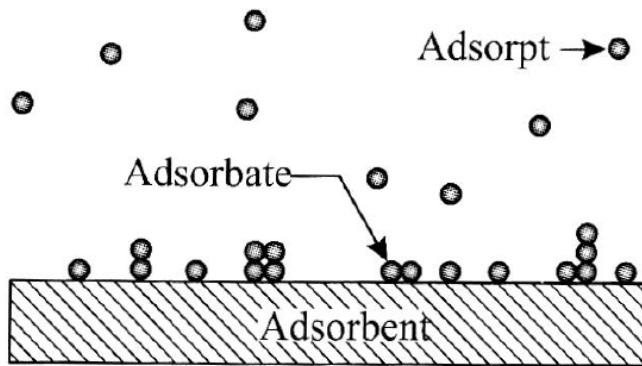
- *adsorbent = substrate* – the solid surface on which adsorption can occur
- *adsorbate* – the general term for the atomic or molecular species which are adsorbed (or are capable of being adsorbed) onto the substrate *(adsorpt* – atomic or molecular species which is not adsorbed but which is capable of being adsorbed)*

Adsorpt ➔ •

Adsorbate

Adsorbent

160

Coverage Θ

Coverage θ'

$$\theta' = N_{ads} / N_s$$

= number of adsorbates / number of surface atoms (both per unit area)

Fractional coverage θ

$$\theta = N_{ads} / N_m$$

N_m = number of adsorbates per unit area in one complete layer

- θ varies usually from 0 to 1, while θ' is commonly less than 1 but may sometimes also exceed 1, e.g. for H on W θ' may be 2: two H atoms on each surface W atom

Adsorbate fate on surface

-move around by surface diffusion
-fragment
-react with substrate
-react with co-adsorbed specie
-react with gas phase specie
-desorb

Products may be volatile and desorb; or form film on surface

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$
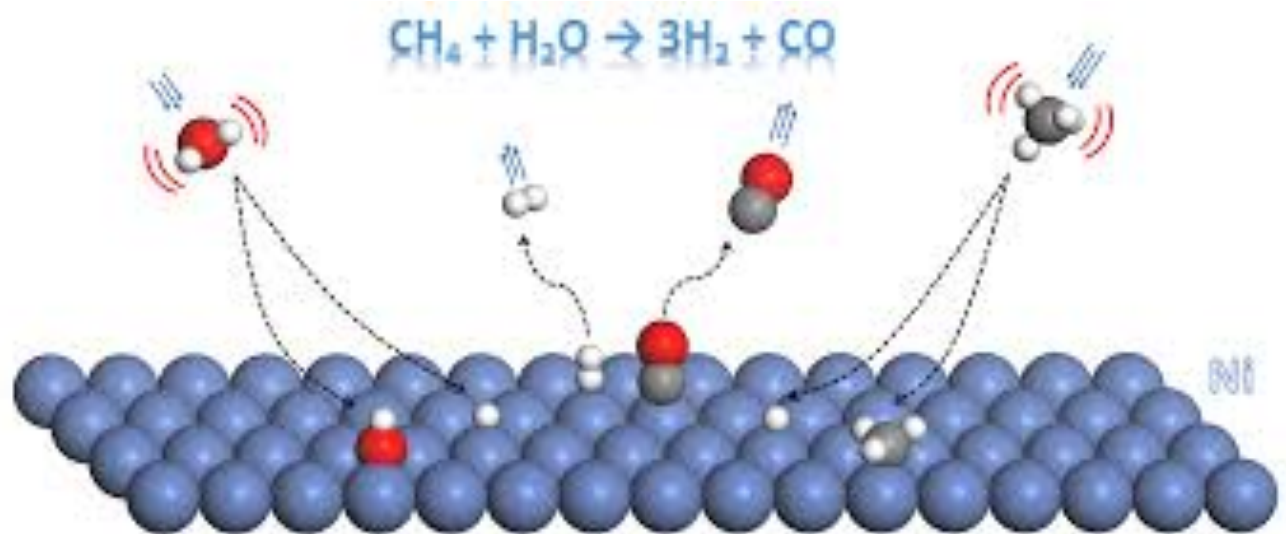
Reactive adsorption

- when adhering to a surface, a molecule also reacts with the surface groups
    - adsorption and surface reaction steps are hard to distinguish experimentally
    - significant effect on the chemical identity of the adsorbate and its capability to desorb
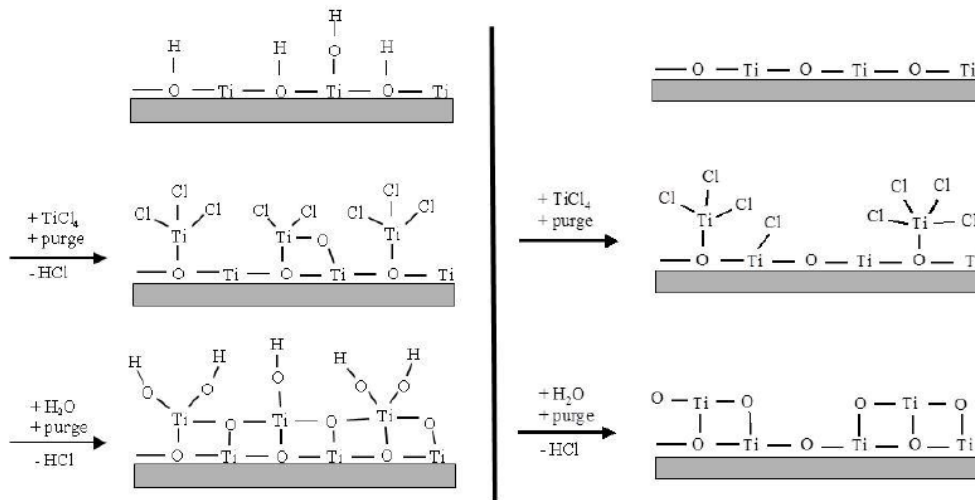
ALD as an example

- at low temperatures mostly exchange reaction – irreversible

- at high temperatures chemisorption (molecular or dissociative) – possibly reversible

196

Physisorption

- physisorption is non-specific: in principle any atom or molecule can adsorb on any surface
- large amounts of physisorption are favoured at low temperature
- physisorption is always exothermic but with low (weakly negative) ΔH_{ads} = - 10 - -40 kJ/mol (about the same magnitude as the heat of condensation)

Xenon atoms physisorbed

Each xenon atom appears as a 1.6-A-high bump on the surface,
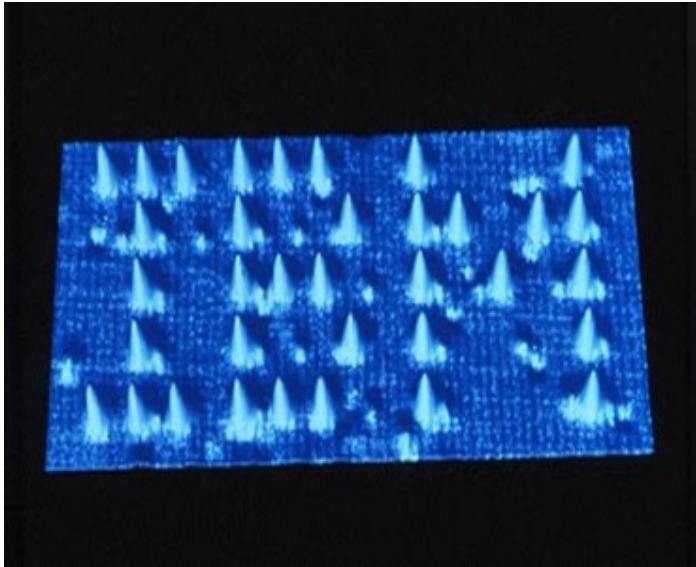
The xenon atoms are spaced on a rectangular grid which is four nickel unit cells long horizontally and five unit cells long vertically, corresponding to 14 x 12.5 A.

"…use of the STM at low temperatures (4 K) to position individual xenon atoms on a single-crystal nickel surface with atomic precision.

The tip of an STM always exerts a finite force on an adsorbate atom. This force contains both Van der Waals and electrostatic contributions. By adjusting the position and the voltage of the tip we may tune both the magnitude and direction of this force. This, taken together with the fact that it generally requires less force to move an atom along a surface than to pull it away from the surface, makes it possible to set these parameters such that the STM tip can pull an atom across a surface while the atom remains bound to the surface."
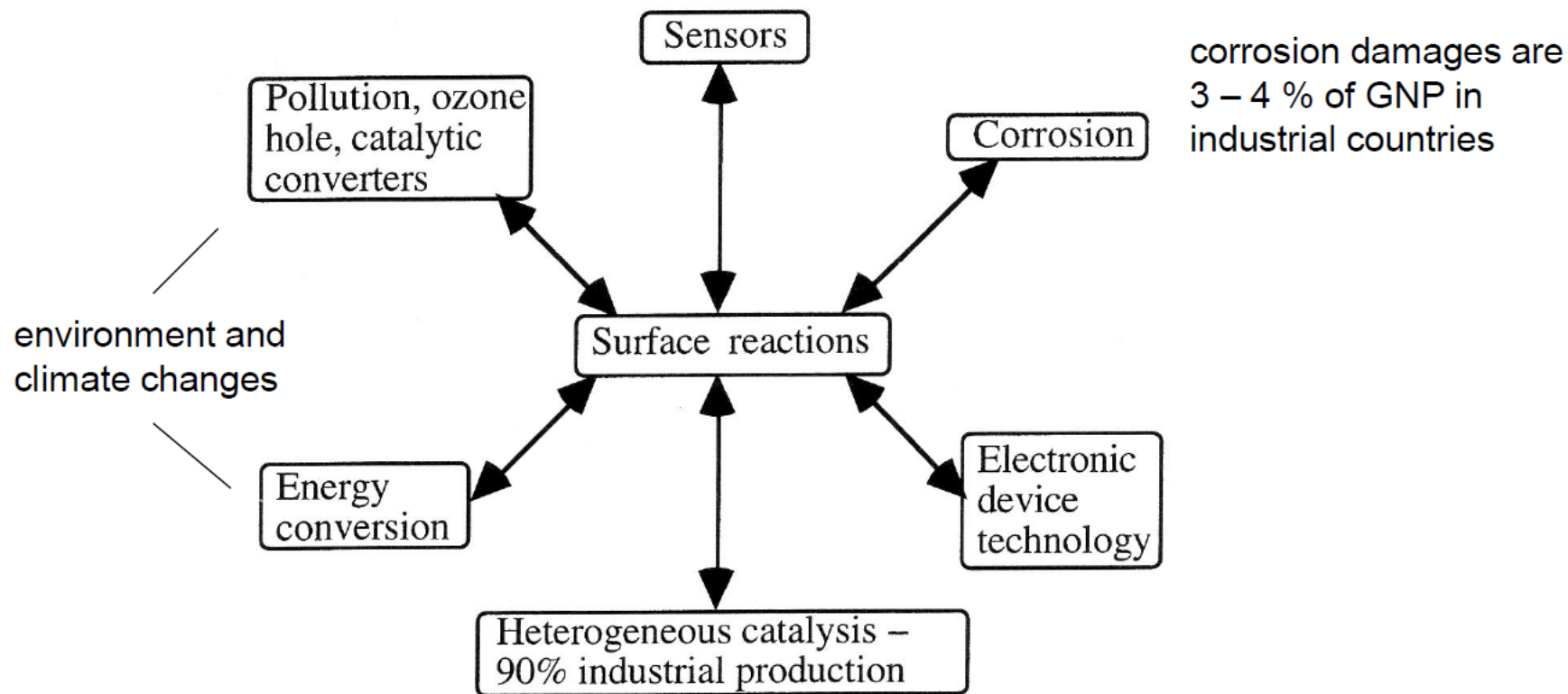
Eigler & Schweitzer, Nature 1990

Chemisorption

- chemisorption involves high degree of specificity, possibly also with respect of crystal planes of the same material
- a strong chemical bond (ionic, covalent or mixture) is formed: exchange of electrons between the adsorbing molecule and surface
- high (largely negative) ΔH_{ads} = - 40 - -1000 kJ/mol (about the same magnitude as the bond energies)
- ΔS_{ads} always negative (increased order, lost freedom)
- chemisorbed layers with high ΔH_{ads} are stable to high temperatures
- ΔH_{ads} is often coverage dependent: $\Delta H_{ads}(\theta)$

Chemisorption vs. physisorption

|	Chemisorption	Physisorption
$-\Delta H_{ads}$	$\sim$40–1000 kJ mol^{-1}	$\sim$10–40 kJ mol^{-1}
Kinetics of activation	Can be activated	Non-activated
Number of layers	One monolayer (assuming no reconstruction or incorporation of adsorbate into the subsurface region)	Monolayers and multilayers
Chemical reactivity	Can cause reactivity changes in the adsorbate	Little change
Specificity	Normally dependent on specific adsorbate–surface interactions	Non-specific, needs low temperature to get substantial amounts
Nature of Adsorption	Often dissociative May be irreversible	Non-dissociative Reversible

Important surface reactions

18

Catalysis

$$SO_2 + 2V^{5+} + O^{2-} \rightarrow SO_3 + 2V^{4+}$$
$$\underline{2V^{4+} + 0.5O_2 \rightarrow 2V^{5+} + O^{2-}}$$
$$SO_2 + 0.5O_2 \rightarrow SO_3$$

$$\Delta H = -90\,\text{kJ/mol}$$

- accelerates the reaction
- does not change the equilibrium
- is not consumed in the reaction
  - catalyst may change during the reaction, but also changes back to its original form
  - in real processes catalyst is consumed
    - covered by coke: less surface accessible, decreased activity; may be regenerated
    - sintering leads to growth of particles: decrease of surface area and activity
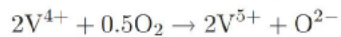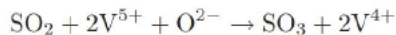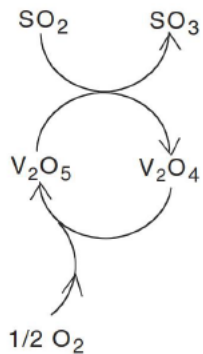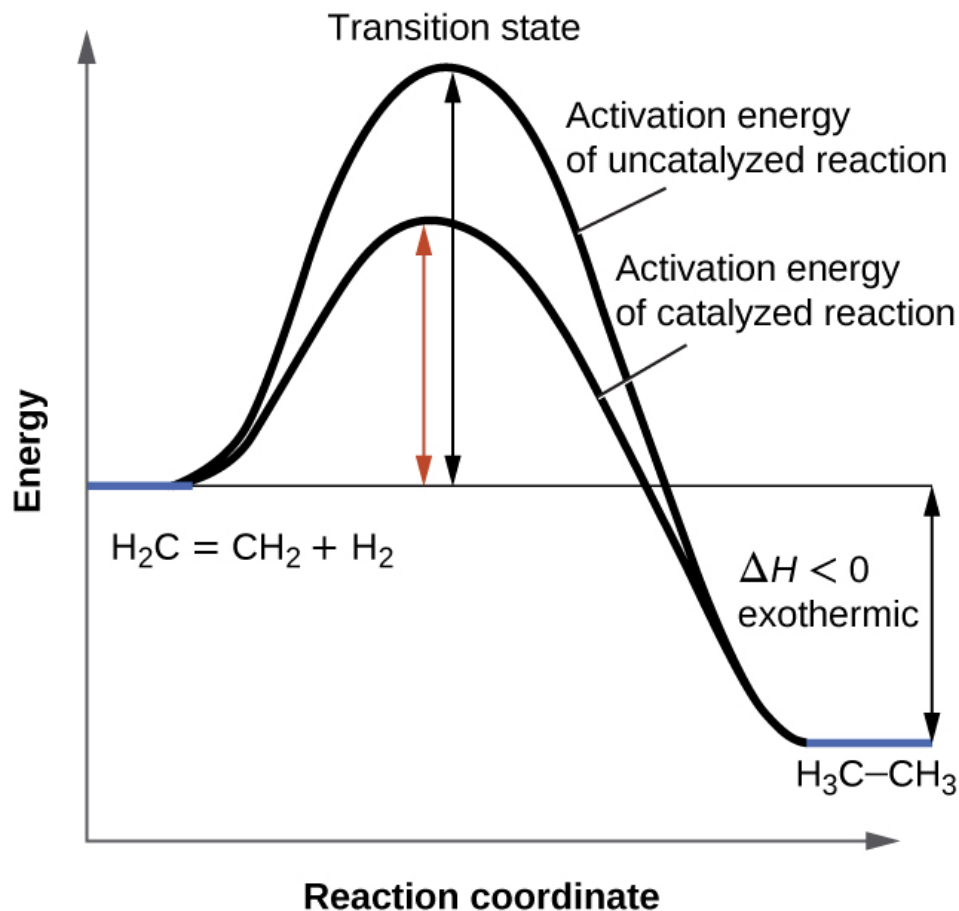
Heterogenous catalysis

in heterogeneous catalysis, the catalyst is present as a solid phase and the reactants and products are in a gas or liquid phase
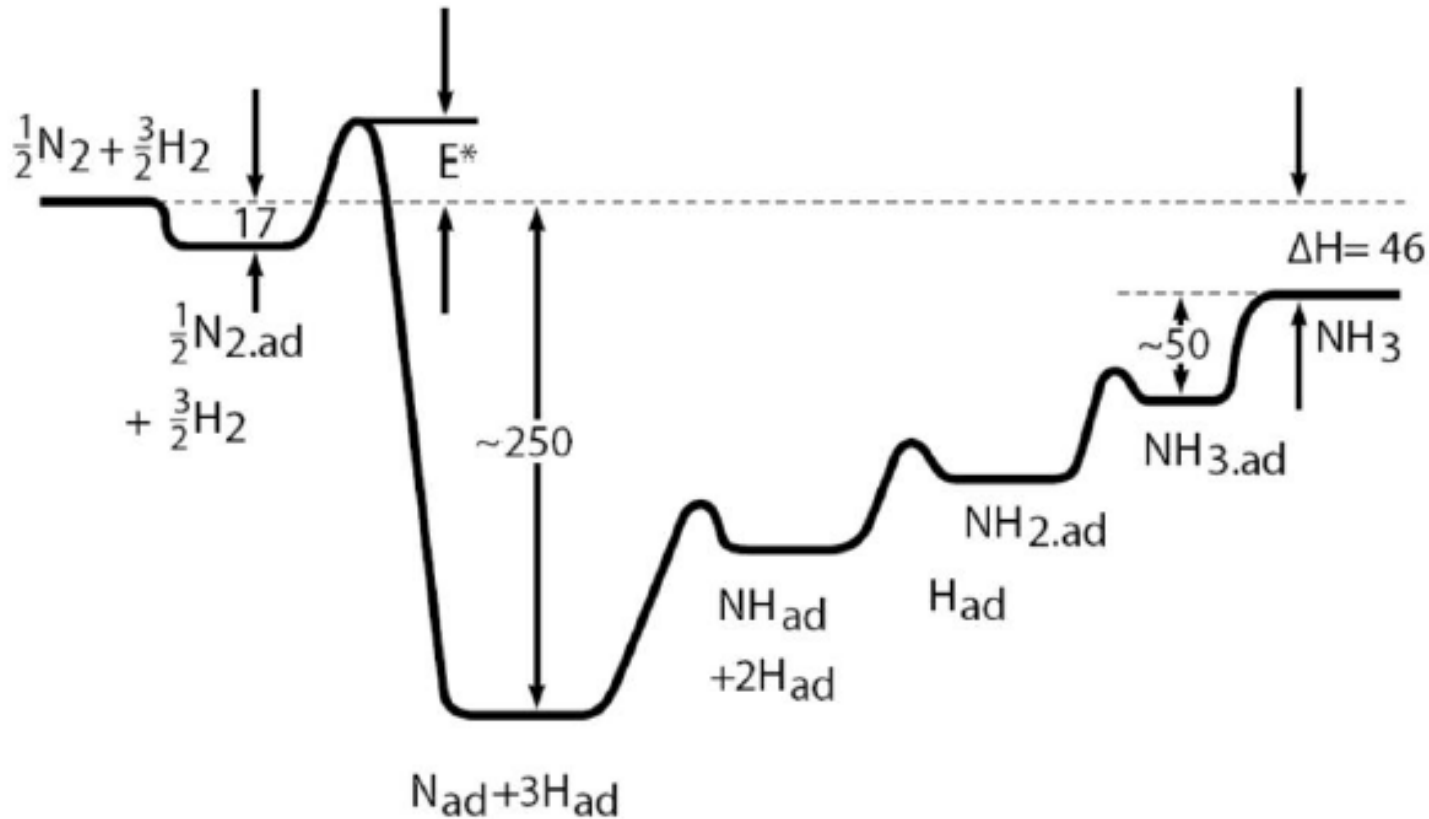
- gas–solid heterogeneous catalysis is often used in the refinery and in the bulk chemicals industry
- liquid–solid heterogeneous catalysis is common in the fine chemical industry, where large batch reactors are filled with an organic liquid and a solid catalyst

Reaction co-ordinates

Transition state

Activation energy
of uncatalyzed reaction

Activation energy
of catalyzed reaction

Energy

$H_2C = CH_2 + H_2$

$\Delta H < 0$
exothermic

H_3C-CH_3
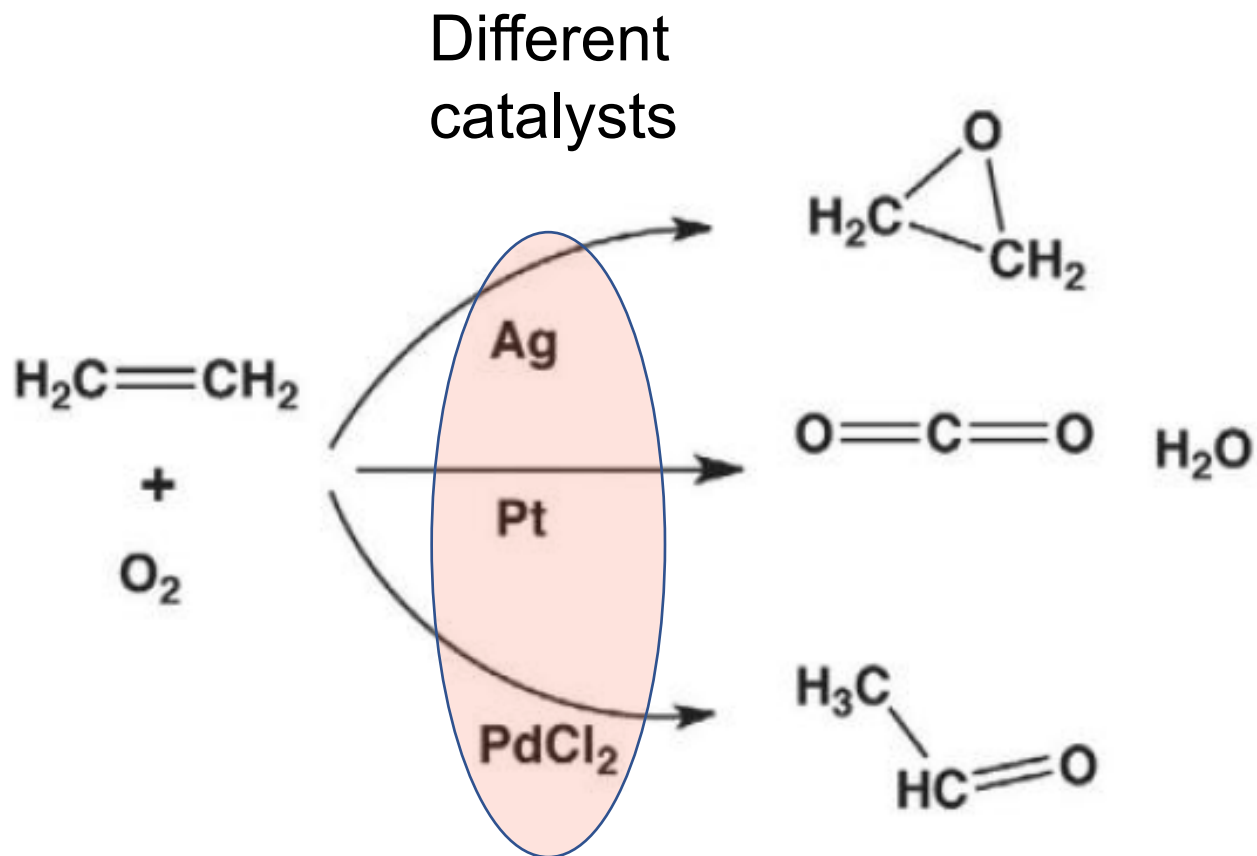
Reaction coordinate

It might be that homogeneous uncatalyzed reaction is replaced by heterogeneous catalyzed reaction.

Nobel prize 2007: Gerhard Ertl

Devil is in the details

Different
catalysts

C. G. Freyschlag and R. J. Madix,
Materials Today 14(4) (2011) 134

Pt/C nanoparticle catalyst
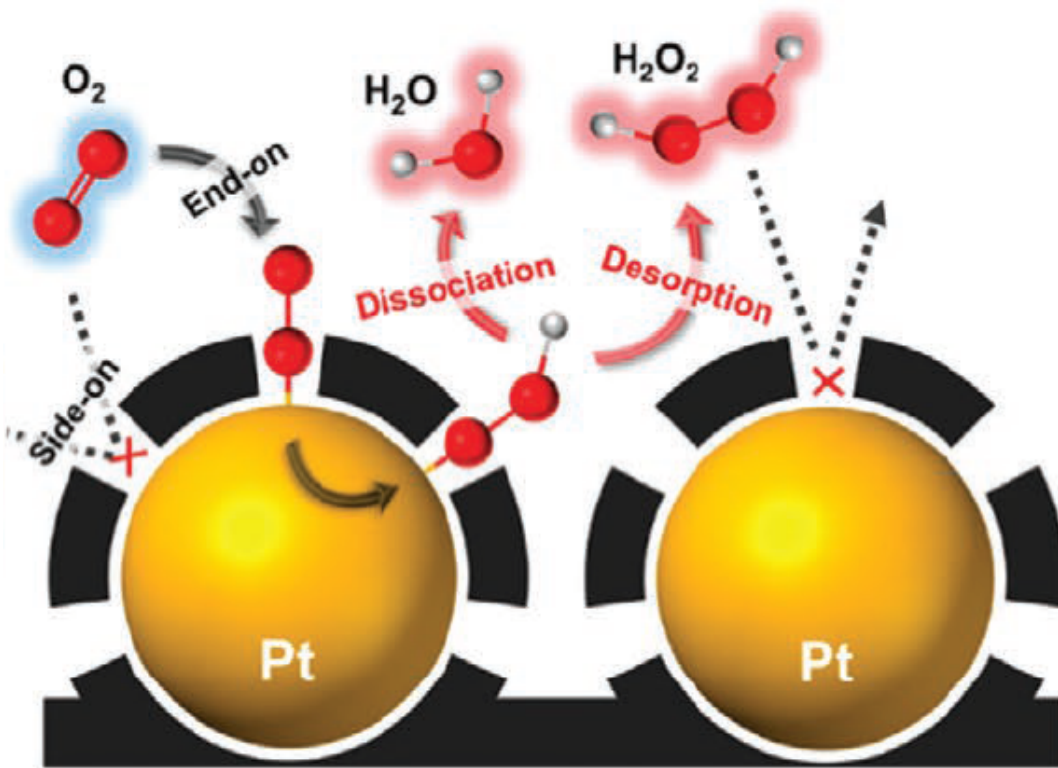
For instance, holes in carbon coating may expose a single Pt-atom; or several ➔ orientation of entering molecule different ➔ different end result

Jiang et al: *Adv. Funct. Mater.* **2020**, *30*, 2003321

ALD-coated Pt-catalyst
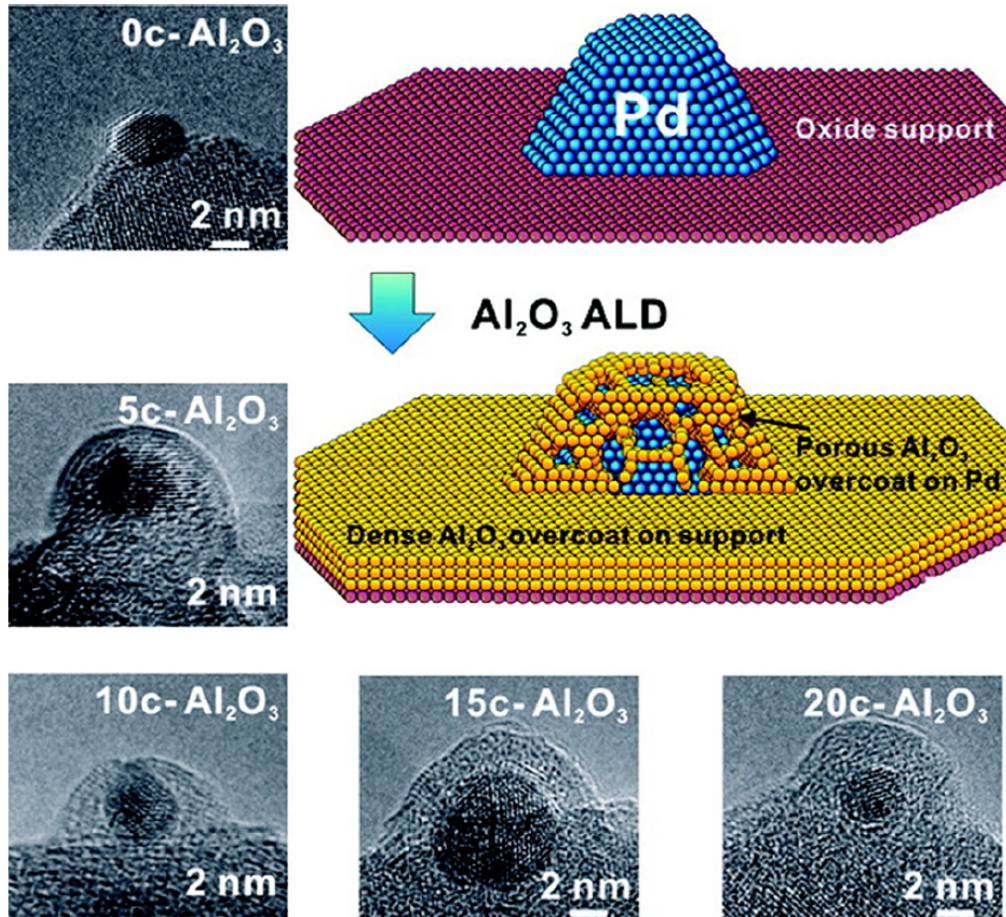
ALD films <1 nm are discontinuous ➜ gas molecules have access to noble metal catalyst.

But reaction product molecules are too big to enter.

Cao et al.: Catalysts design and synthesis via selective ALD, JVST A 2018

Stabilization by coating

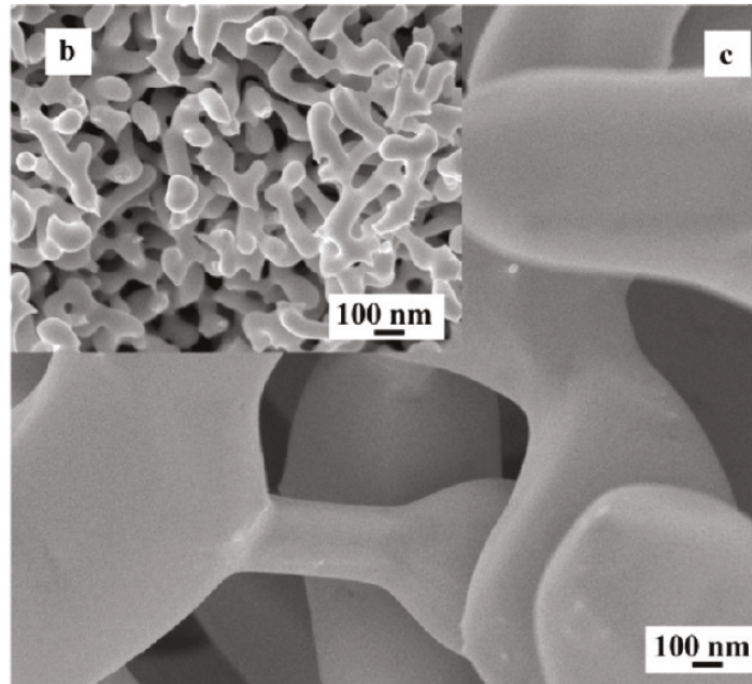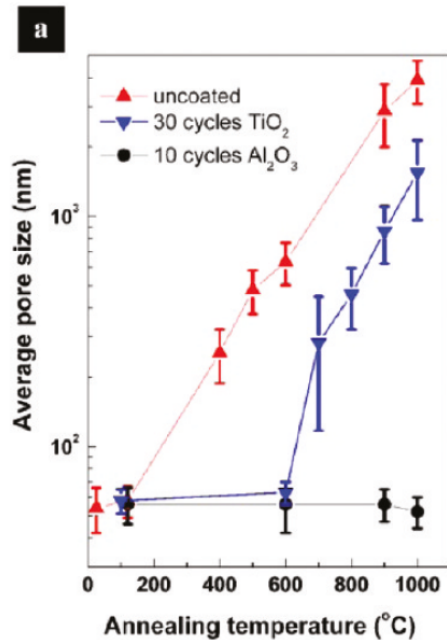b and c – samples both 600ºC anneal

Nanoporous gold wants to minimize area, but ALD films prevent this.

In b) nanoscale structures protected by ALD film remain;
In c) unprotected nanoscale structures have coalesced into larger microstructures

Biener et al: ALD Functionalized Nanoporous Gold: Thermal Stability, Mechanical Properties, and Catalytic Activity, Nanoletters 2011

Facet selective deposition
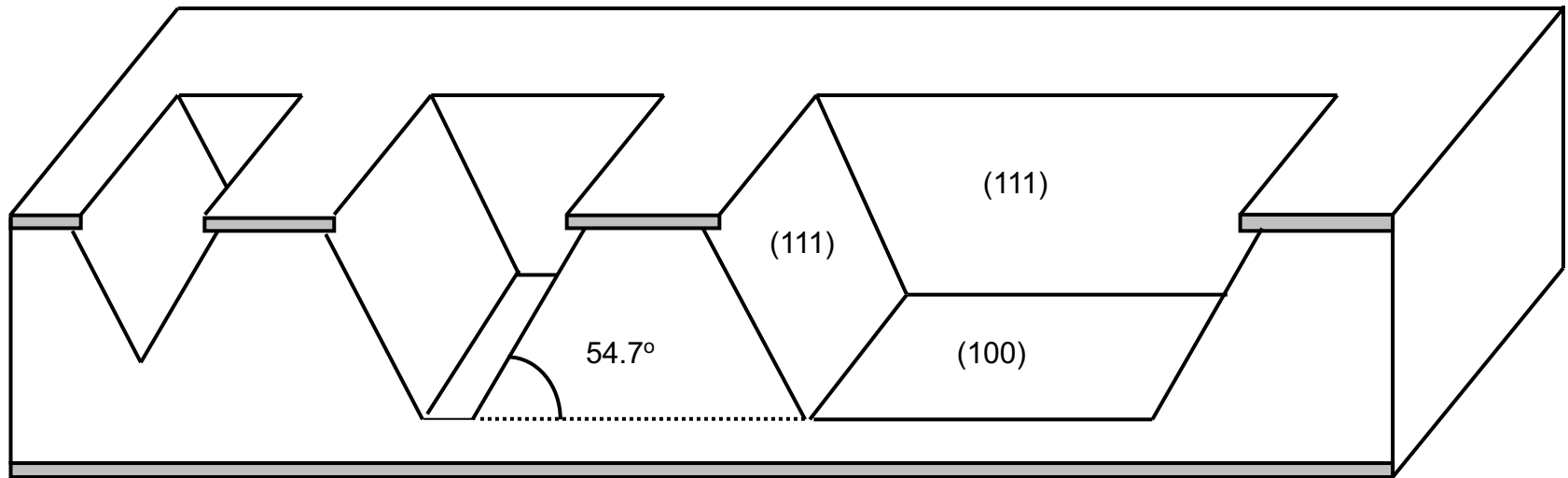

The facet selectivity was realized through the intrinsic differences in binding energies of Ce precursor fragments chemisorbed on Pt surfaces.

Fe_3O_4 on Pt, and TiO_2 on Au, there is a strong tendency to first nucleate on the egde/low coordinated sites.

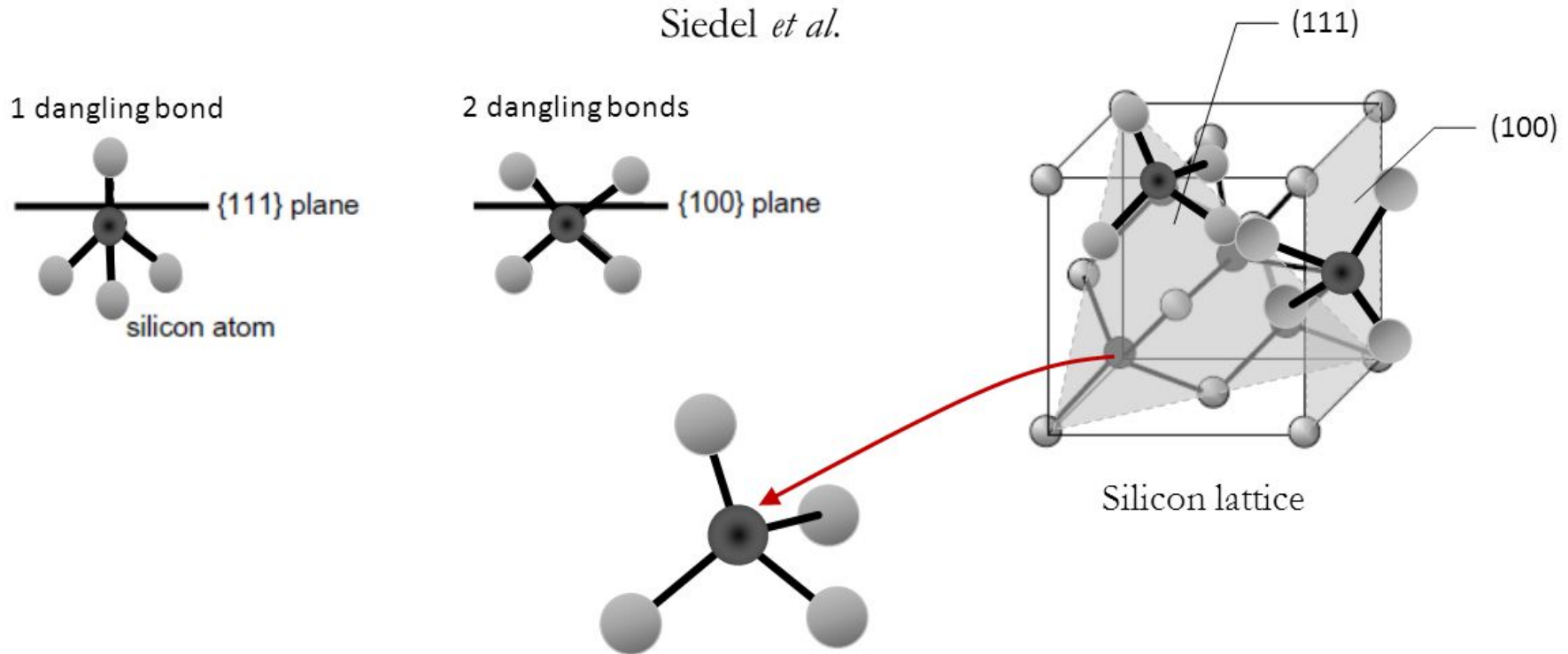Cao et al.: Catalysts design and synthesis via selective ALD, JVST A 2018

Crystal plane dependent etching

Some crystal planes etch much faster than others. In silicon, (100) planes etch 100X faster than (111) planes.

Bond density at surface

Siedel *et al.*

1 dangling bond — {111} plane — silicon atom

2 dangling bonds — {100} plane

(111), (100) — Silicon lattice
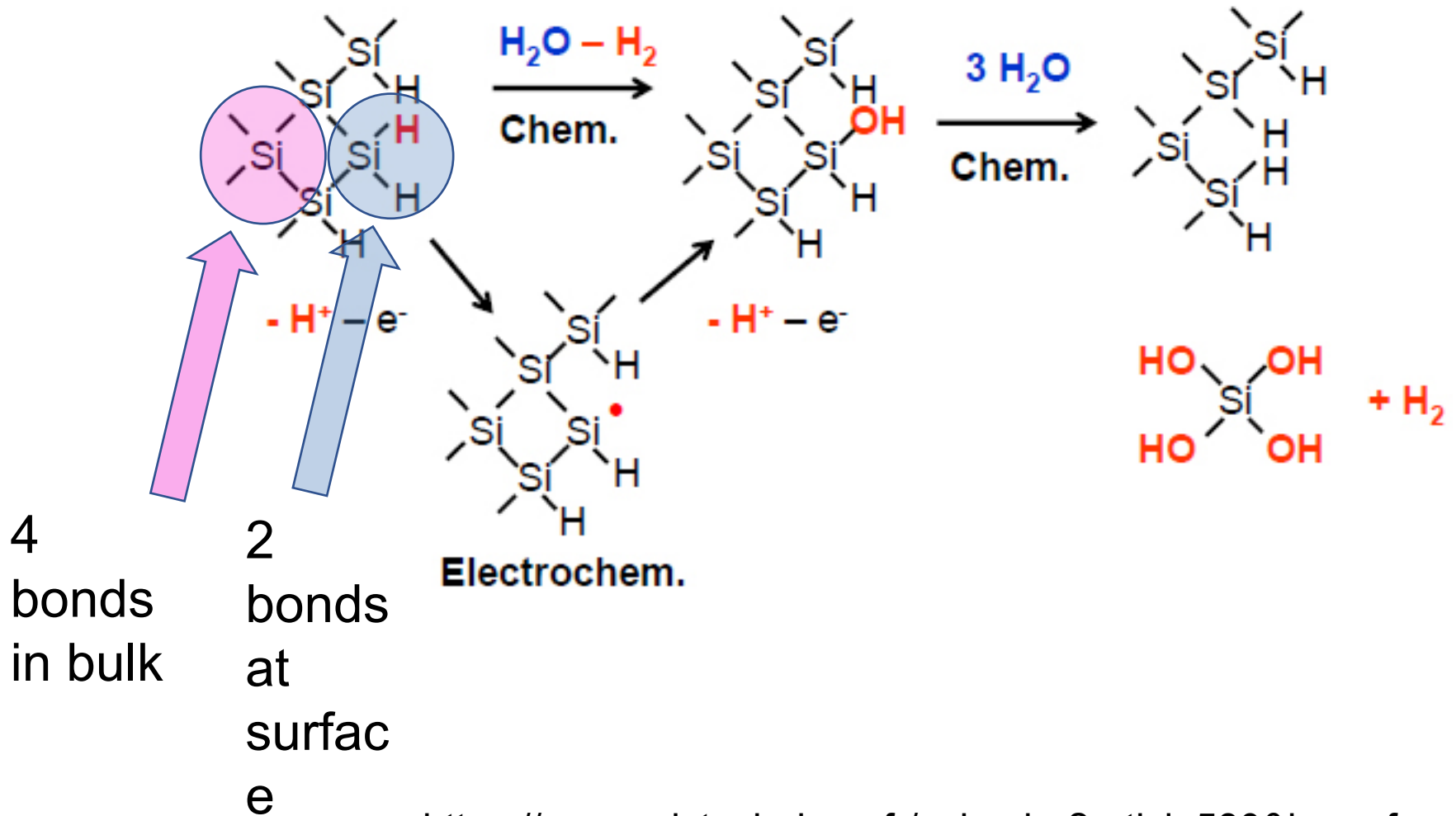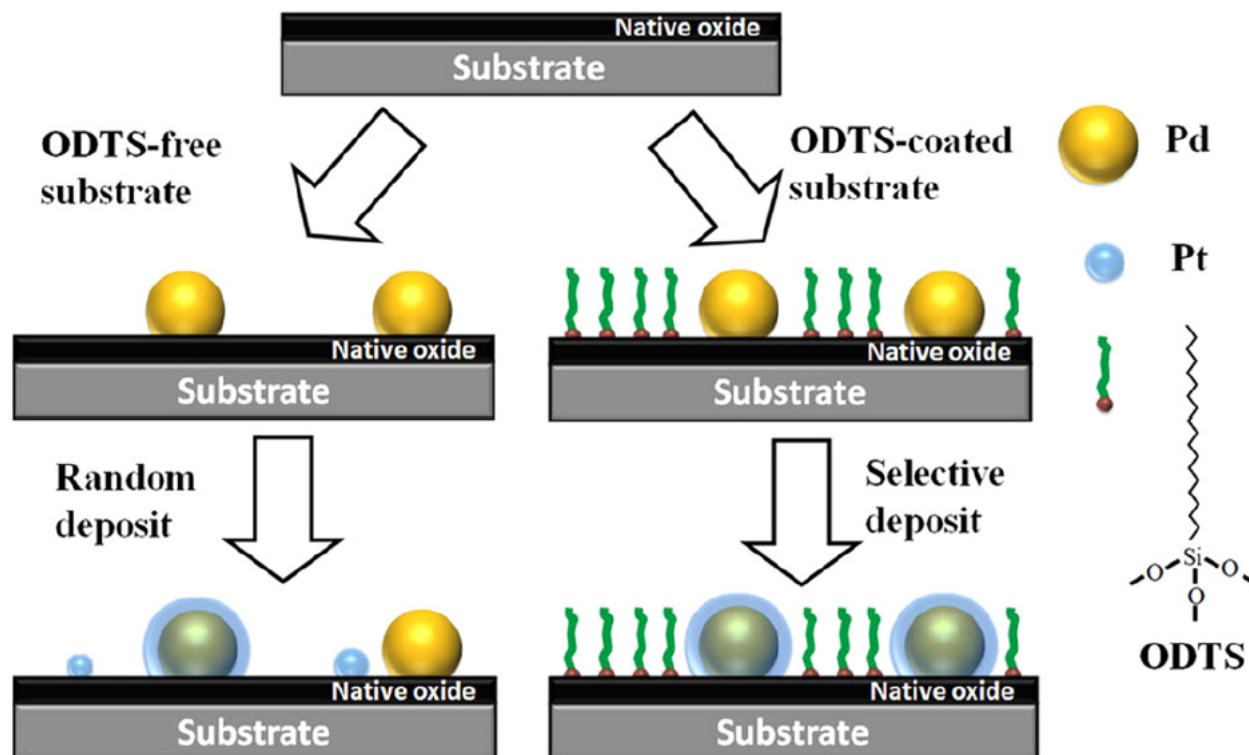
The lower reaction rate for the {111} planes is caused by the larger **activation energy** required to break bonds behind the etch plane. This is due to the larger bond density of silicon atoms behind the {111} plane.

One layer at a time

4 bonds in bulk

2 bonds at surface

Patterning of catalyst

Cao et al.: Catalysts design and synthesis via selective ALD, JVST A 2018

Graphene oxide catalyst

Carbon · **Cobalt** · **Hydrogen** Co–N$_4$(O)

Nitrogen · **Oxygen**

Mild reduction
NH$_3$, 500 °C

GO → Co$_1$–NG(O)
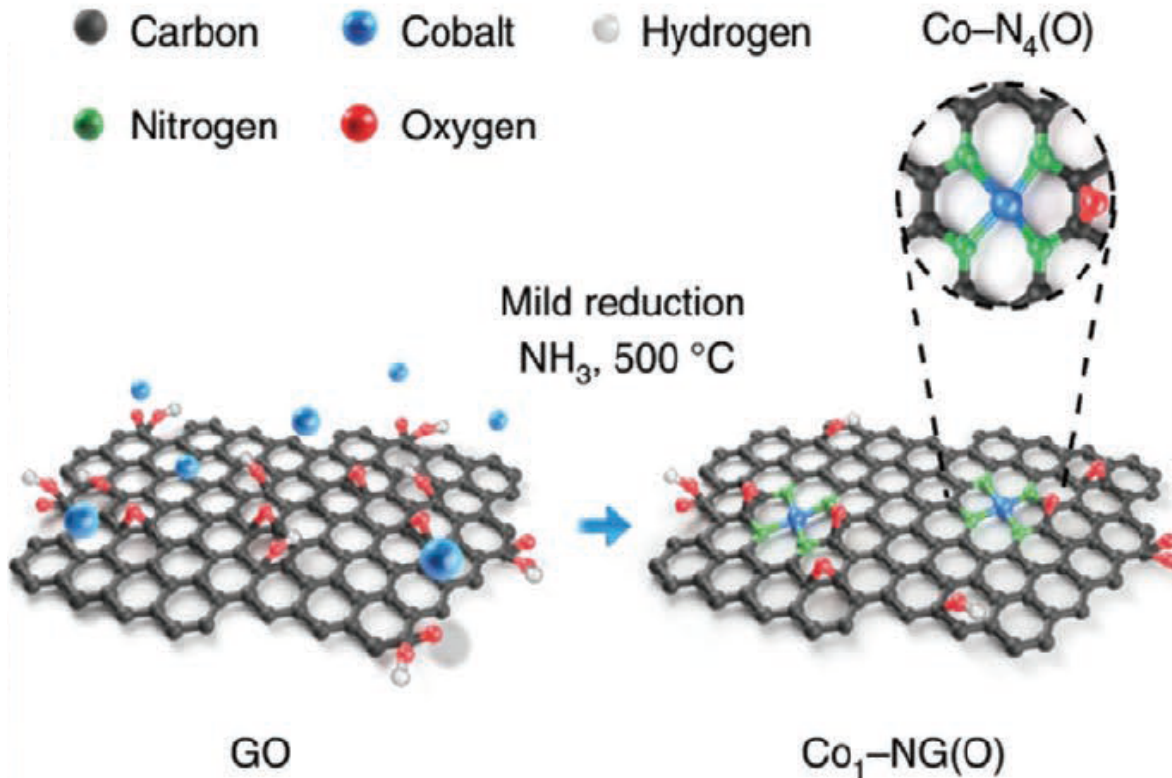
"Co–N$_4$ moieties are surrounded by the desired configuration of electron-rich oxygen atoms from graphene oxide substrates."

Industrial catalytic processes

- Haber Bosch process: $N_2 + 3H_2 \Rightarrow 2NH_3$
  - alkali-metal-promoted iron catalyst

- three-way catalyst: NO_x, CO and $C_xH_y \Rightarrow H_2O + CO_2 + N_2$
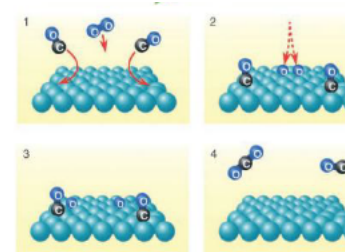 - destroys harmful molecules from automobile exhaust
  - with catalyst composed of Pt, Rh and Pd

- Fischer-Tropsch chemistry: $H_2 + CO$ (synthesis gas from natural gas or coal) • methanol or liquid fuels or other hydrocarbons and oxygenates
  - typically iron or cobalt catalysts

Size scales of catalysis

active sites

pore geometry

crystal

shaped catalyst

packing

reactor

10^{-10}m

10^{-9}m

10^{-7}m

10^{-3}m

10^{-1}m

$>10^1$m

accessibility

diffusion

heat transfer

pressure gradient

Chemistry & physics & computational science

Materials science

Chemical engineering

Real surfaces…

Layer III (mobile water, removable at 50 °C)

Layer II (relatively mobile water, removable at 80 ~ 100 °C)

Layer I (stabilized water, removable at 100 ~ 160 °C)

Physisorbed water

Chemisorbed water

300 ~ 500 °C

Two terminal OH groups condense and evolve into water at 300 ~ 500 °C.

C.-Y. Wu et al. Materials 2017, 10, 566

More real surfaces

Metal strip
- 0.3-10 nm — temporary water film hydrocarbons
- 1-10 nm — oxide layer
- > 5 µm — working layer by skin rolling
- bulk material roughness: 0.1 – 10 µm

Sheet glass
- ~50 nm — temporary water film (physically bound)
- ~10 nm — permanent water film (chemically bound)
- bulk glass roughness: ~ 0.1 nm

Si wafer
- ~50 nm — temporary water film (physically bound)
- ~ 0.5 nm — native oxide
- bulk glass roughness: ~ 0.5-1 nm

Surface functionalization
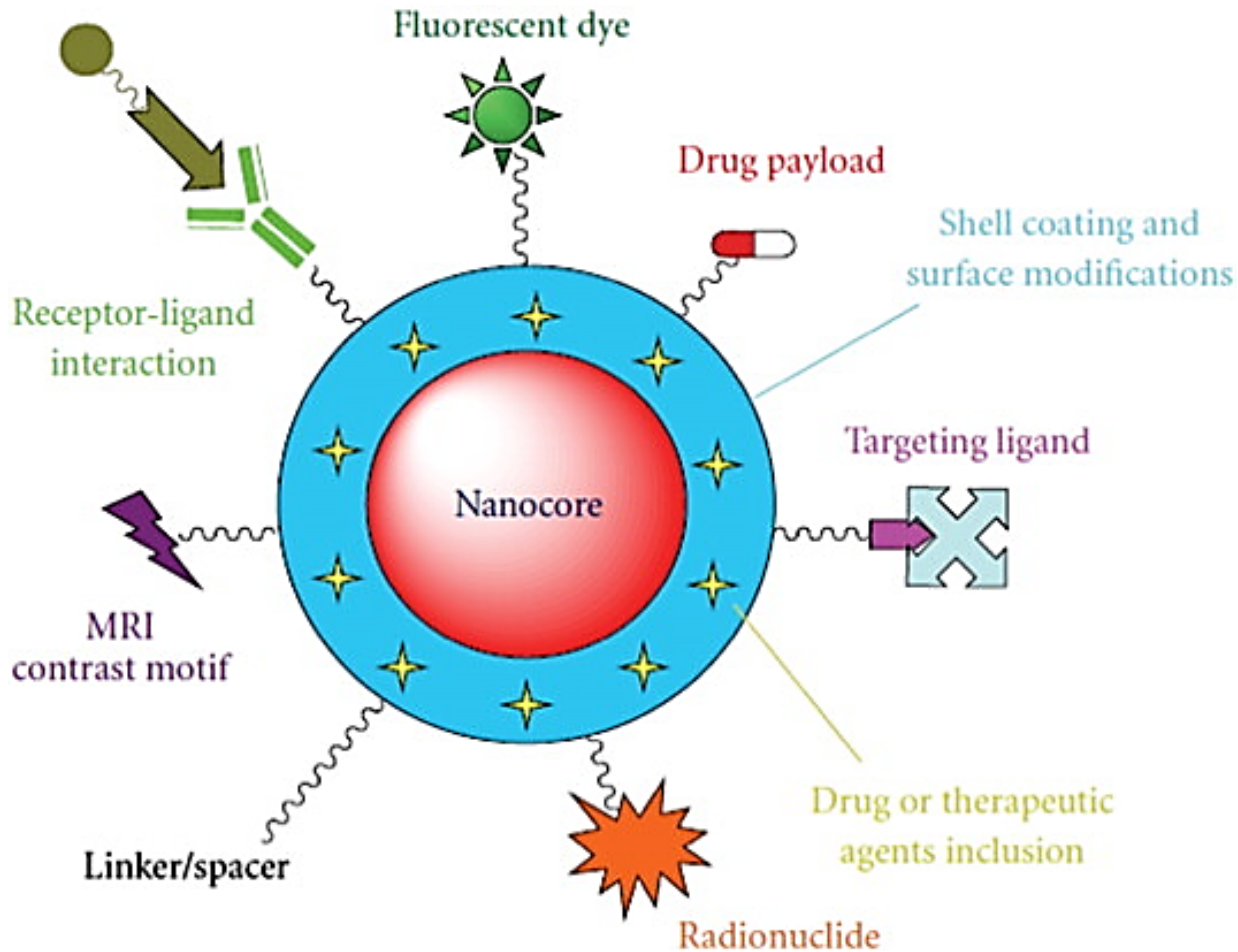
Chatterjee et al:
Core/shell nanoparticles
in biomedical
applications, 2014