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What is a Surface / Interface?

• Common Sense: A **surface** is the shell of a macroscopic object (the inside) in contact with its environment (the outside world). An **interface** is the boundary between two phases.

The surface of an object determines its optical appearance, stickiness, wetting behavior, frictional behavior, and chemical reactivity, e.g.

- in **large** objects with small surface area *A* to volume *V* ratio (*A*/*V*) the physical and chemical **properties** are primarily defined by the **bulk** (inside)

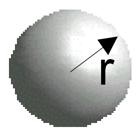
- in **small** objects with a large *A*/*V*-ratio the **properties** are strongly influenced by the **surface**

⇒ in a solid the density of atoms is in the order of 10^{23} atoms cm^{-3}, so only a small number of surface atoms compared to the number of bulk atoms

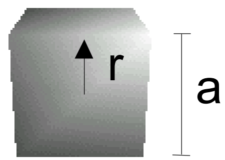
$$V = c_V \left(\frac{r}{r_0}\right)^3 \qquad A = c_A \left(\frac{r}{r_0}\right)^2$$

$$\frac{A}{V} = \frac{c_A}{c_V}\left(\frac{r_0}{r}\right) = r_0 \frac{c_A}{c_V} \cdot \frac{1}{r}$$

sphere: $V = \frac{4}{3}\pi r^3 \qquad A = 4\pi r^2$



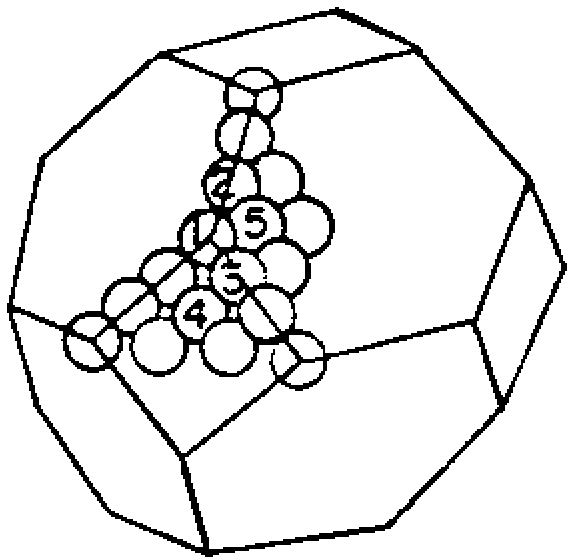
cube: $V = 8 r^3 \qquad A = 24 r^2 \qquad r = \frac{1}{2} a$

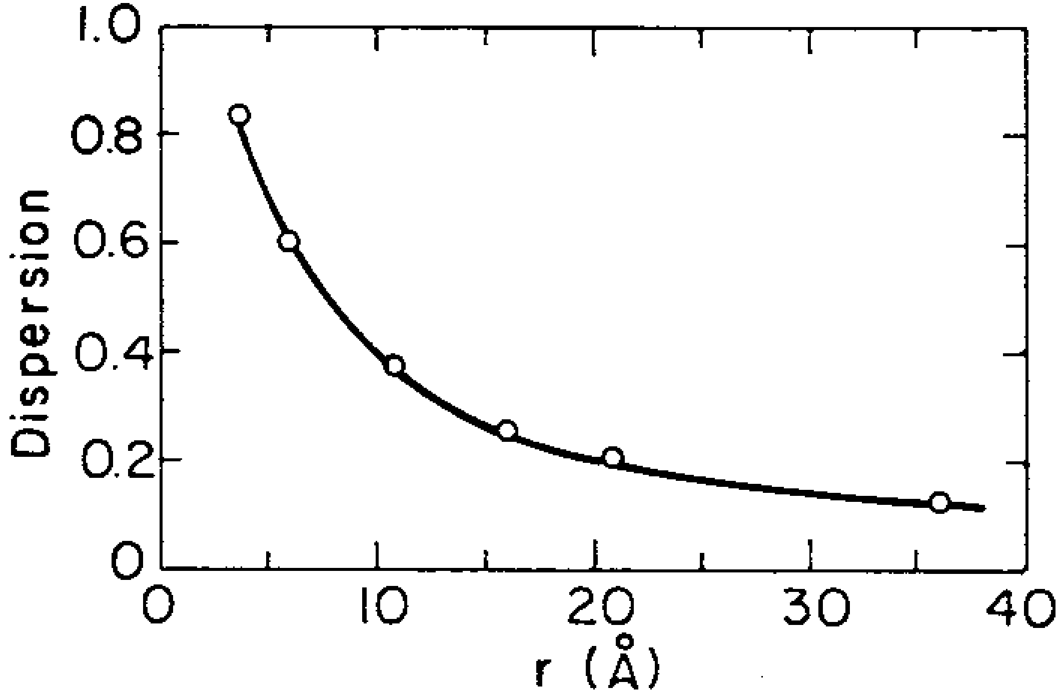


r_0 relates to the radius of a structure element (atom, e.g.)

"Dispersion", the Other *A*/*V* Relation

"dispersion": The **ratio** of the number of **surface** atoms to the **total** number of the atoms in a particle.

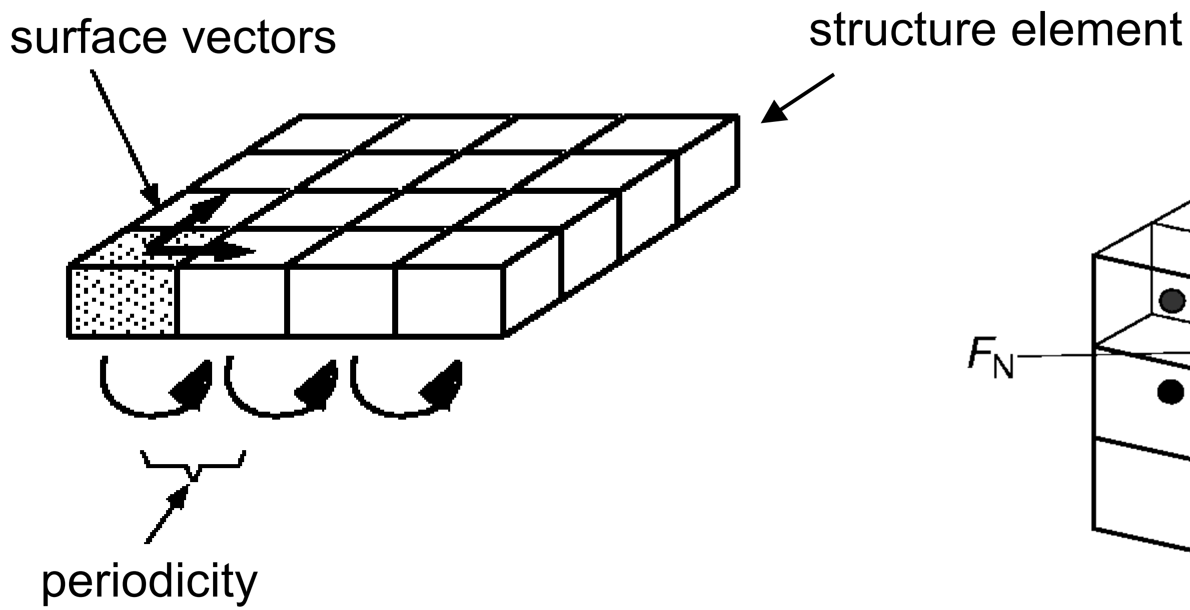


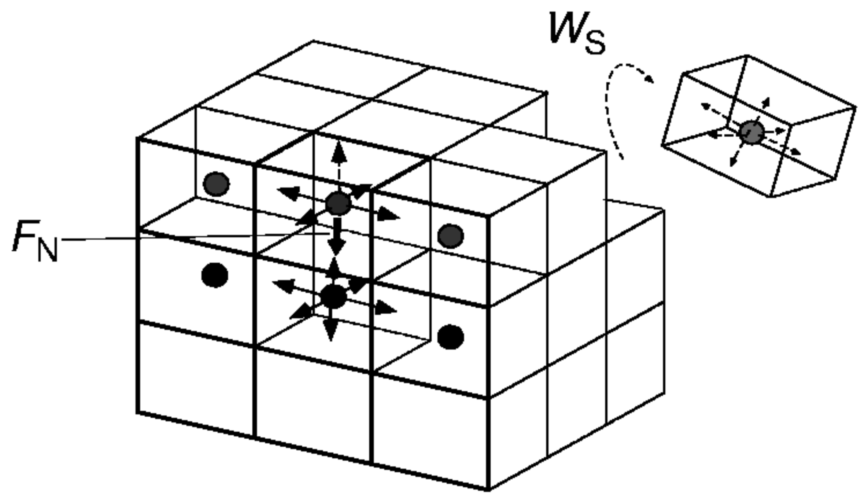


example: variation of the dispersion with particle size for close-packed cubic packing (fcc) of spherical particles

Schematic Representation of a Surface

Translational symmetry of structure elements in an ordered surface: idealized crystal lattice



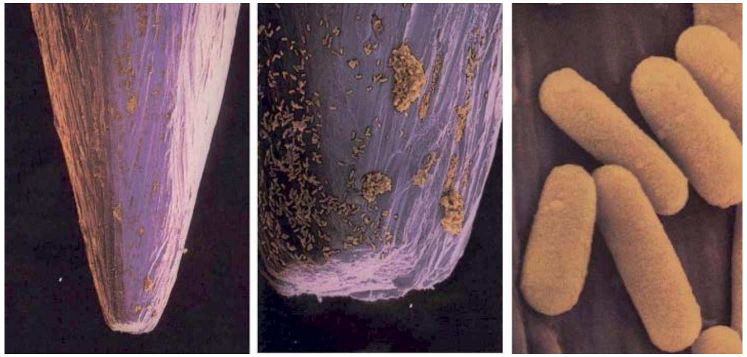


In three dimensions the structure extends to one side of the surface into the bulk.

F_N is the normal force acting onto a surface element towards the bulk, due to missing elements at the exterior.

W_s is the work to transfer a surface element into the gas phase.

What is the Structure of a Surface?



courtesy of Dr. Marx: http://www.siu.edu/~cafs/surface/file1.html

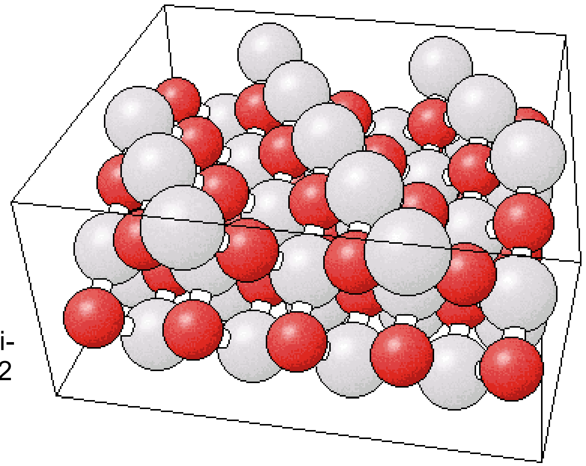
The **morphology** of a surface is a **macroscopic** or **ensemble** propery that defines its **form** and **shape**.

example: grainy structure of wooden table top

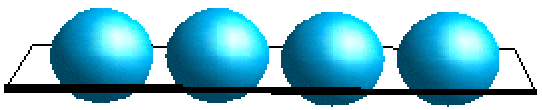
The **structure** of a surface is given by the **atomic** and **molecular composition** and arrangement of the atoms in space.

Geometry of AgBr(111)-(2x1) ->

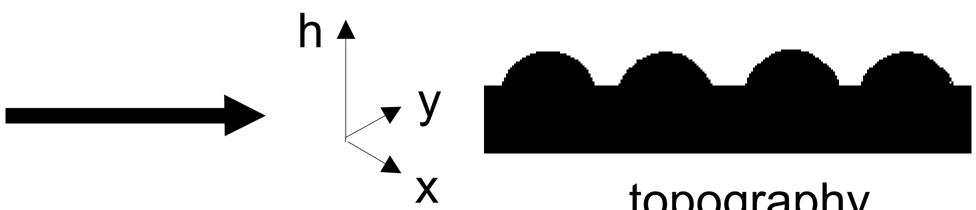
courtesy of P. R. Watson, M. A. Van Hove, and K. Hermann: http://www.fhi-berlin.mpg.de/th/personal/hermann/img_title.cgi?var1=./SSDfig151.gif&var2=AgBr(111)-(2x1)



The **topography** of a surface is its **profile** determined by "valley", "planes" and "hills".



structure

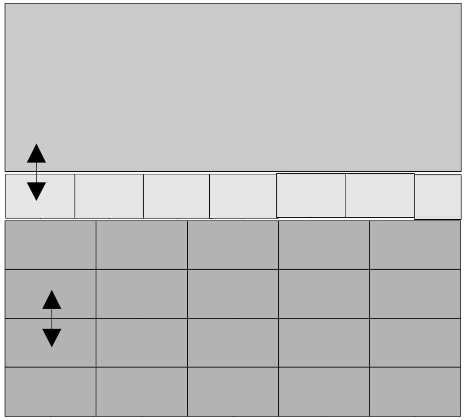


topography

What is an Interface

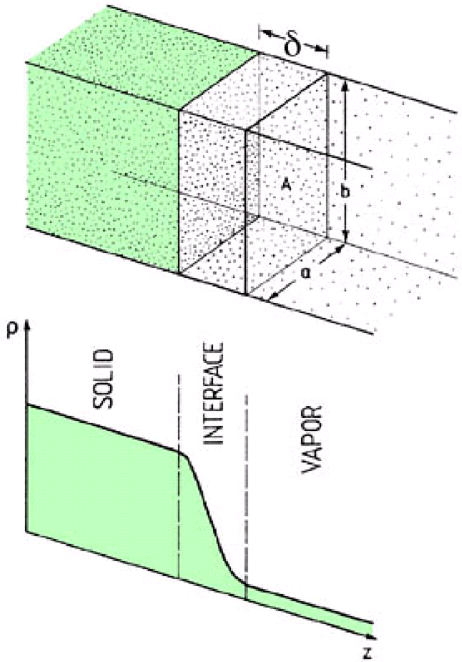
An **interface** is the separating **layer** between two condensed phases (usually molecular dimensions).

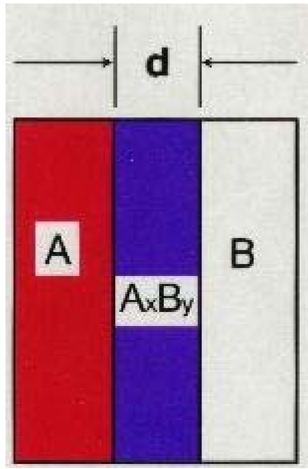
adhesion: attractive interactions between two different media



cohesion: attractive interactions within a phase (solid or liquid)

At the border of a solid or liquid in contact with vapor there is usually no abrupt change in density, but a more or less continuous transition from high density to low density. The interface consists either of evaporating bulk material or condensing material from the gas phase.

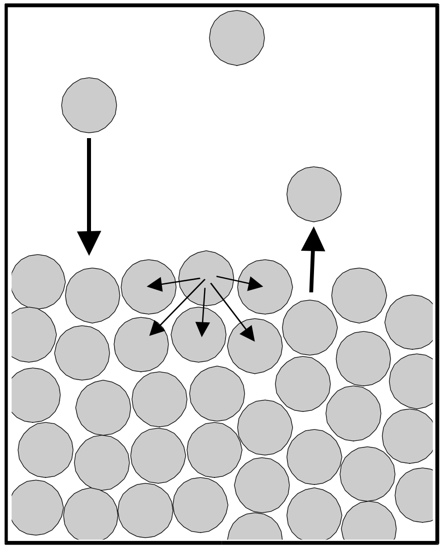




An **interphase** is a chemical **compound** composed of the two sourrounding phases.

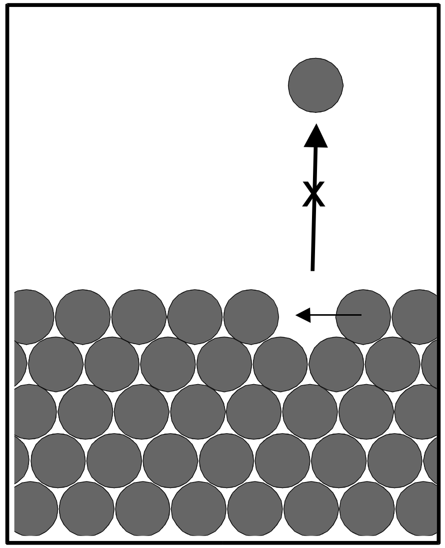
Different Surface & Interface Scenarios

liquid / vapor



- liquid highly mobile & disordered
- constant evaporation and recondensation at surface

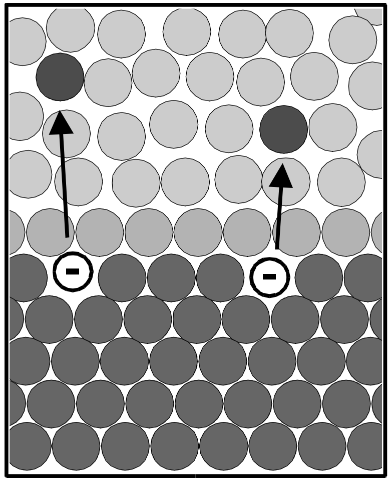
solid / vapor (vacuum)



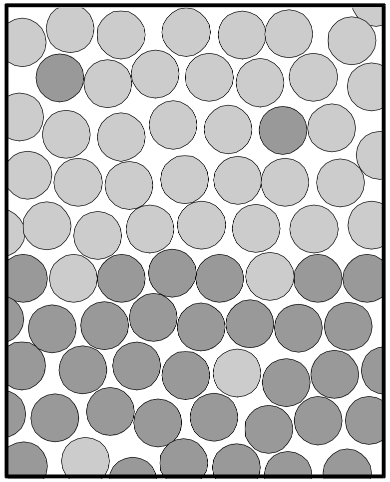
- solid highly immobile
- crystalline solids highly ordered / structured
- usually no evaporation of surface atoms & molecules, only lateral diffusion (depends on T)

Different Surface & Interface Scenarios (2)

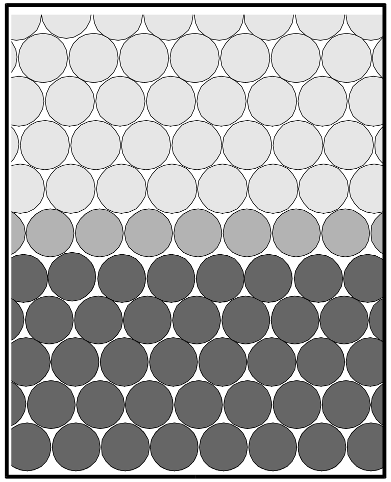
solid / liquid



liquid$_1$ / liquid$_2$



solid$_1$ / solid$_2$



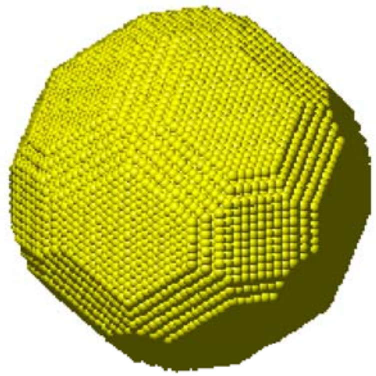
- liquid can dissolve surface atoms → may lead to surface charges
- liquid molecules at the interface can be much higher ordered than in the bulk

- both phases highly mobile → shape of interface is controlled by surface tension
- depending on solubility molecules will migrate from one phase to the other → controlled by chemical potential (partition coeff.)

- if two crystalline solids are in atomic contact the different lattice constants will generate strain @ interface
- if both materials react together new compound will be formed in contact region → **interphase**
- at high T interdiffusion possible (e.g. Cr & Au)

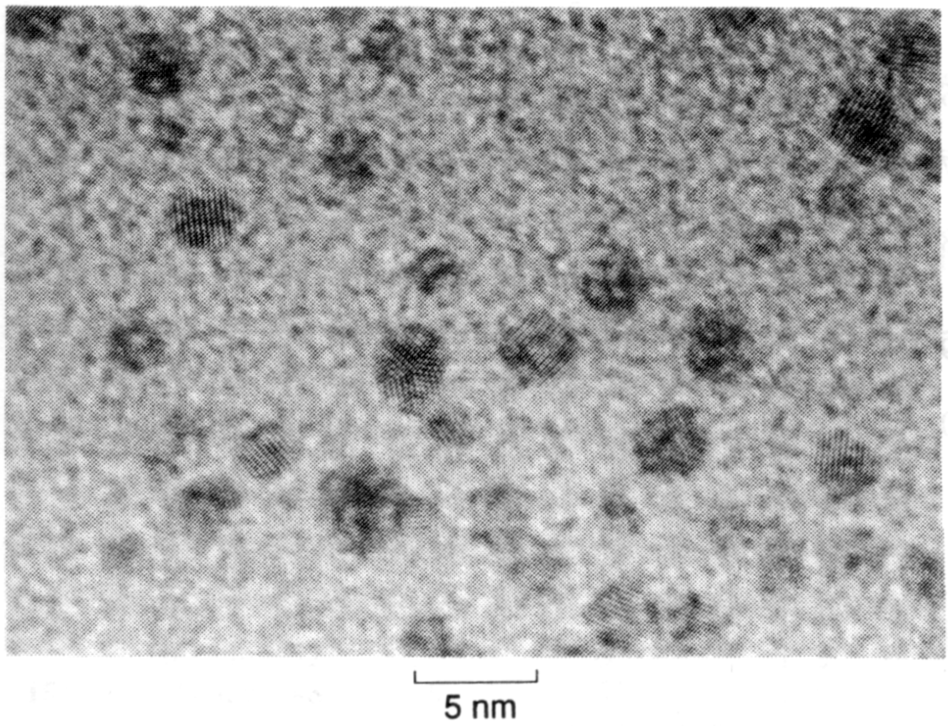
Example: Gold Nanoparticles

Gold nanoparticles are composed of small **crystalline Au clusters** with dimensions usually around 2 nm in diameter.



example for material with **high *A*/*V* ratio**, **quantum** structures (size effects)

surface coating with molecular layer to prevent **aggregation** (alkylthiols or PPh_3)

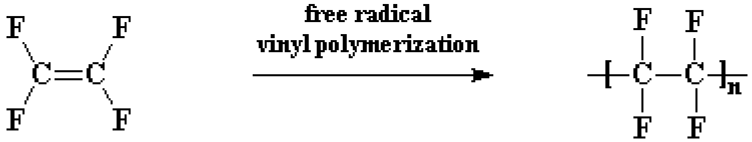


synthesis (two phase system H_2O / toluene):

$HAuCl_4$	gold (III) salt
+ $NaBH_4$	reducing agent
+ $(C_8H_{17})_4NBr$	phase transfer reagent
+ $C_nH_{2n+1}SH$	capping reagent
	(n=12,14,...20)

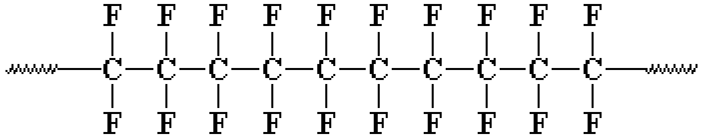
Teflon Frying Pan

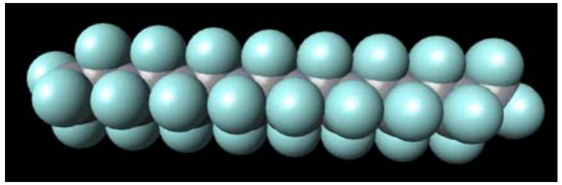
Polytetrafluoroethylene (PTFE, Teflon) is obtained by **free radical polymerization** of tetrafluoroethylene.



tetrafluoroethylene

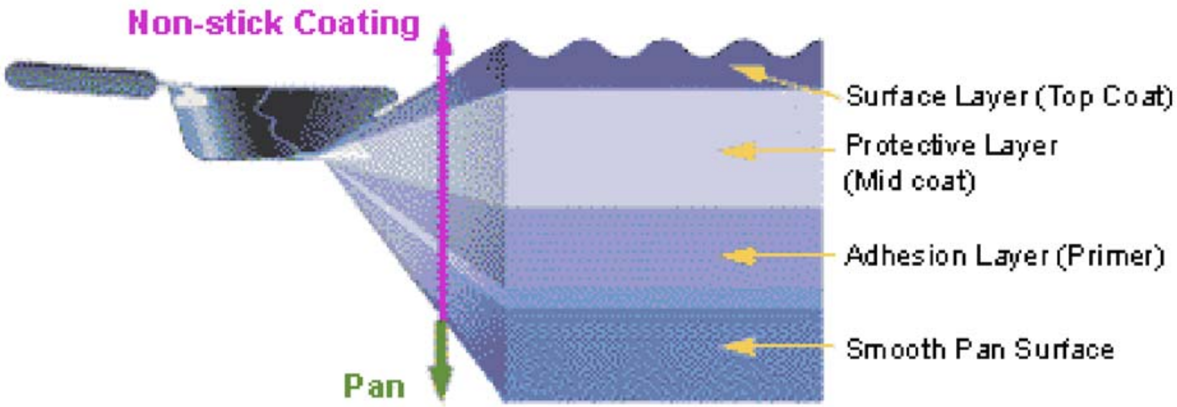
polytetrafluoroethylene





PTFE has very **low surface energy** (non-sticking), is very **apolar**, is highly **chemically resistant**, and shows **low friction.**

"How does Teflon stick to the frying pan when nothing sticks to Teflon???"



The Lotus Leaf Effect

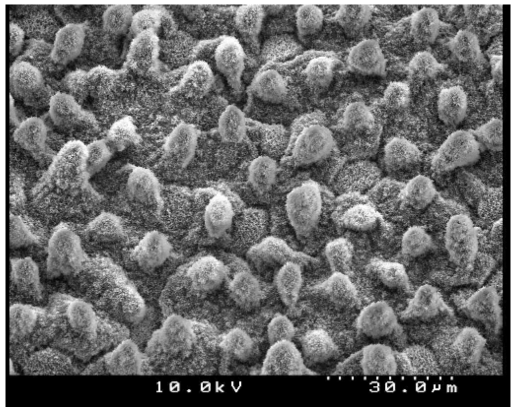
The **surface** of plant **leafs**, especially of the **lotus** flower, can show **extreme hydrophobicity** to water (large water contact angles > 150°C).



Such **hydrophobic surfaces** also show a remarkable **self-cleaning** effect.

explanation:

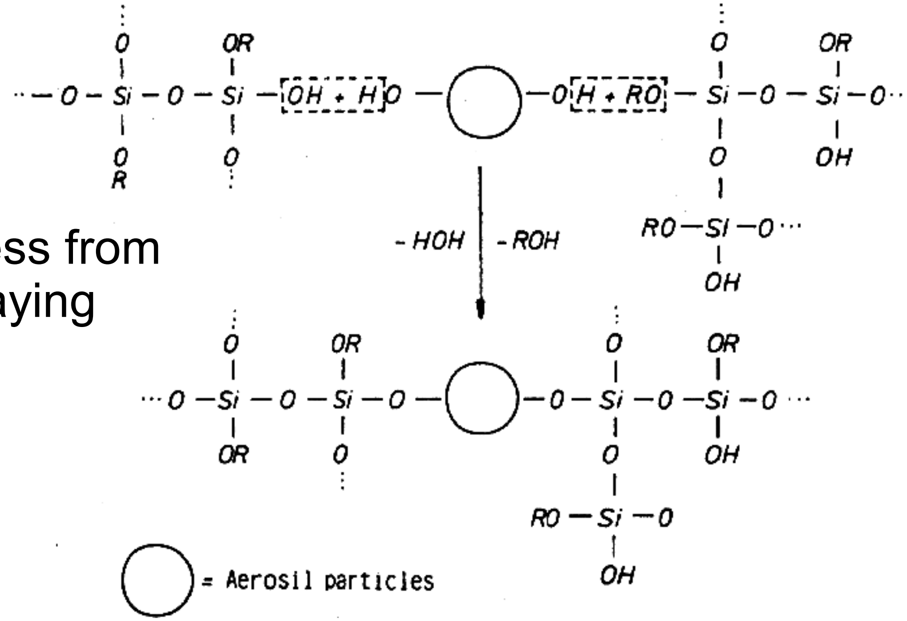
- hydrophobic material
- surface structure (20-100µm)



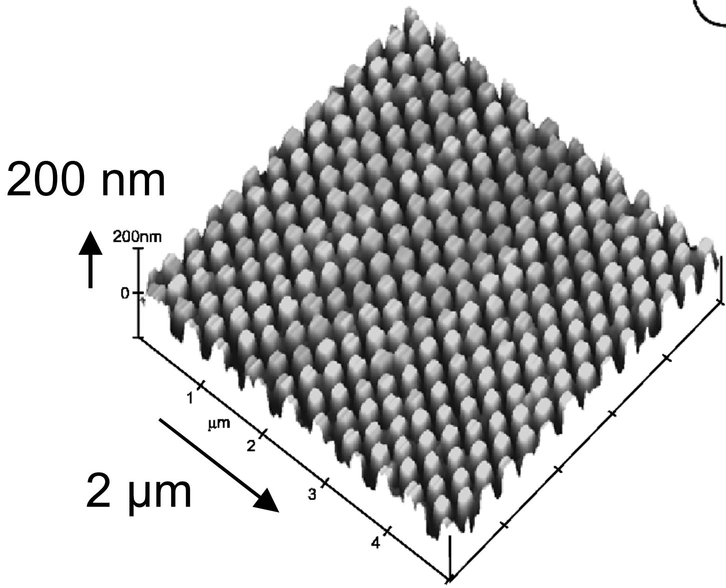
Antireflecting Surfaces

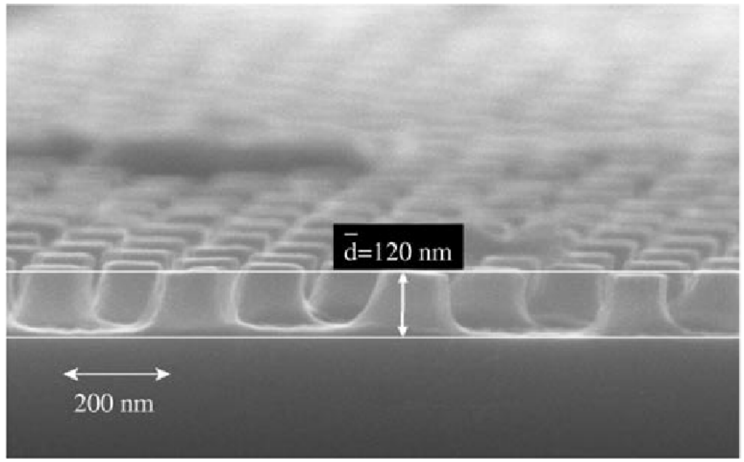
Structured surfaces with **feature** sizes **below** the **wavelength** of visible light (ca. < 200 nm) show **antireflecting** behavior.

surface roughness from sol-gel cold-spraying process

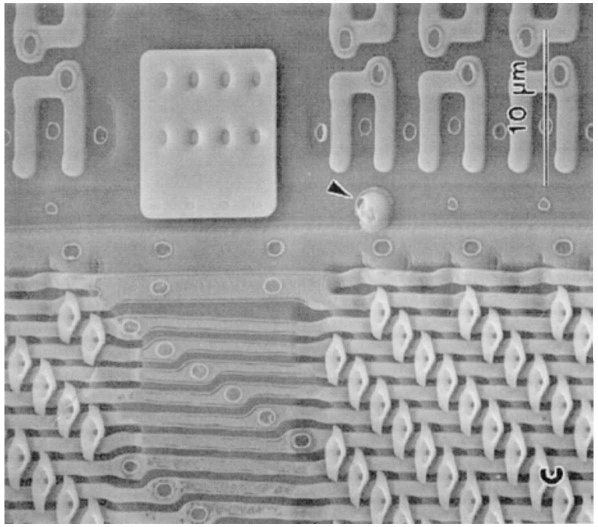


surface roughness by lithographic patterning and etching





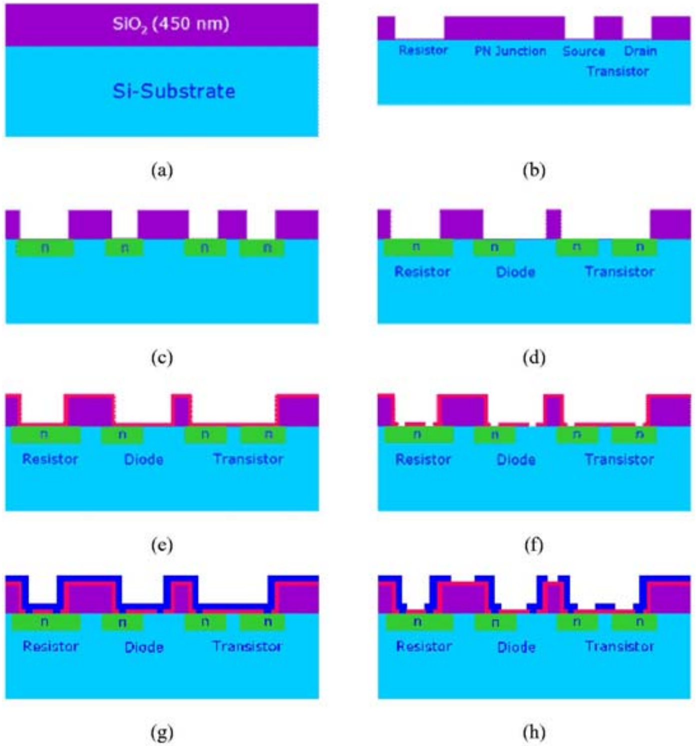
Semiconductor Chips

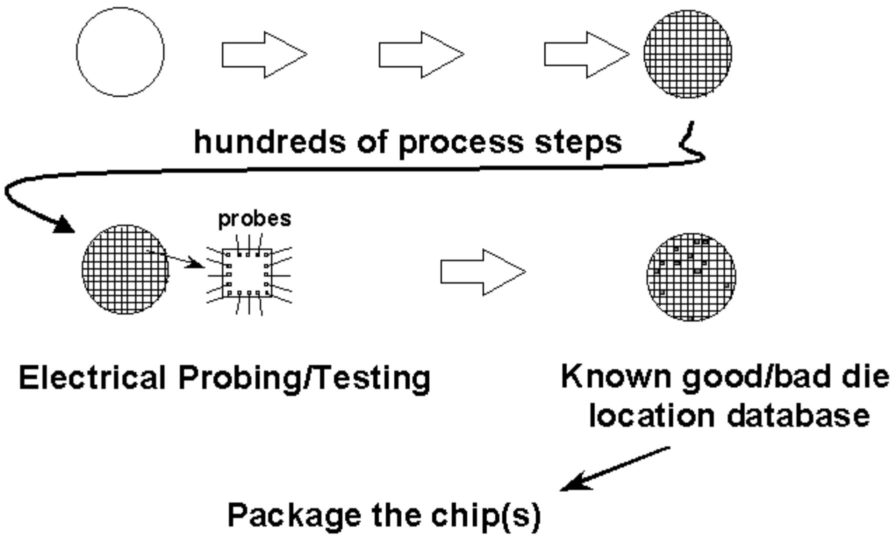


Many **different** processes:

- photolithography / masking
- etching
- material deposition
- chemical surface reaction
- atom implanting

...

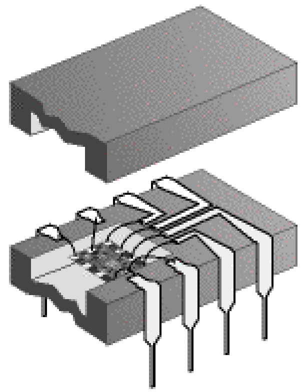




Multistep processes:

e.g. photolithography

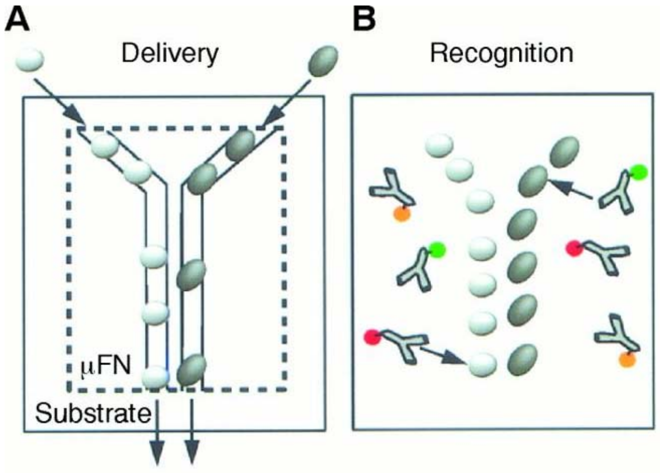
1) spin coating
2) exposure to light (mask)
3) developer step
4) etching
5) remover step



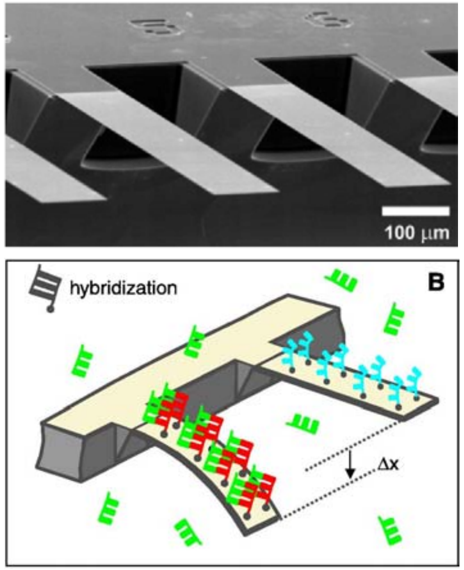
Biochips

- **immobilized biomolecules** for **sensors** and **diagnostics**:

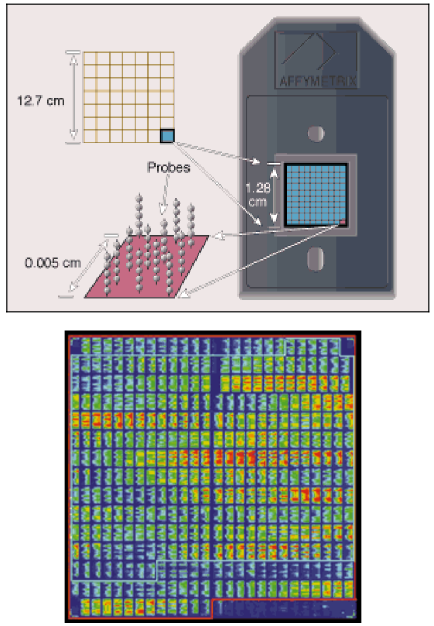
immunoassay in microfluidics:



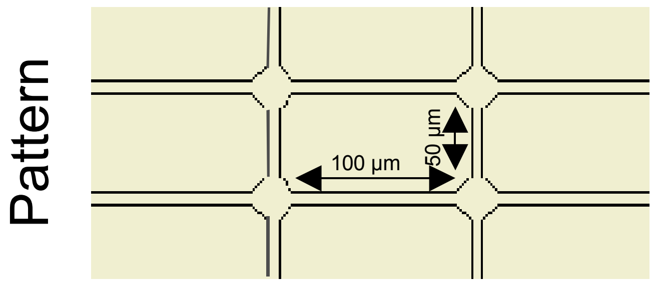
the "chemical nose":



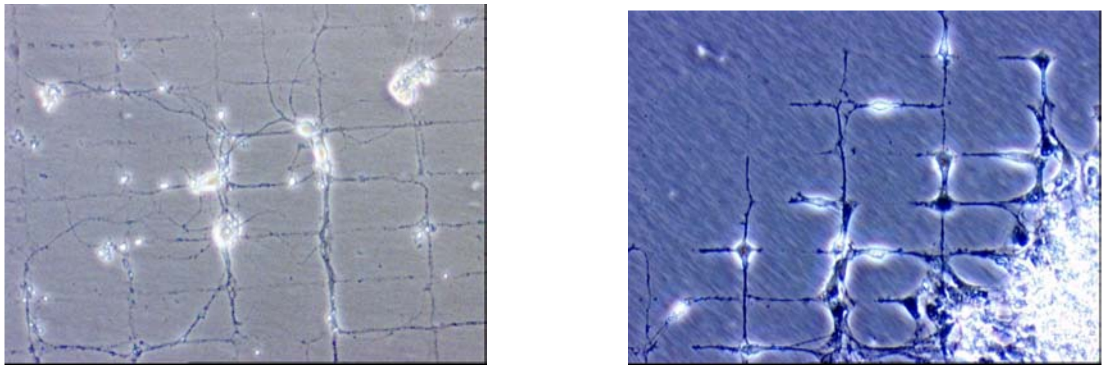
DNA chips:



- **specific surface modification** for site-selective adsorption / growth of **cells**:



line width 6 μm, node diameter 14 μm
ECM-gel printed on polystyrene



courtesy of Angela Vogt, MPIP 2002

Important Key Features of Surfaces

- **surface material (chemical composition)**:

-> determines chemical behavior (reactive / inert)
-> physical materials behavior (conducting / insulating)
-> polarity (hydrophilic / hydrophobic)
-> surface structure on a molecular scale
...

- **topography ("valleys and hills")**:

-> determines chemical "reactivity" / kinetics (fast / slow reaction, reactive sites)
-> physical surface behavior (reflectivity, effective wetability)
-> tribological behavior (friction on "rough" or "smooth" surface)
-> surface morphology on a microscopic to macroscopic scale
...

Application Examples of Surface Science

- understanding and design of catalysts (industrial production of NH_3 e.g., car exhaust)
- understanding and inhibition of corrosion (ships, cars, buildings)
- modification of surface properties like:
  - friction (tires, bearings)
  - wear (polymer lenses of glasses → ormocers)
  - stickiness (frying pan, adhesive tape)
  - wetting, condensation (scuba diving goggles, outdoor gear, inkjet printing)
  - anti-reflection (picture frames, displays)
  - color (paint)
- chip manufacturing / microelectronics
- hard disks (anti-friction, ultra-smooth,...)
- biological surfaces (biocompatibility, patterned cell growth)
- sensors (chemical, biological)
- microfluidics ...