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WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS IN NANOSCIENCE AND NANOTECHNOLOGY

(7 - 18 February 2005)

"Fabrication and Properties of Metal Nanoparticles"-I

presented by:

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Preparation and Characterisation of Metal Nanoparticles

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„There's Plenty of Room at the Bottom“

An Invitation to Enter a New Field of Physics

http://www.zyvex.com/nanotech/feynman.html

“Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?”

by Richard P. Feynman (1959)

Richard P. Feynman

1918 – 1988

There's Plenty of Room at the Bottom

- Miniaturisation of circuits, computers, storage media, etc. down to an atomar/molecular level
- Biological systems as an example how to store information and function
- Writing the entire information of all books in the world in a cube of material of the size of a piece of dust
- Imaging and manipulation of single atoms and molecules

Nanostructure Science

1 Nanometer = 1 nm = 0,000000001 m

How many atoms are inside one Nanoparticle?

Example: Sodium

20 Atoms: Ø = 1,1 nm
500 Atoms: Ø = 3,3 nm
10^7 Atoms: Ø = 100 nm

number of atoms per cluster	number of atoms on the surface of the cluster
20	> 90 %
100	86 %
500	50 %
1000	40 %
10 000	20 %

Why nanostructures ?

- ultimate miniaturisation
- new properties of materials, phenomena and processes
- single elements and nano-systems:
  building blocks of natural and artificial matters
- efficient fabrication: little energy, little waste

Why Nanoparticles

- basic scientific interest
- ☞ transition from
  atoms → molecules → solid state,
  "quantum size" effect

How do parameters like

- ionization potential
- vibrational spectra
- geometric arrangement
- melting temperature
- magnetic properties
- electronic spectra
- ⋮

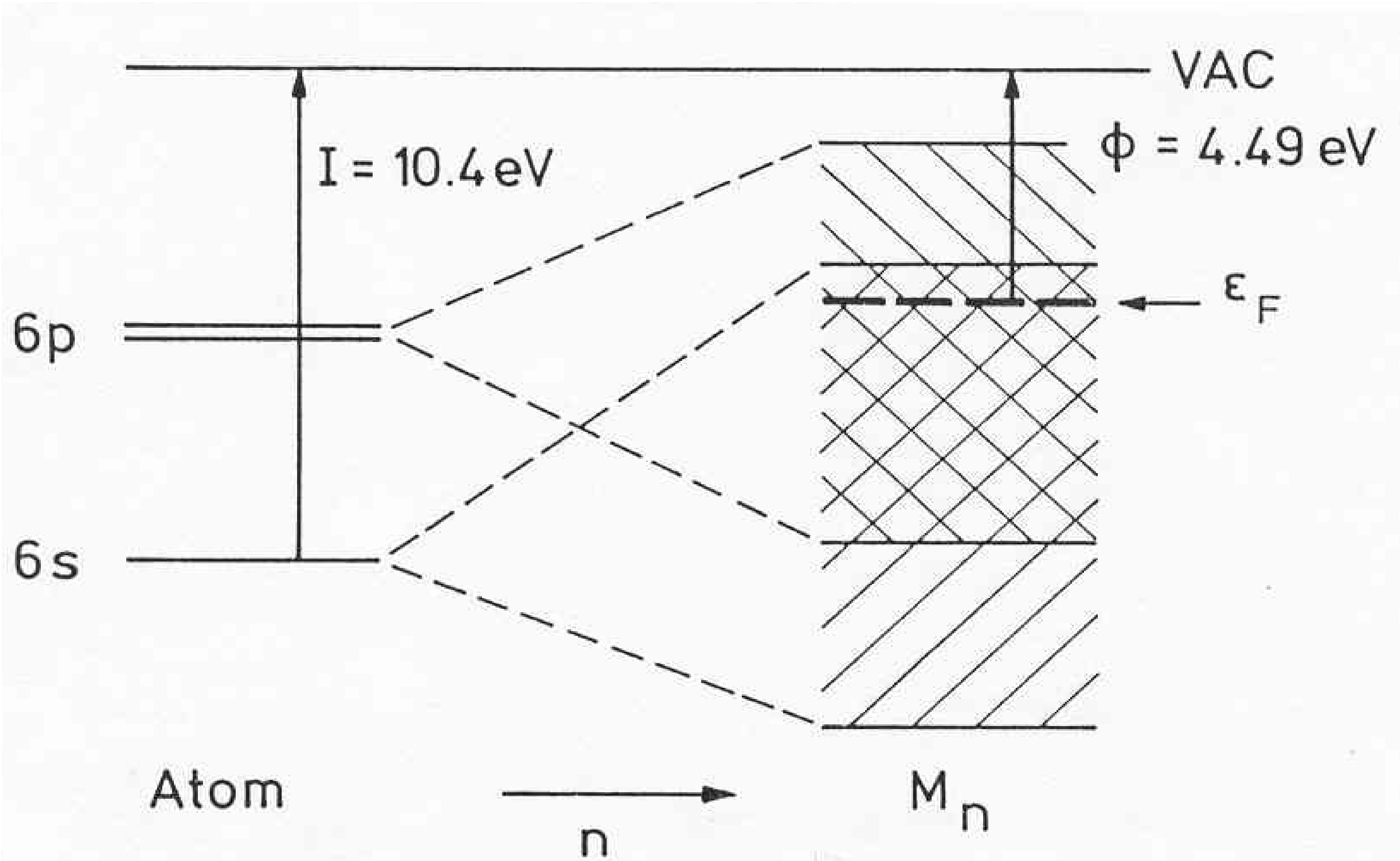
changes as a function of size and shape ?

- Applications of clusters

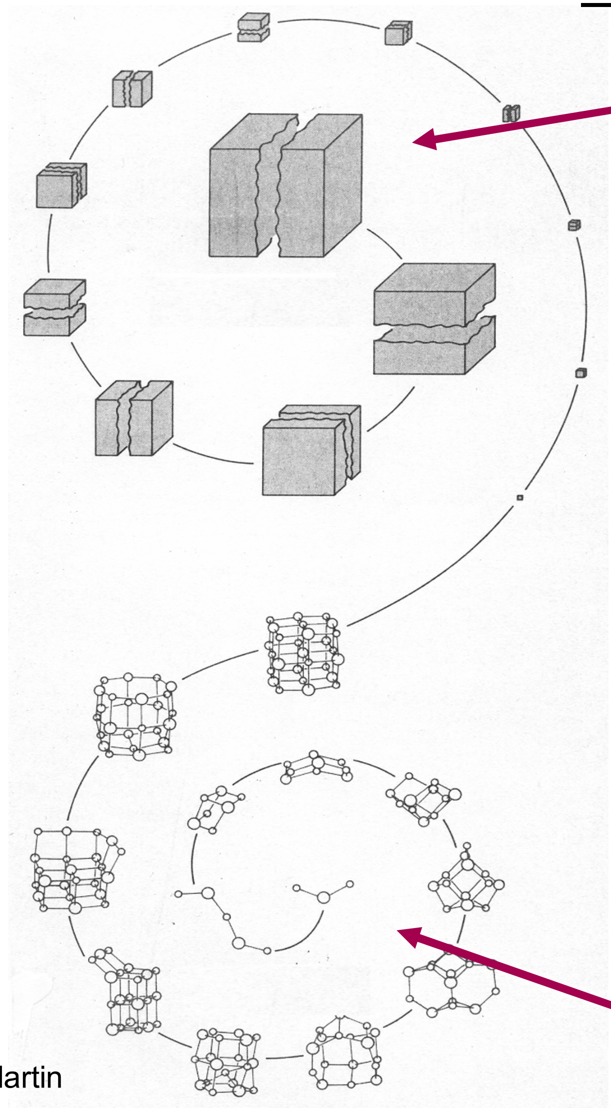
- thin film production
- catalysis
- microelectronics
- photography
- chemistry
- optical filters
- ⋮

☞ close connection between cluster physics and surface science

Ionisation potential and work funktion of mercury



Preparation



Macroscopic Matter

⇓ top-down, lithography, structuring

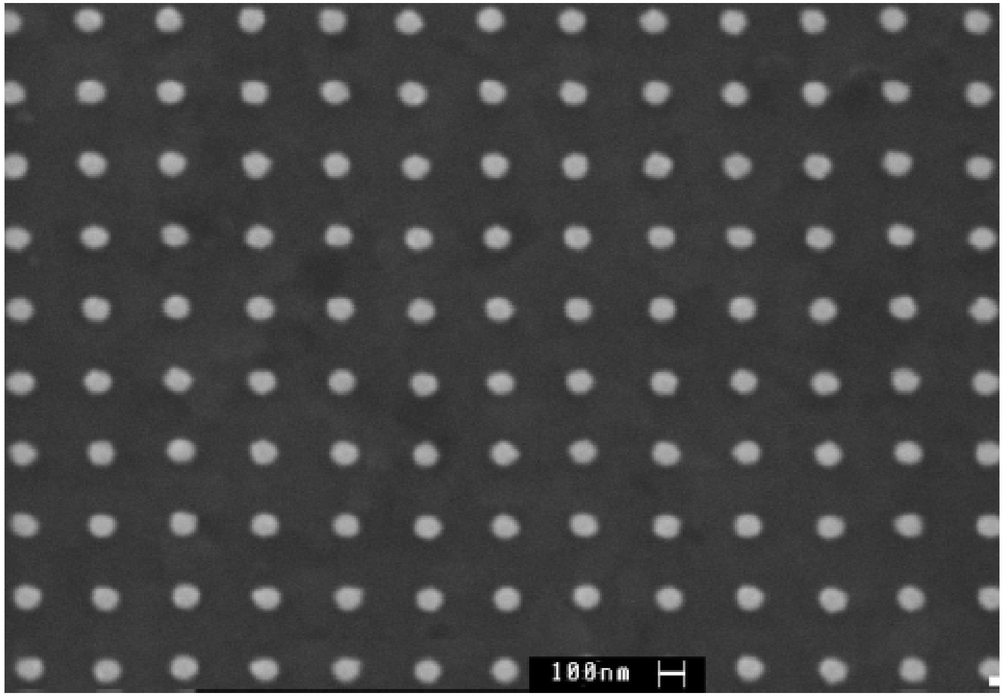
- exciting fundamental research
- tailored materials for applications
- huge technological potential

⇑ bottom-up, self organization, controlled growth

Atoms, Molecules

T.P. Martin

Electron Beam Lithography



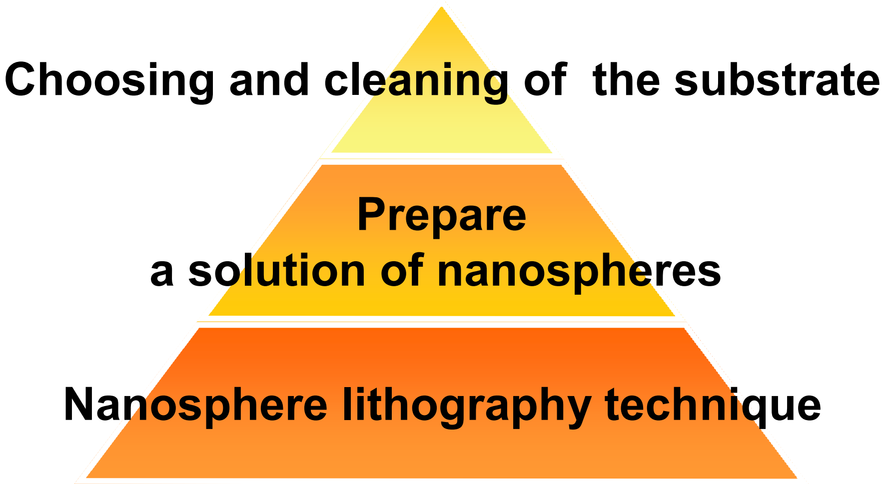
Scanning electronic microscope (SEM) image of a gold particle square grating produced by electron beam lithography. The diameter of the particles parallel to the substrate is 110 nm and the particle height is 60 nm.

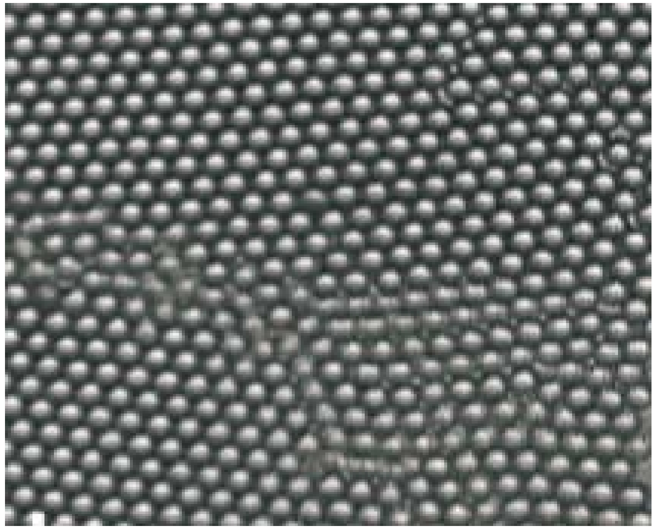
limited to structures with

R > 20 nm

N. Felidj, J. Aubard, G. Levi, J.R. Krenn, M. Salerno,G. Schider, B. Lamprecht, A. Leitner, F.R. Aussenegg, Phys.Rev.B. 65, 075419 (2002).

Nanosphere Lithography





V. Ng, Y. V. Lee, B. T. Chen and A. O. Adeyeye, Nanotechnology **13,** 554-558, 2002.

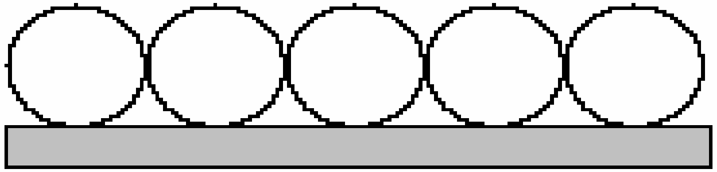
Substrate Preparation

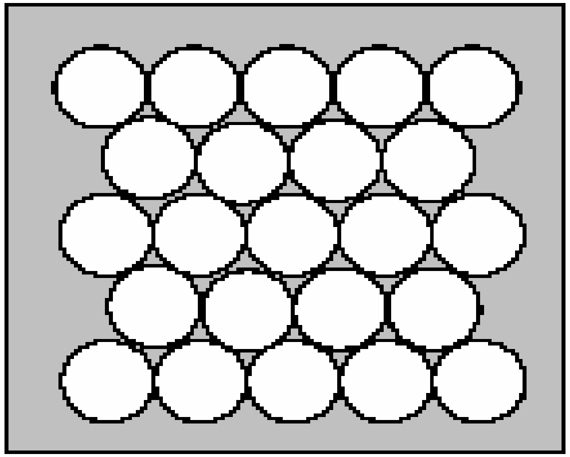
- The mean surface corrugation should be much smaller than the particle diameter.
  - ❖glass plates;
  - ❖polished silicon wafers;

- Cleaning the substrate:
  - ❖piranha solution (3:7 H_2O_2:H_2SO_4);
  - ❖alkaline solution (NaOH, KOH) 20 minutes, after that 5 minutes in 1 M hydrochloric acid, finally 20 minutes in pure water;
  - ❖combine piranha solution with alkaline solution

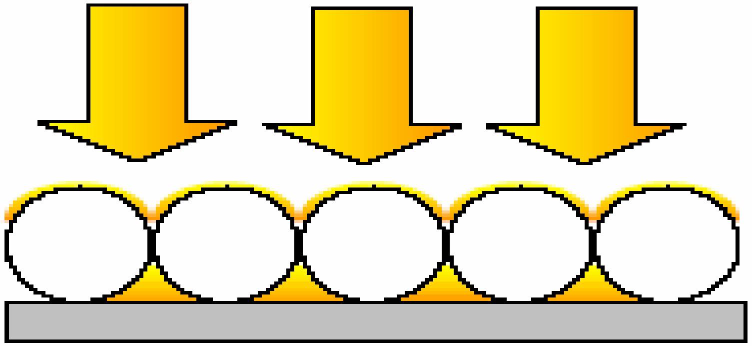
NSL procedure

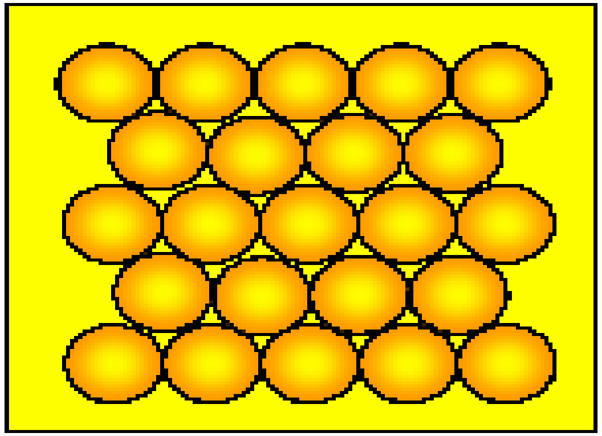
Step 1: Nanosphere Apllication



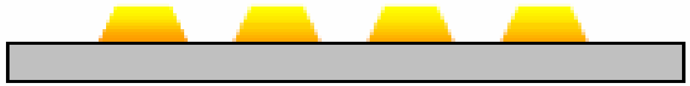


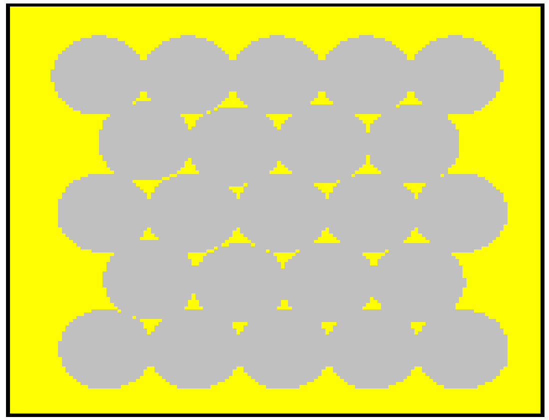
Step 2: Gold Deposition



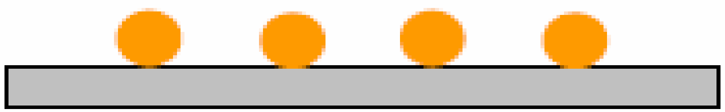


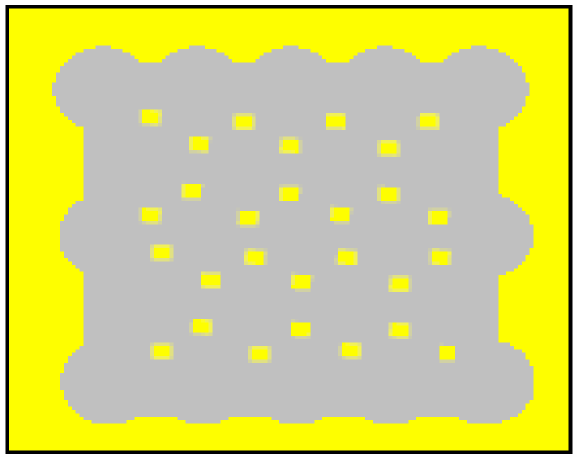
Step 3: Nanosphere Removal



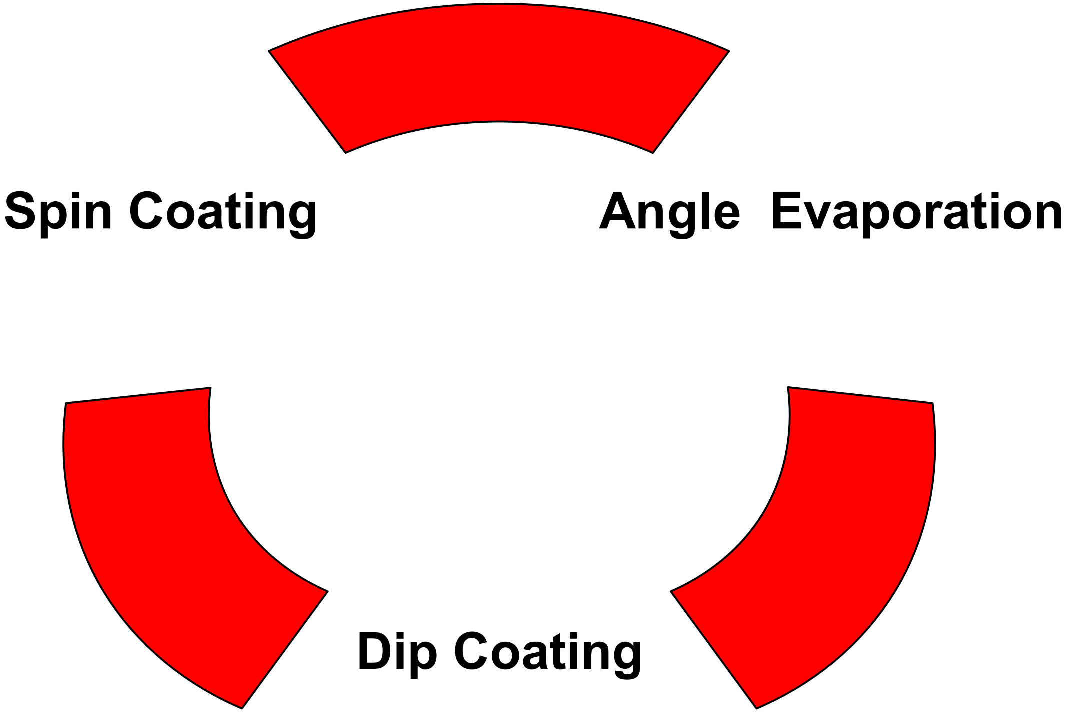


Step 4: Annealing





Preparation Methods



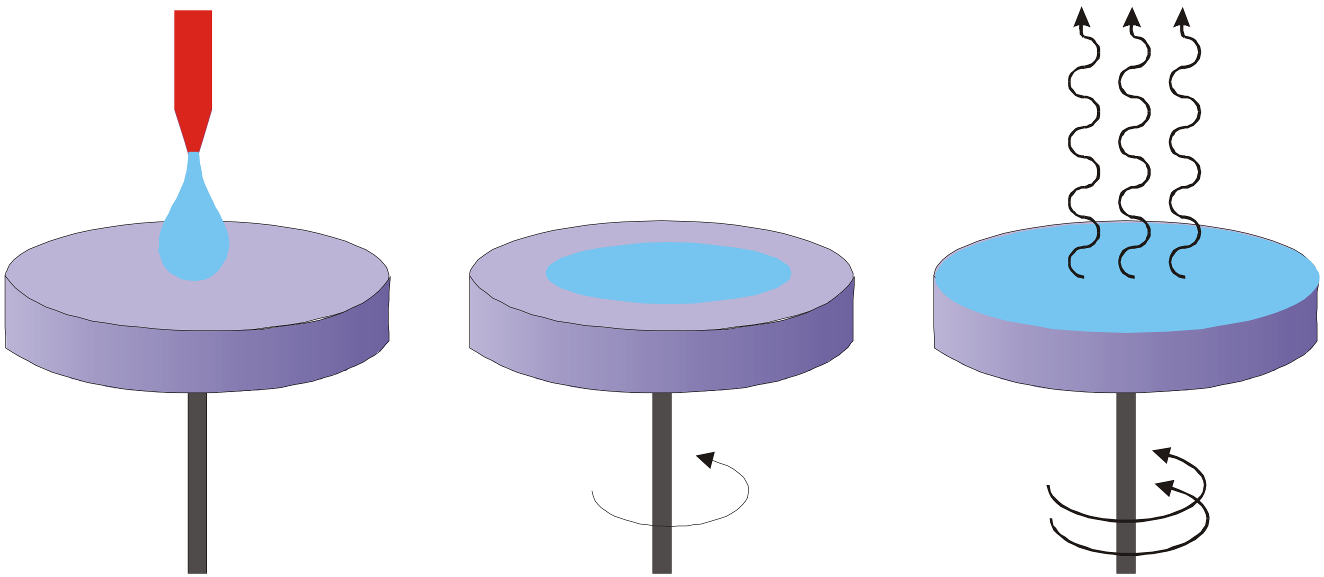
Spin Coating

- The thickness of the monolayer can be calculated by:

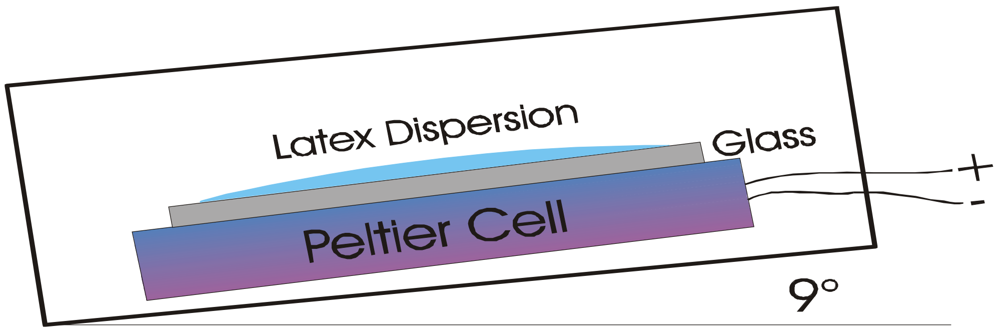
$$h = \sim \left(\frac{3\eta \cdot m}{2\rho_{A_0} \cdot \omega^2} \right)^{1/3}$$

- Spin speed: 100-2000 rpm;

h = coating thickness, ω = angular speed
ρ_{A0} = initial value of the density of the solution
η = viscosity, m = evaporation rate of the solvent



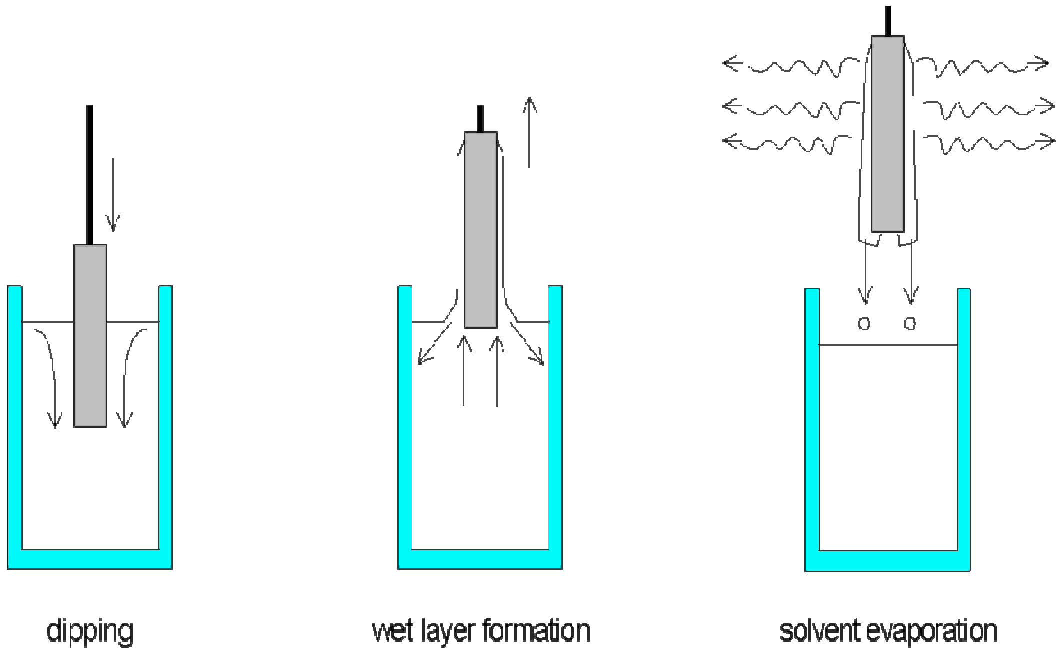
Angle evaporation



- Investigate the monolayer formation by varying the angle of the tilt plane from 5° to 15°.
- Use of a Peltier cell for a good thermal stability.
- To control the evaporation rate, means to control the temperature.

Dip coating method

- Controlled dipping and pulling of the substrate with a constant velocity smaller than 1mm/s;
- The coating thickness can be calculated by the Landau-Levich equation:



$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}}$$

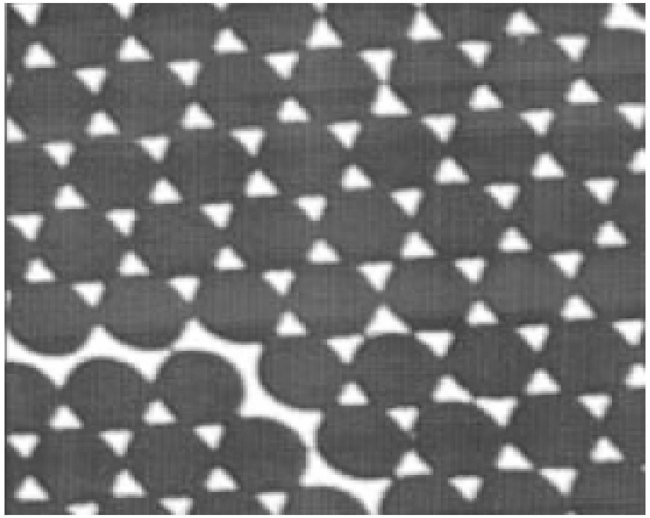
h = coating thickness, ν = velocity
γ = Surface tension, ρ = density
η = viscosity, g = gravity constant

L.D. Landau, B.G. Levich, Acta Physiochim **17**, 42-54 , 1942.

Nanosphere removal

- Dissolved in Tetrahydrofuran (THF)
- Soaking in dichlormethane for one minute
- Ultrasonic bath in pure water for five minutes
- Adhesive tape

Also limited to sizes larger than R_{eq} = 20 nm



F. Burmeister, W. Badowsky, T. Braun, S. Wieprich, Applied Surface Science **144**, 461-466, 1999.

Examples of bottom-up techniques for the preparation of metal nanostructures

- Deposition of atoms and molecules
  - Pulsed laser deposition
  - Electron beam evaporation
  - Chemical vapour deposition
- Adiabatic expansion
- Wet-chemically

Chemical reduction

- 1857: Faraday's colloidal solutions of gold (The Royal Institution's Faraday Museum, London)
- Reduction of hydrogen tetrachloraureate $HAuCl_4$ by sodium citrate
- Negative citrate ions adsorb on the nanoparticles surface and prevent aggregation

$$H(AuCl_4)\ .\ 3H_2O\ +\ C_6H_8O_7$$

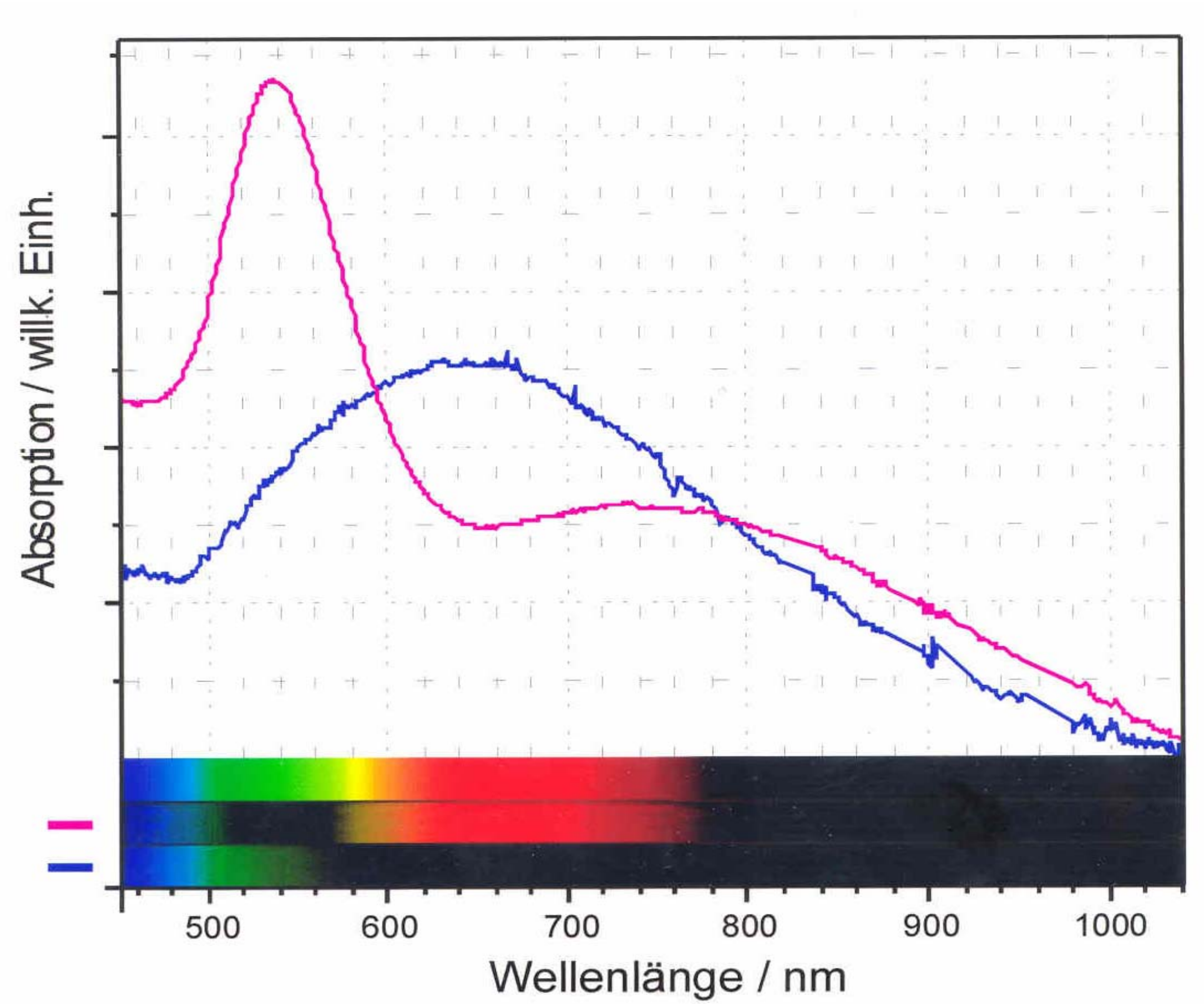
$$\downarrow$$

Au-NP, size: 30 nm – 40 nm

J. Turkevich, P.C. Stevenson, J. Hiller: *Discuss. Faraday Soc.* **11**, 55 (1951).

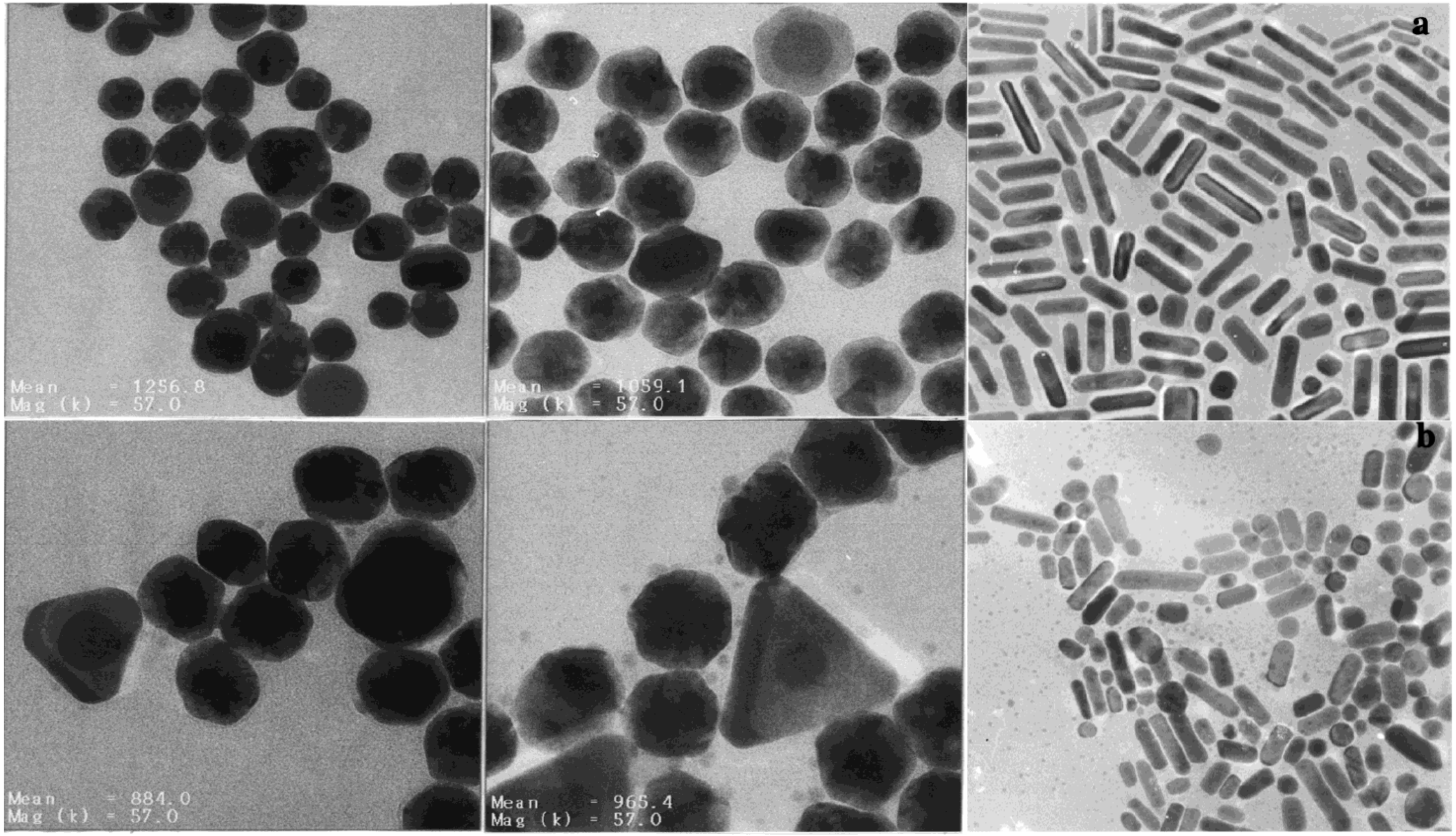
Frens, G.: *Nat. Phys. Sci.* **241**, 20 (1973).

Different Methods – Different Properties



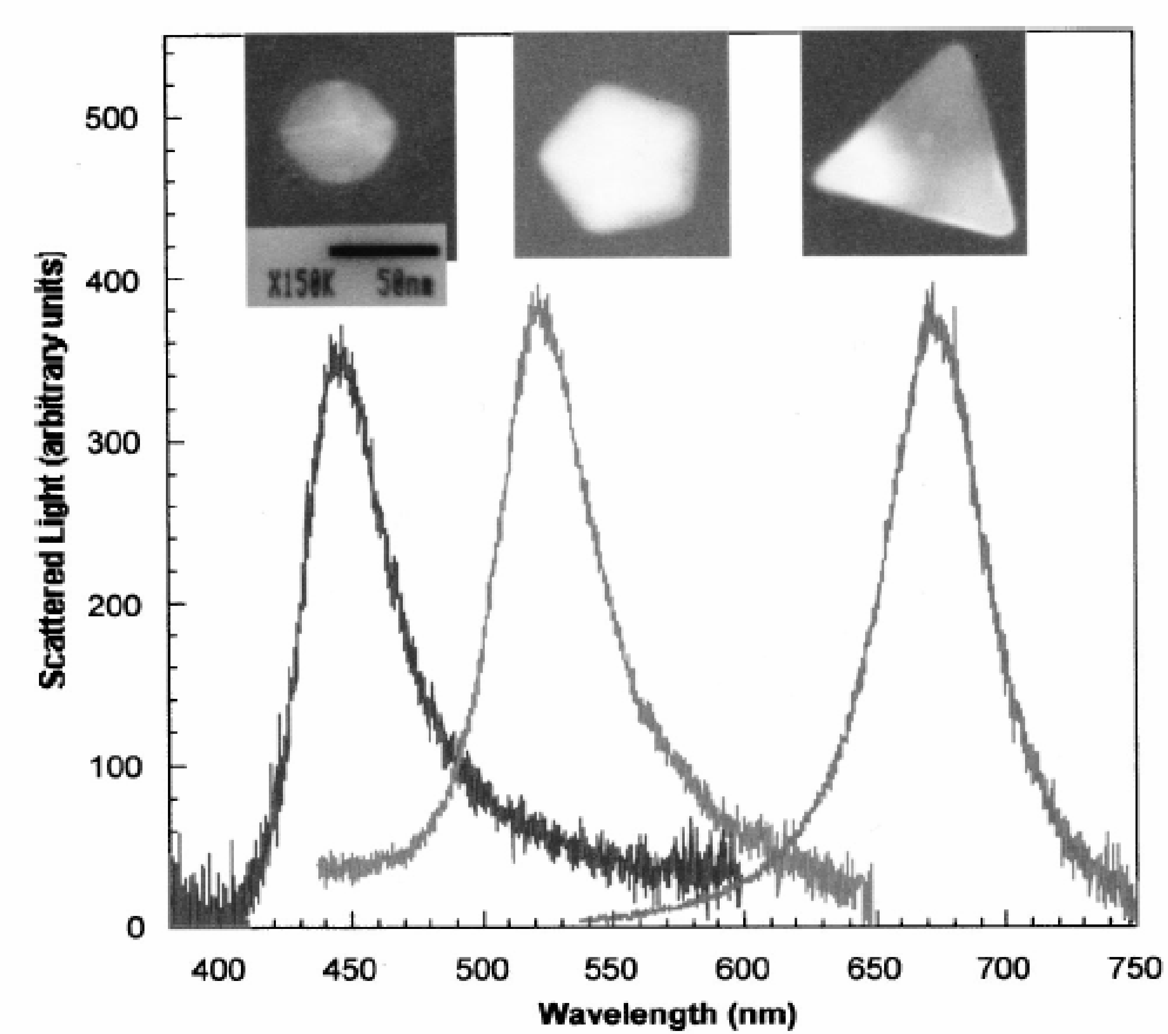
- purple solution: tetrachloraureate and sodium citrate at 90ºC
- blue solution: tetrachloraureate and hydrazine sulfate solution

Chemically prepared nanoparticles



Hodac et al. *J. Phys. Chem. B* **2000,** *104*, 11708-11718
Link et al. *J. Phys. Chem. B* **2000,** *104,* 6152-6163

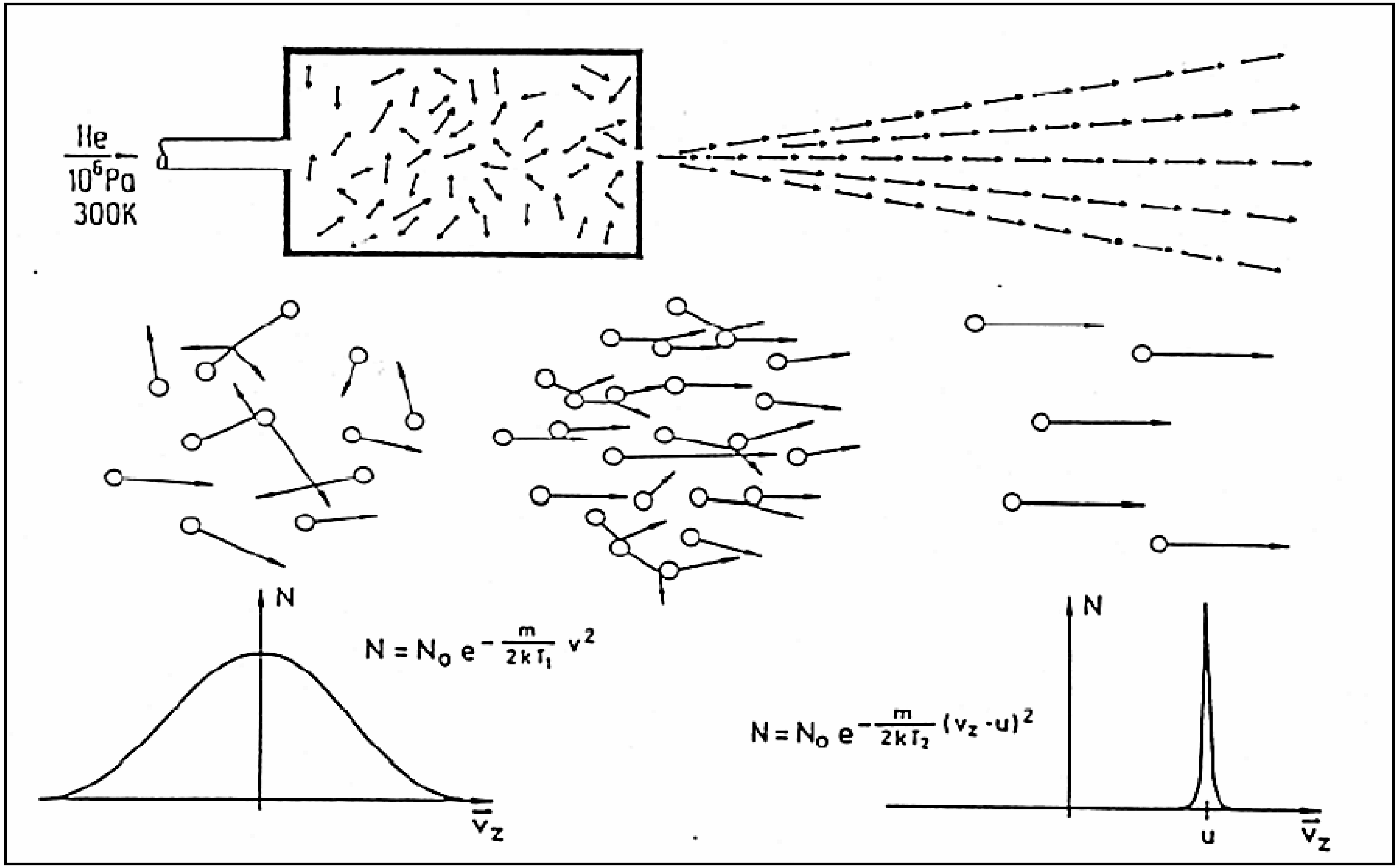
Optical properties (Ag-NP)



Mock et al. J. CHEM. PHYS. 116, 2002

Colours

Preparation of clusters by means of adiabatic expansion

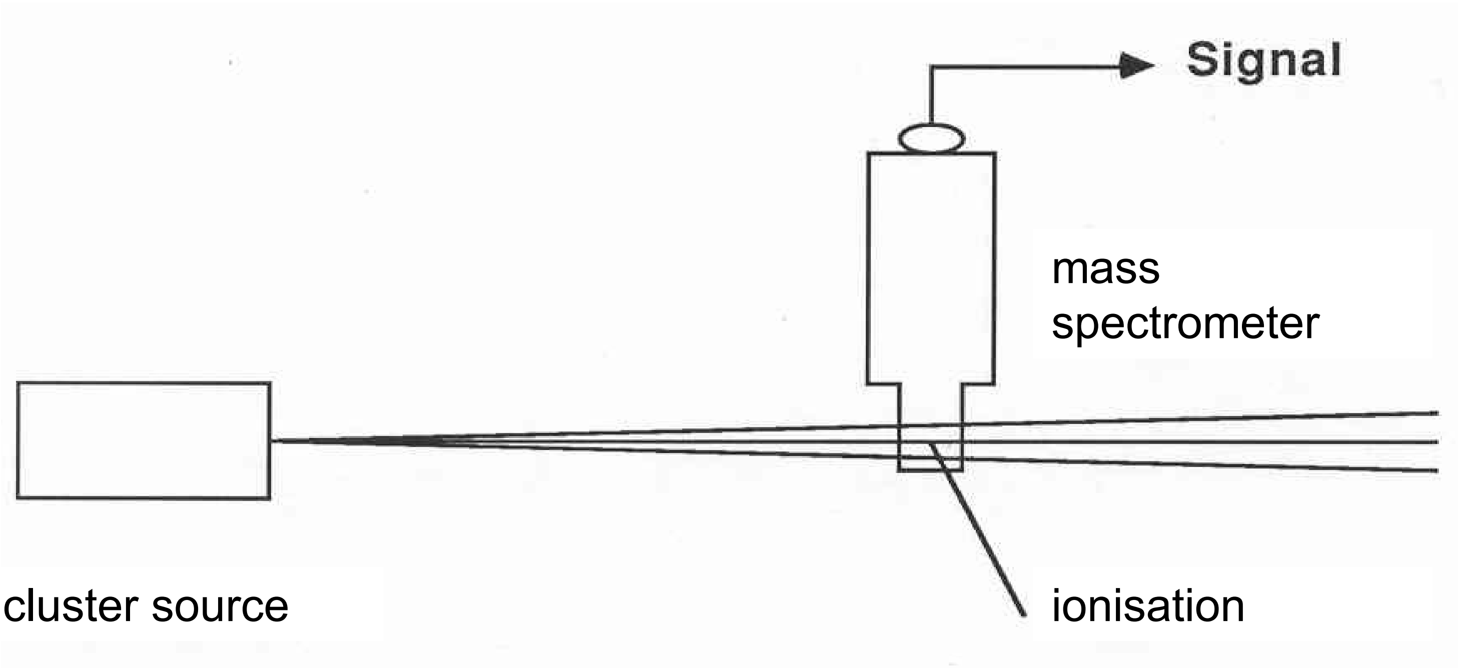


http://e-diss.uni-kiel.de/diss_473/d473.pdf

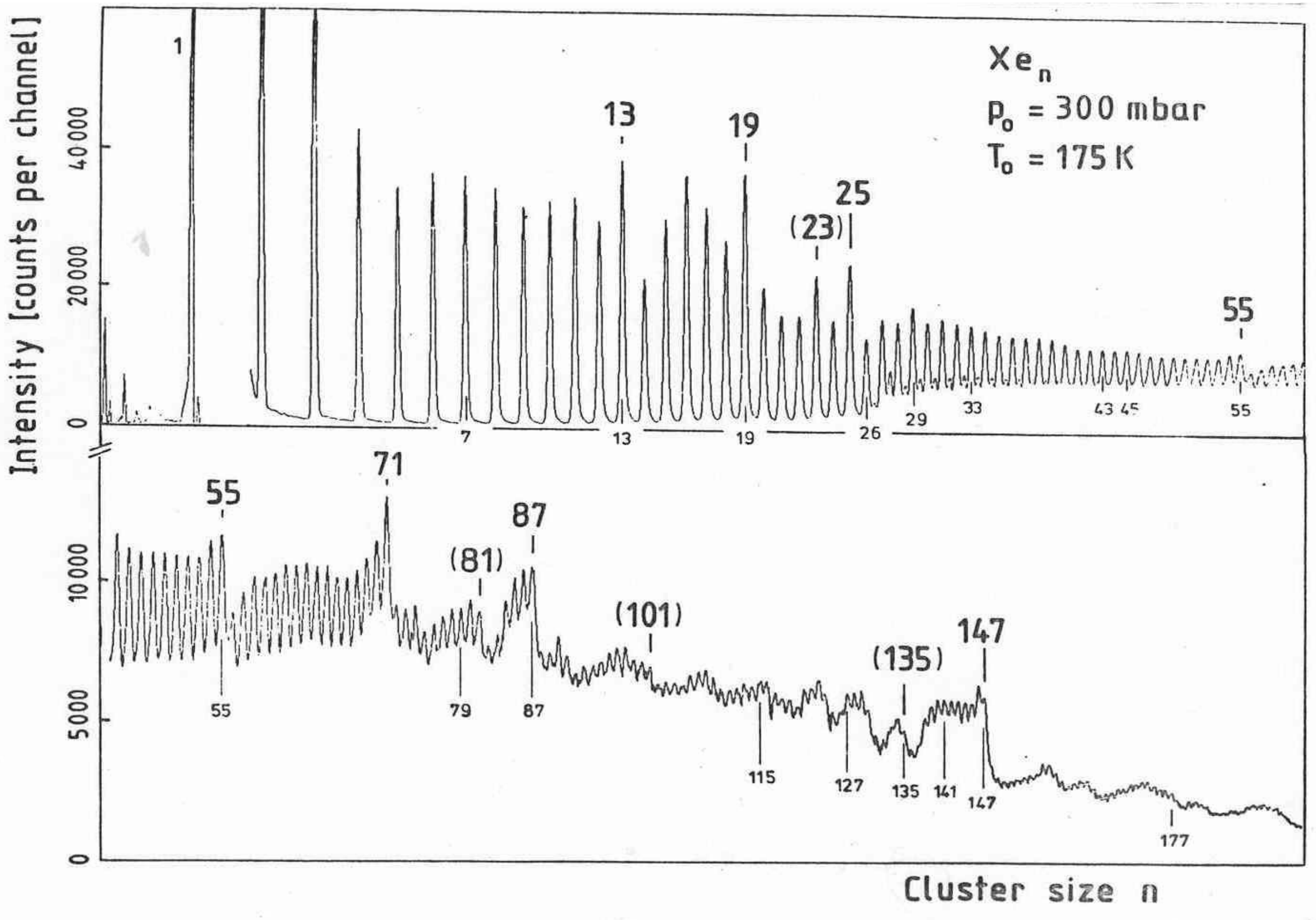
adiabatic expansion

http://www.ebepe.com/html/310_div.html

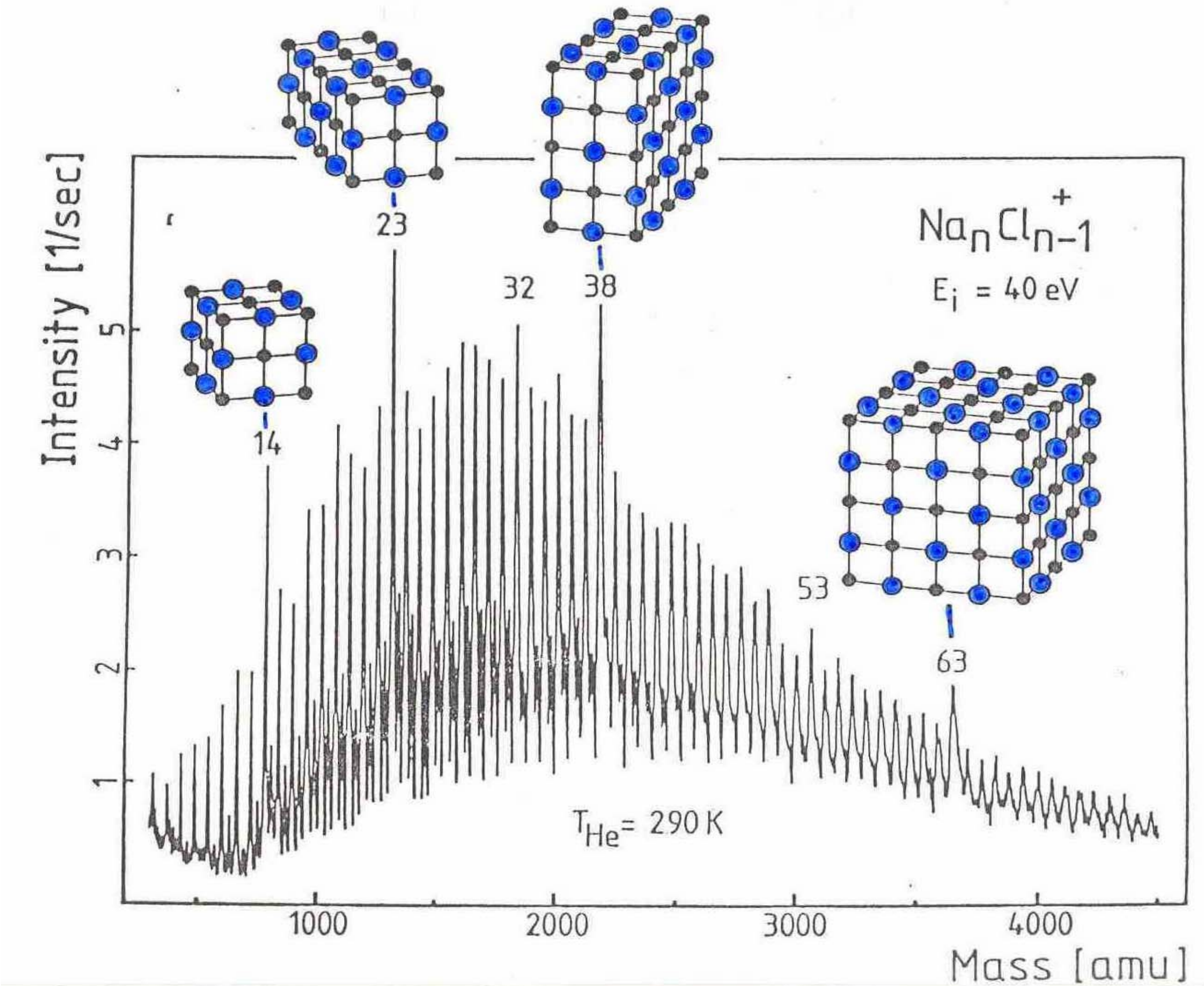
Mass separation



Mass spectrum for Xe

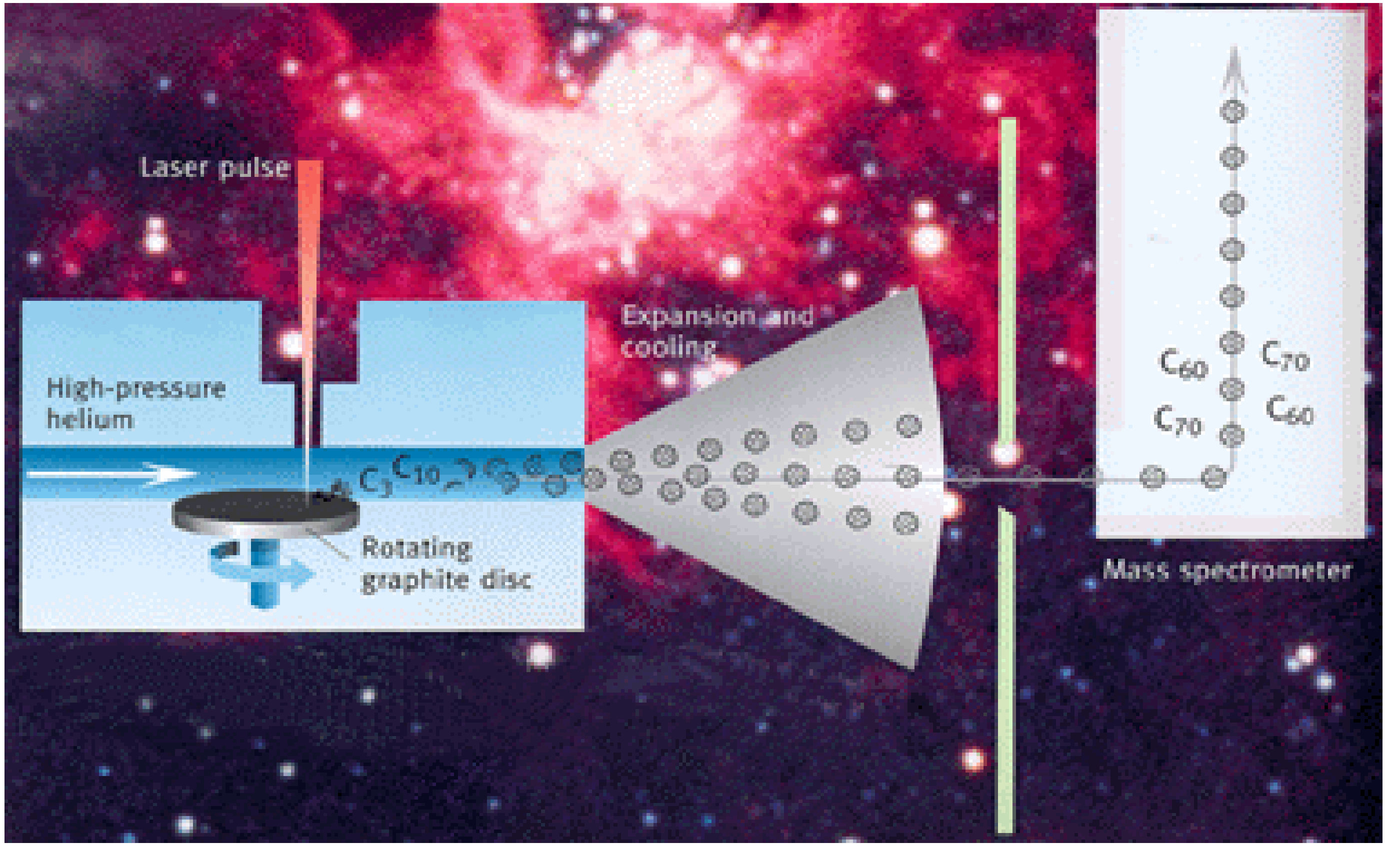


Mass spectrum for NaCl

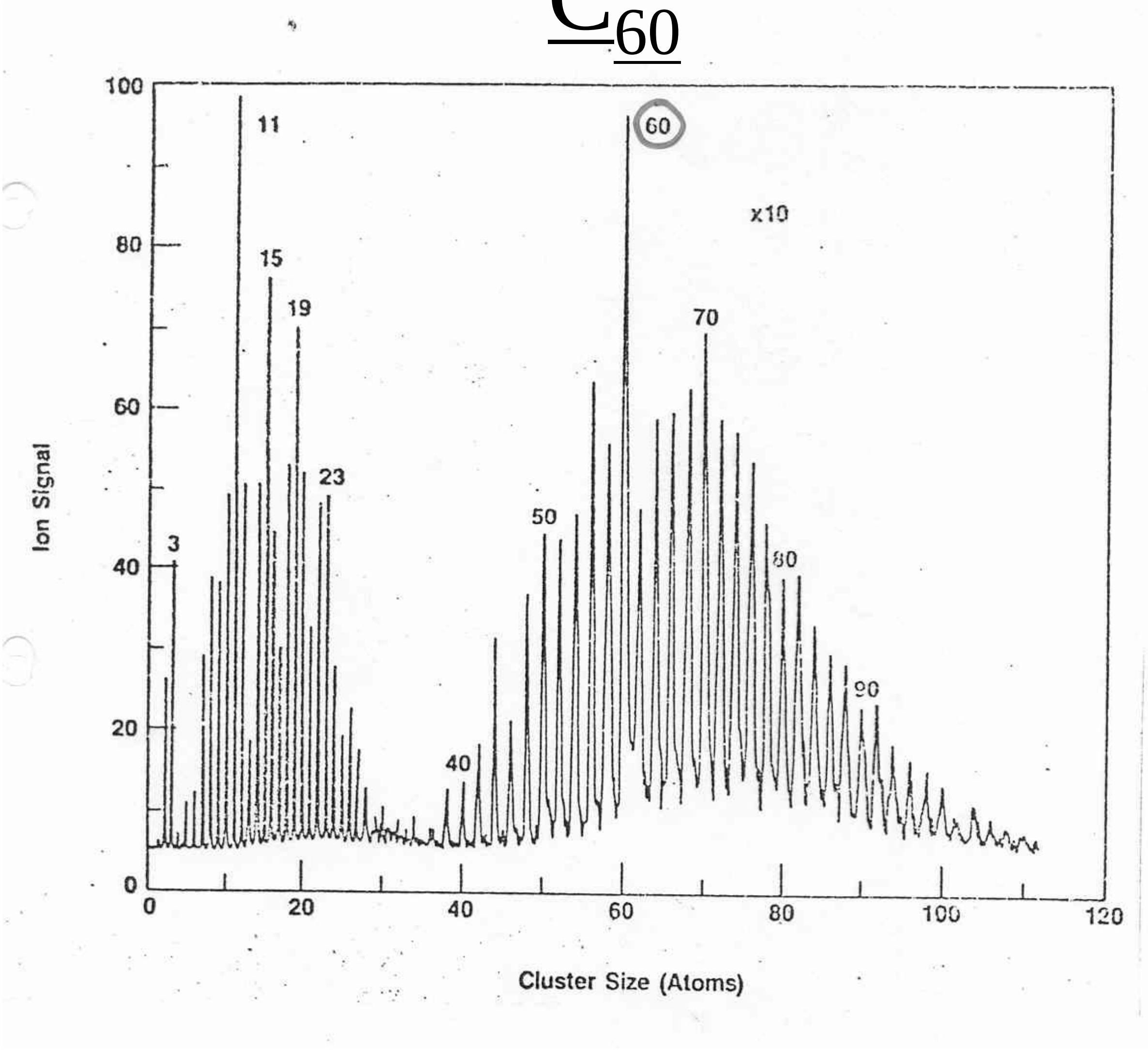


Example: C_{60}

Preparation by means of Laser evaporation

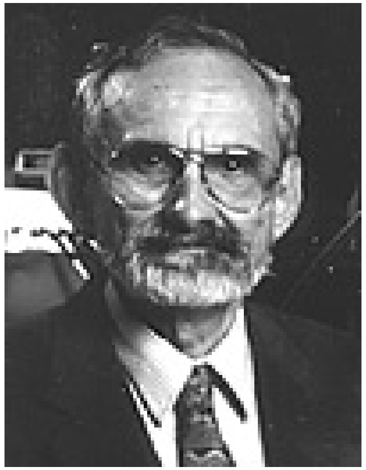


C_{60}

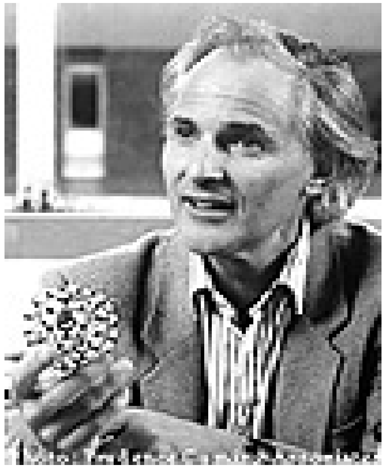

Ion Signal
100
80
60
40
20
0
11
15
19
23
3
60
x10
70
50
80
40
90
0
20
40
60
80
100
120
Cluster Size (Atoms)

The Nobel Prize in Chemistry 1996

„for their discovery of fullerenes“



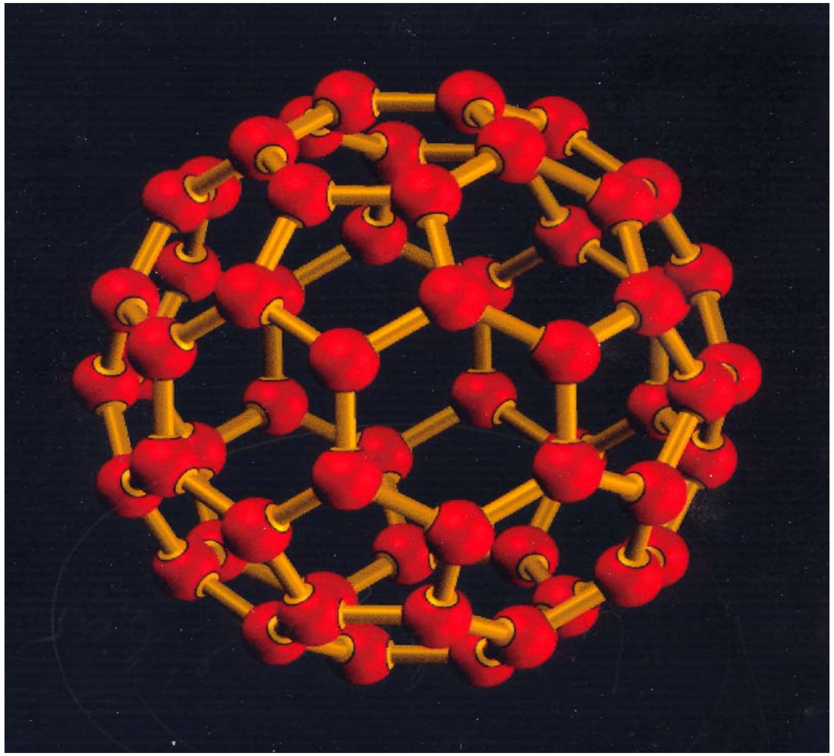
Robert F. Curl Jr.



Sir Harold W. Kroto

Richard E. Smalley

C_{60}



also called buckyball

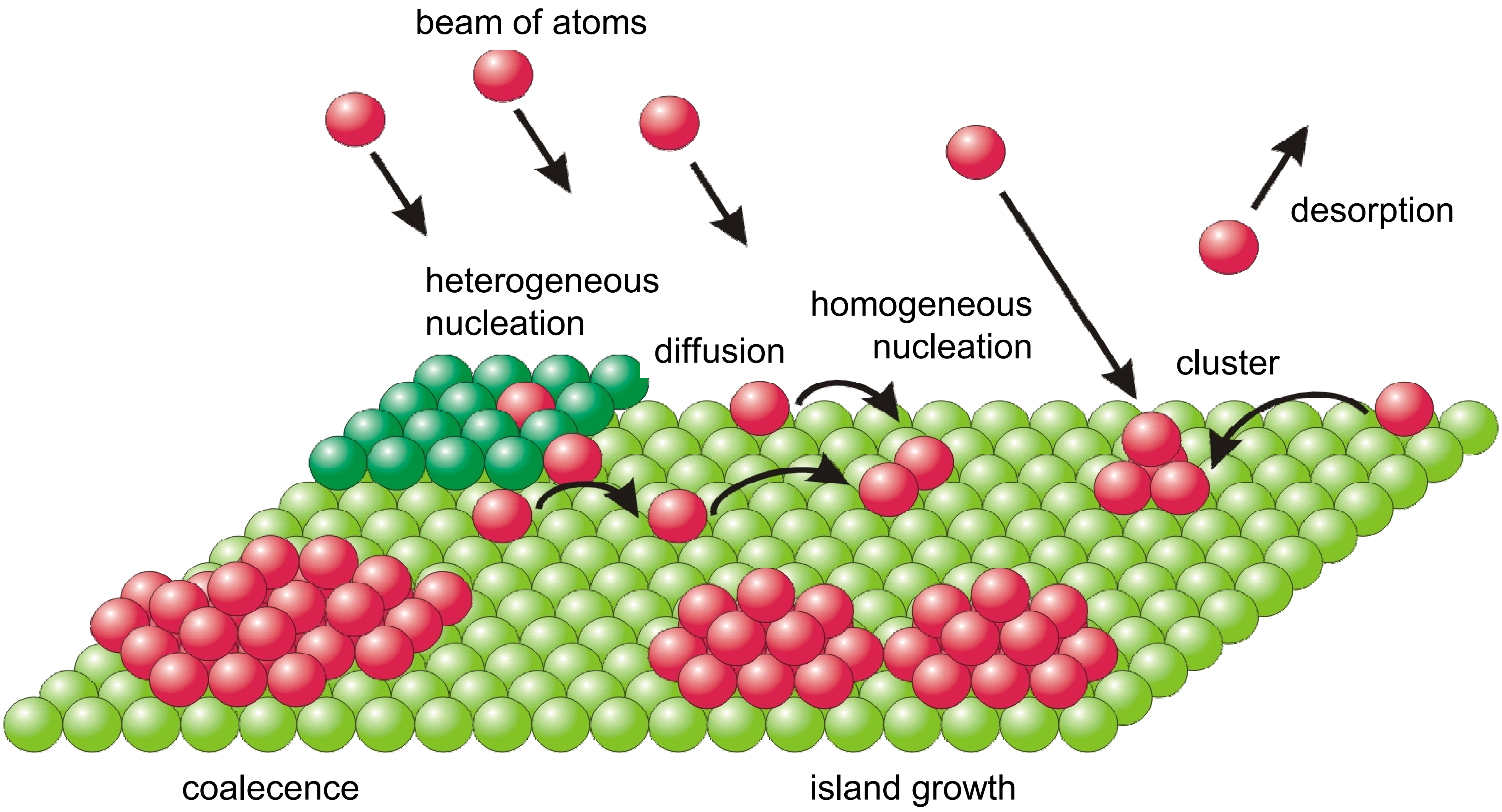
Third allotropic form of carbon

- graphite
- diamond
- fullerene

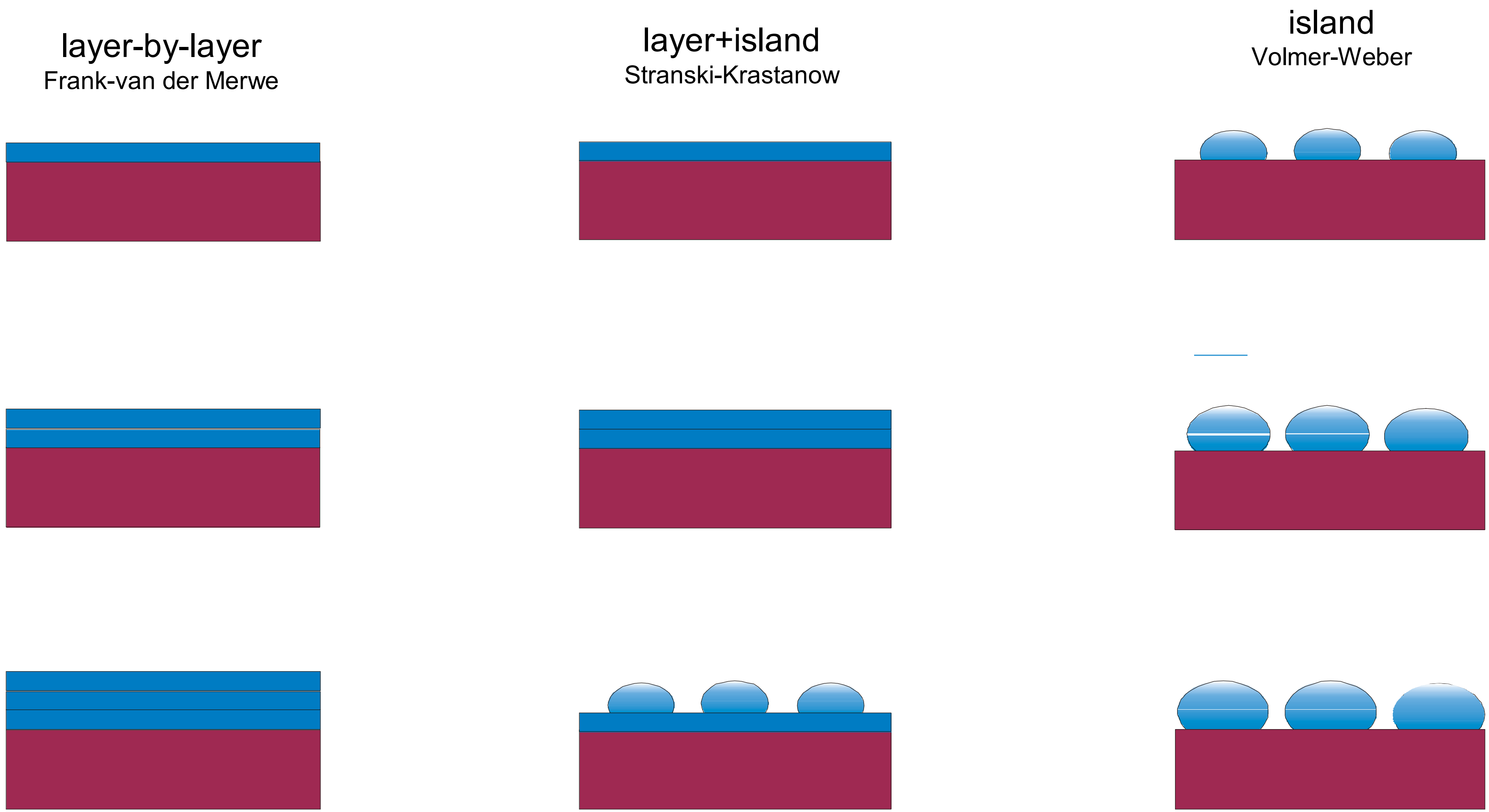
Geodesic Dome

American Pavillion (Biosphère), Expo '67,from
Richard Buckminster Fuller, Ile Sainte-Hélène, Montreal

Deposition of Atoms



Growth modes



Atomic processes responsible for nucleation and growth of thin films on substrate surfaces

Step 1: Adsorption of adatoms

Atoms arrive from the gas phase at rate R or at an equivalent vapor pressure p such that

$$R = \frac{p}{\sqrt{2\pi mkT}}$$

with: m atomic mass
k Bolzmann constant
T absolute temperature of vapor source

This creates adatoms the areal density of which increases initially as n(t) = R * t

The adatoms remain on the surface only for a certain period of time given by the Frenkel equation:

$$\tau = \tau_0 \, e^{\frac{E_a}{kT}}$$

↑ mean residence time

with: $\tau_0 \approx 10^{-12}$ s oscillation period of atoms in surface potential
E_a adsorption energy

Atomic processes responsible for nucleation and growth of thin films on substrate surfaces

Step 1: Examples

1. mean residence time as a function of binding energy with
   T = const. = 100 K

E [eV]	τ
0,1	$2{,}2 * 10^{-8}$ s
0,3	10 s
0,4	64 h
0,5	164 a
2,0	10^{67} s

2. mean residence time as a function of temperature with
   E = const. = 1 eV

T [K]	T
100	10^{39} s
300	$2 * 10^{4}$ s
600	$5 * 10^{-5}$ s

Atomic processes responsible for nucleation and growth of thin films on substrate surfaces

Step 2: Surface diffusion of adatoms

The diffusion constant D is given by:

$$D = \frac{\nu_d a^2}{4} e^{-\frac{E_d}{kT}}$$

with:

with:	ν_d	jump frequency
	E_d	diffusion energy
	$a \approx 0{,}2 - 0{,}5$ nm	jump distance

$$\mathbf{E_d \leq 0{,}4\ E_a}$$

The mean square path S covered by diffusing atoms in time t is given by (Einstein and Smoluchowski):

$$\mathbf{S^2 = D * \tau}$$

During typical residence times τ, S can be very large and the atoms migrate over considerable distances of micrometers or more.

Atomic processes responsible for nucleation and growth of thin films on substrate surfaces

Step 3: Nucleation and cluster growth

During their random walk on the surface the atoms collide with other atoms or surface defects

☺ ☺

✡ homogenous and / or heterogenous nucleation
(high deposition rate) (low deposition rate)

☺

atoms „decorate“ surface defects that act as nucleation centers

☺

defect density: 10^9 – 10^{10} cm^{-2} on annealed single crystal surfaces

☺

well-defined relation between mean cluster size and number of deposited atoms

Each growing cluster is surrounded by a „capture area“. Atoms impinging on the substrate in this area are tapped at the cluster perimeter after surface diffusion and thus contribute to particle growth.

Diffusion of clusters is usually neglected.

Process depends on temperature:

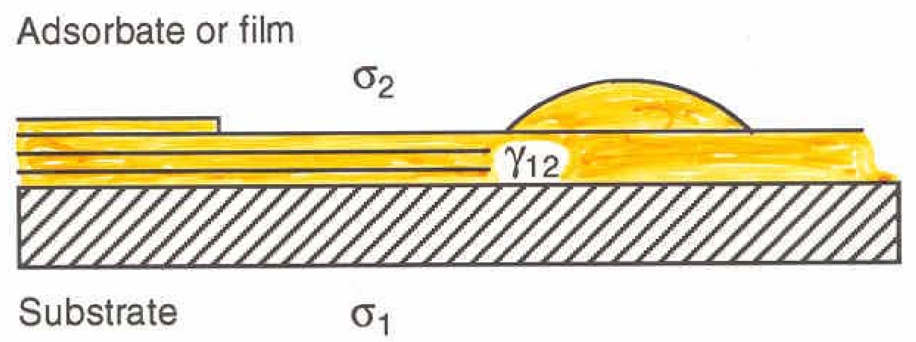
Since most growth processes take place more or less far from thermal equilibrium

- metastable growth modes are possible
- at low temperature usually fairly homogenous films can be deposited even if 3-dimensional islands are favorable

Alternative points of view:

- Do the adsorbed atoms bind more strongly to each other or to the substrate atoms?
- Does or does not wet the film the substrate?

Heteroepitaxy of lattice matched systems



Substrate surface energy	σ_1
Adsorbate surface energy	σ_2
Interface energy	γ_{12}

- Island/clusters are thermodynamically favorable and formed if

$$\sigma_2 + \gamma_{12} < \sigma_1$$

- Layer-by-layer growth is thermodynamically favorable and occurs if

$$\sigma_2 + \gamma_{12} > \sigma_1$$

Heteroepitaxy with lattic mismatch

In reality the substrate and the film have different lattice constants ⇒ mismatch

⇒ epitaxial strain

⇒ interface energy γ_{12} changes as a function of film thickness

⇒ initial growth is layer-by-layer, however, with increasing strain energy

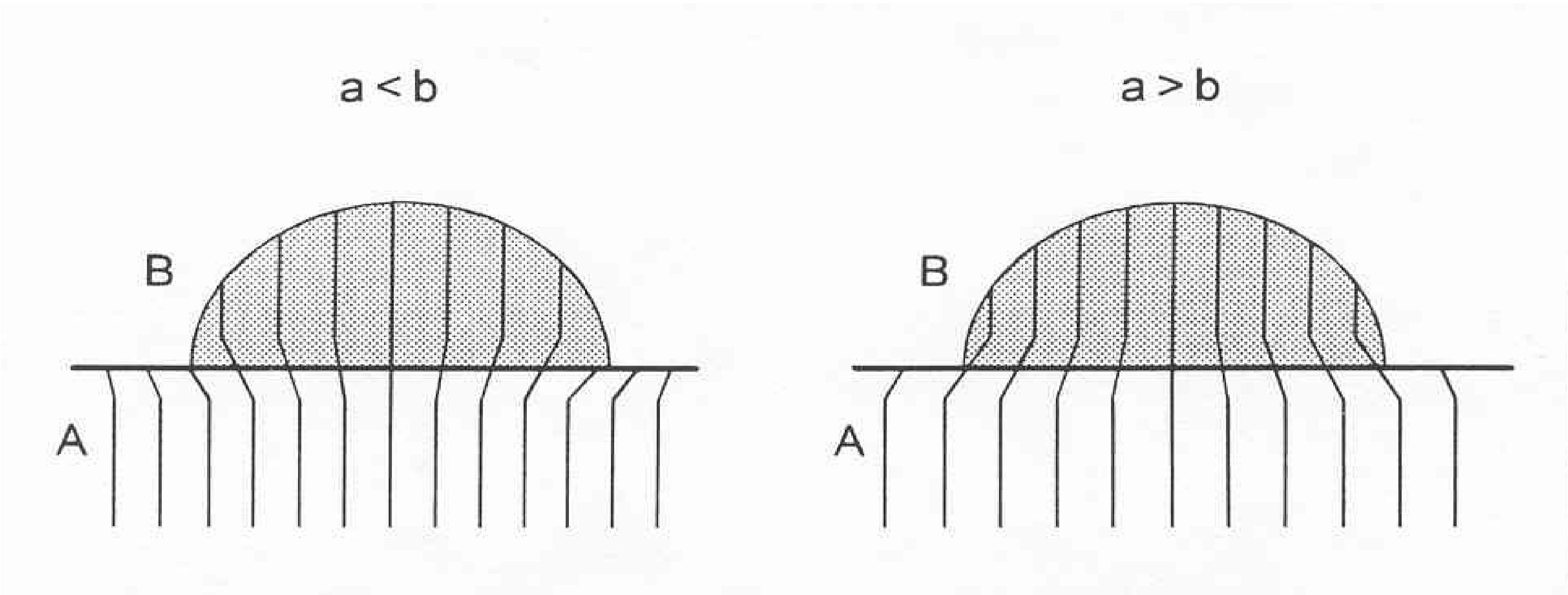
the system can lower the strain energy that increases with tickness by strain relaxation

⇒ island formation

⇒ transition from Frank van der Merwe to Volmer-Weber growth

(resulting in Stranski-Krastanow growth for the complete system)

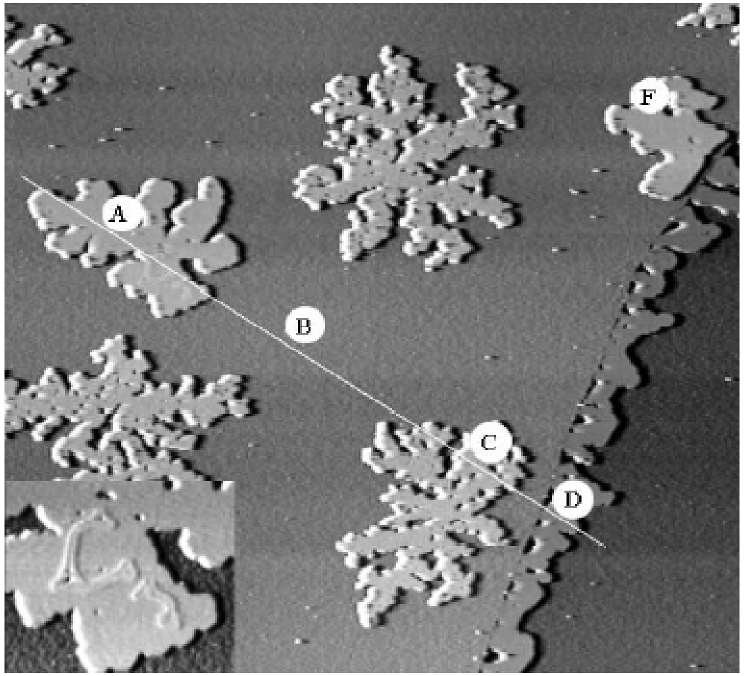
Lattice mismatch between clusters and substrate surface

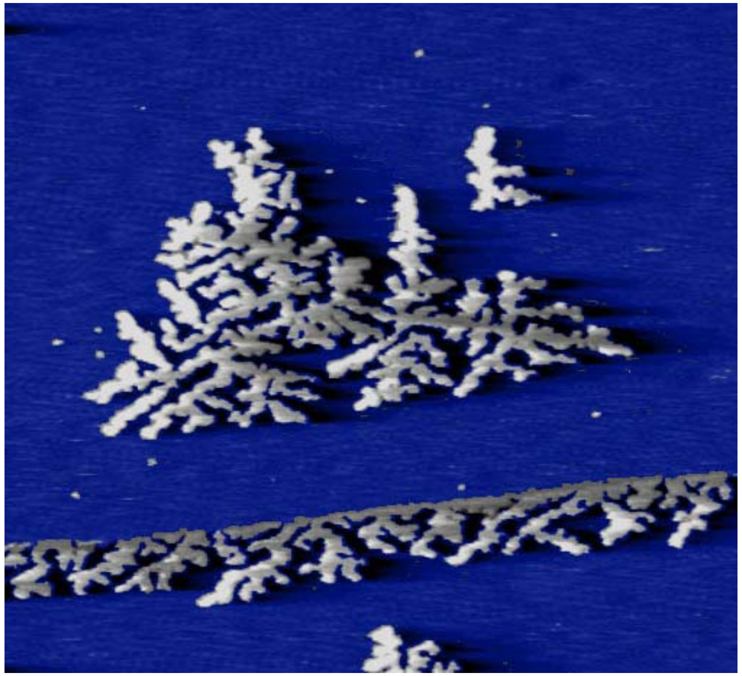


J.J. Métois, J.C. Heyraud, R. Kern, Surf. Sci. 78, 191 (1978)

Frank-van der Merwe growth

copper on ruthenium and silver on platinium





so-called dendritic or fractal structure

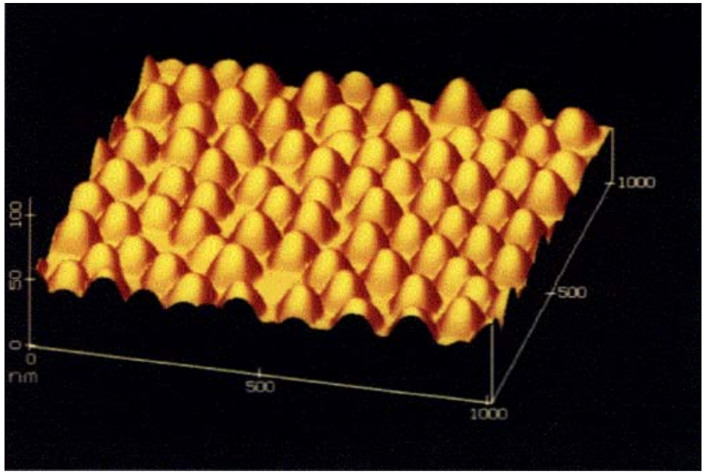
http://sundoc.bibliothek.uni-halle.de/diss-online/01/02H034/prom.pdf
http://www.fkf.mpg.de/kern/lectures/lectures_pic.html

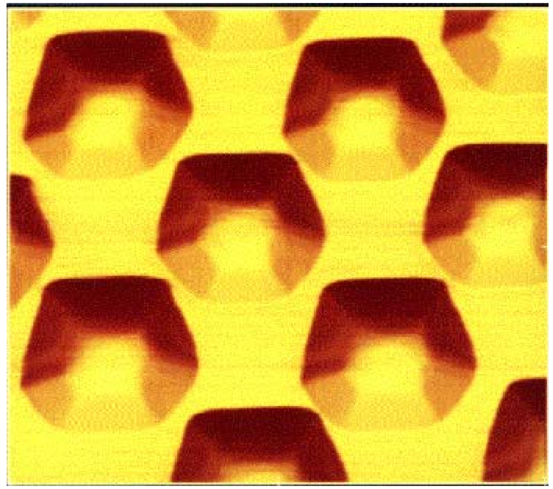
Dendritic structures in nature

ice crystals

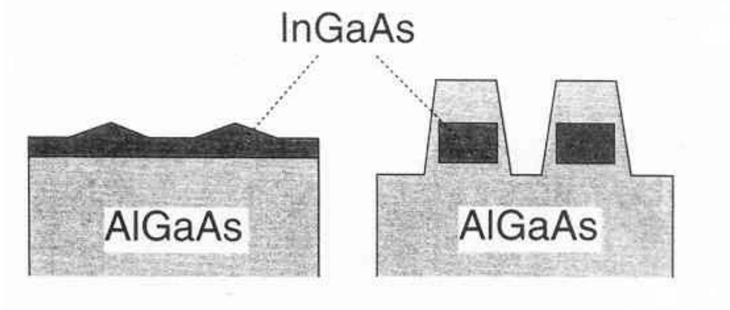
http://www.digicamfotos.de/index3.htm?http://www.digicamfotos.de/4images/details.php?image_id=24482&mode=search

Stranski-Krastanow-Growth

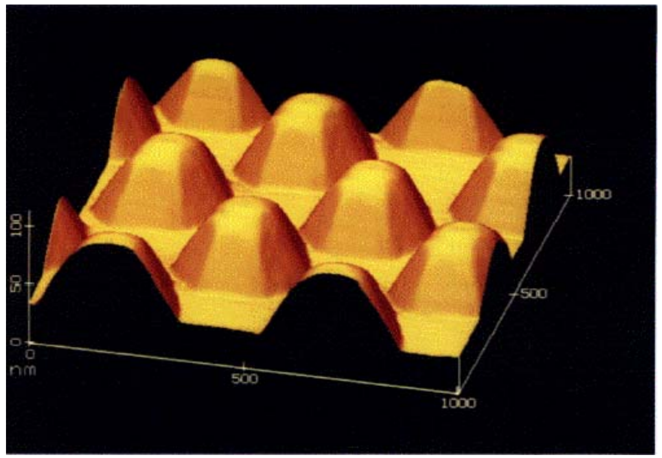




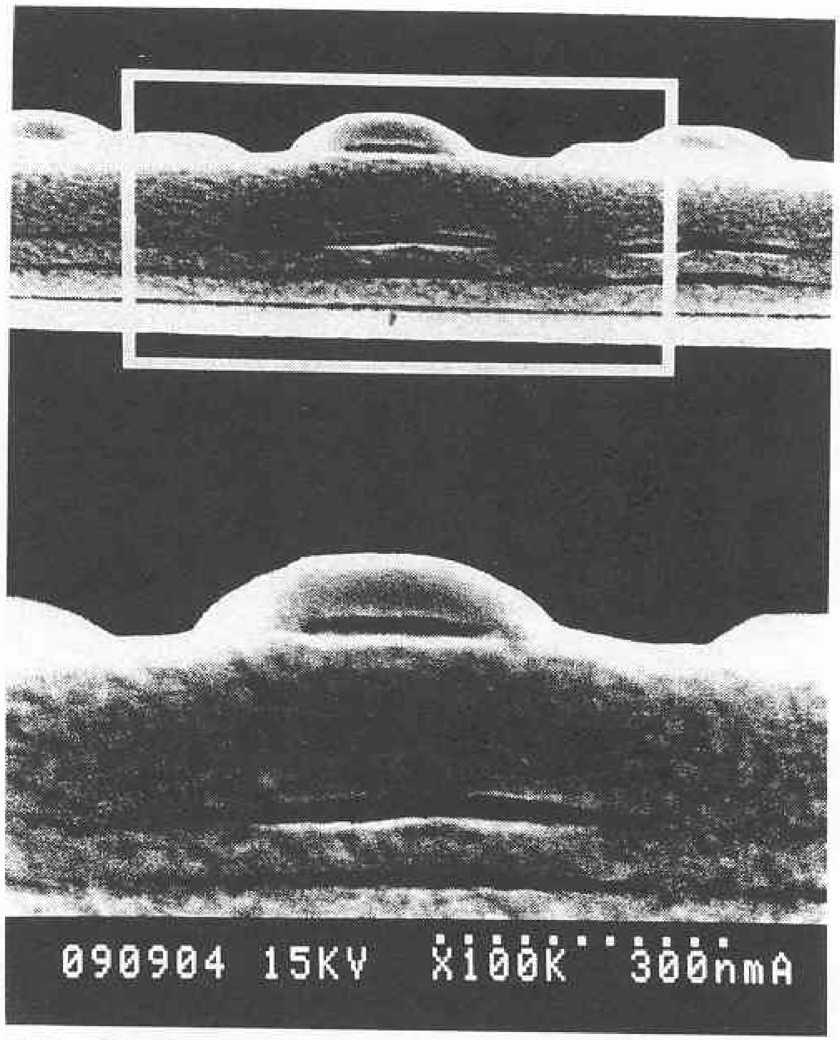
$In_{0,2}Ga_{0,4}As$ covered with
AlGaAs on GaAs (311)B substrate



GaAs (311)B substrate



R. Nötzel, Semicond. Sci. Technol. **11** (1996) 1365–1379.



Size of AlGaAs dots depends on In content of InGaAs overlayer

In content 0,2 → <r> ≈ 220 nm
In content 0,4 → <r> ≈ 70 nm

R. Nötzel, Semicond. Sci. Technol. **11** (1996) 1365–1379.

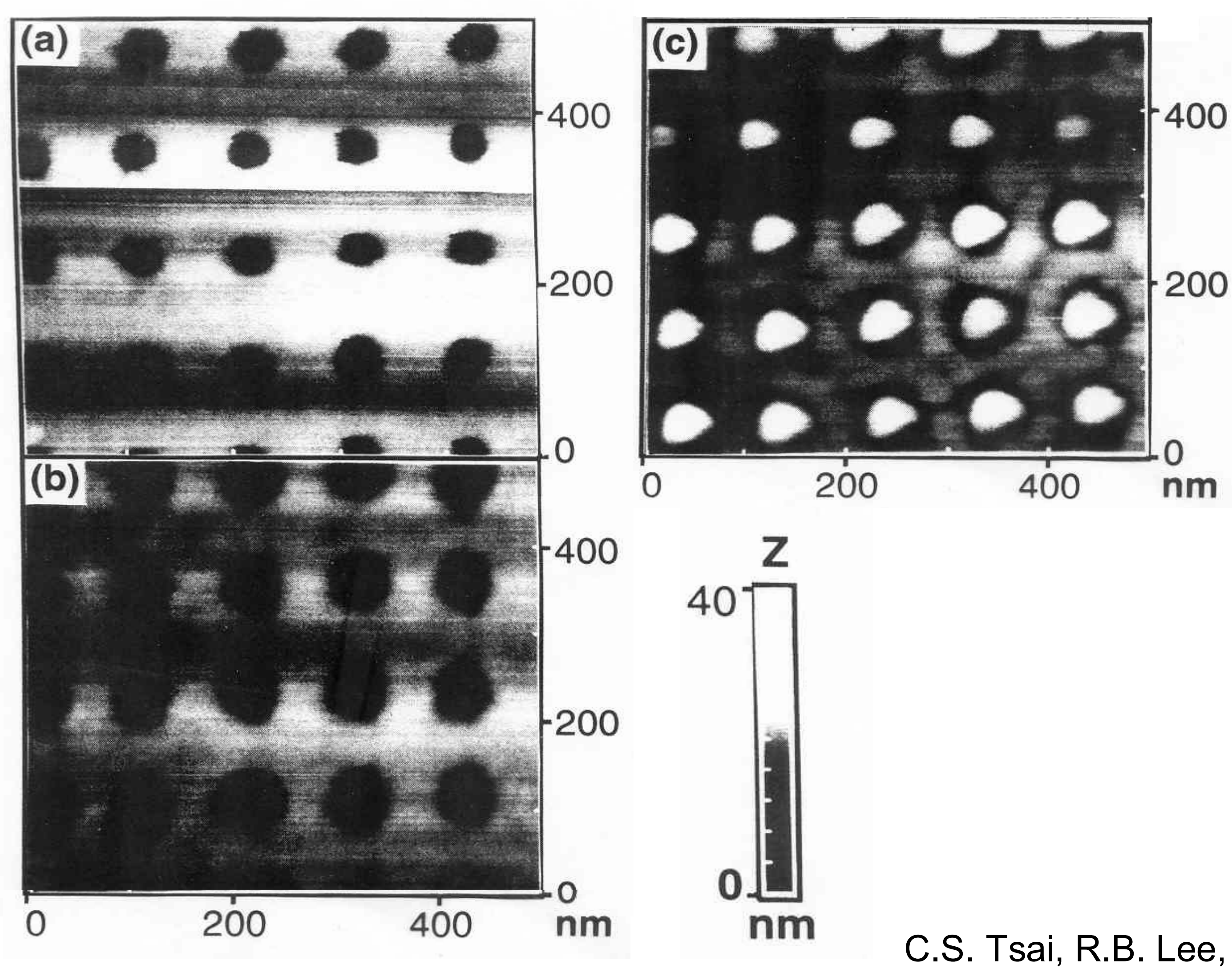
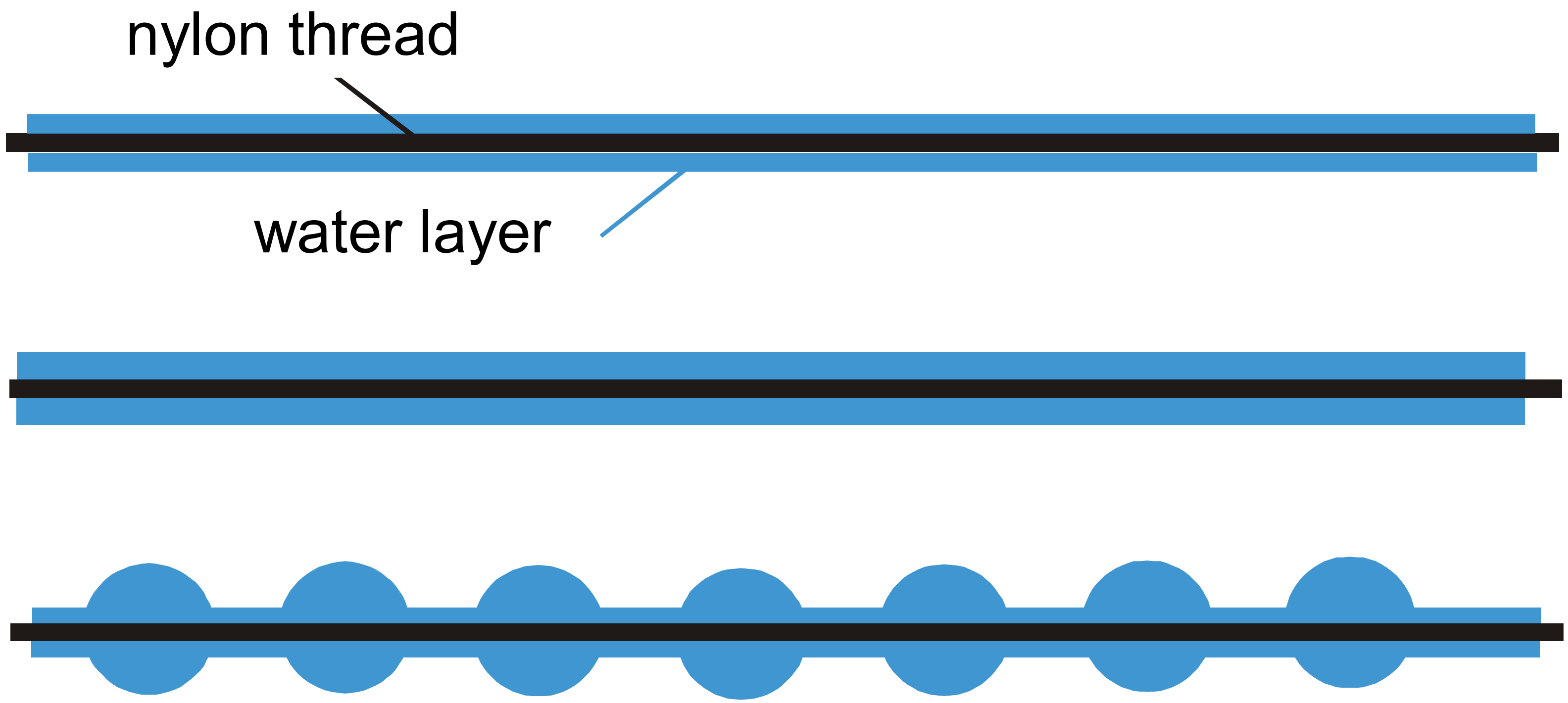


FIG. 1. Atomic force micrographs in plane view of arrays of (a) small, (b) medium, and (c) large GaAs dots after growth. The actual scan area is 500 nm x 500 nm. The height (Z) is represented by gray scale. The dot center-to-center spacing is 100 nm.

C.S. Tsai, R.B. Lee, K.J. Vahala,
Mat. Res. Soc. Symp. Proc. 358, 969 (1995)

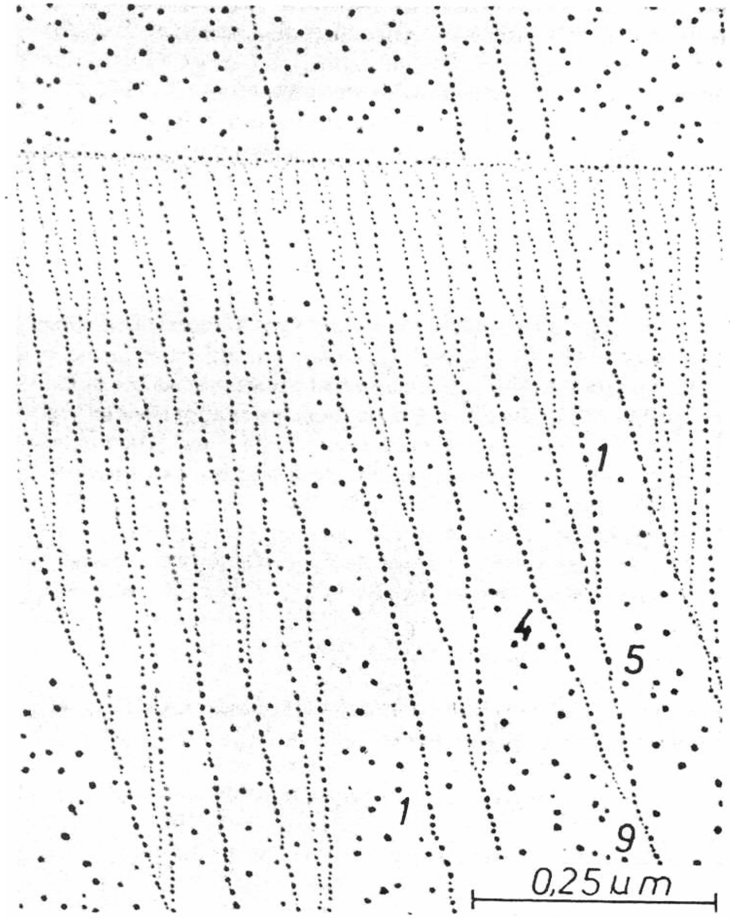
Stranski-Krastanow in nature

Self-organisation of a breaking water layer

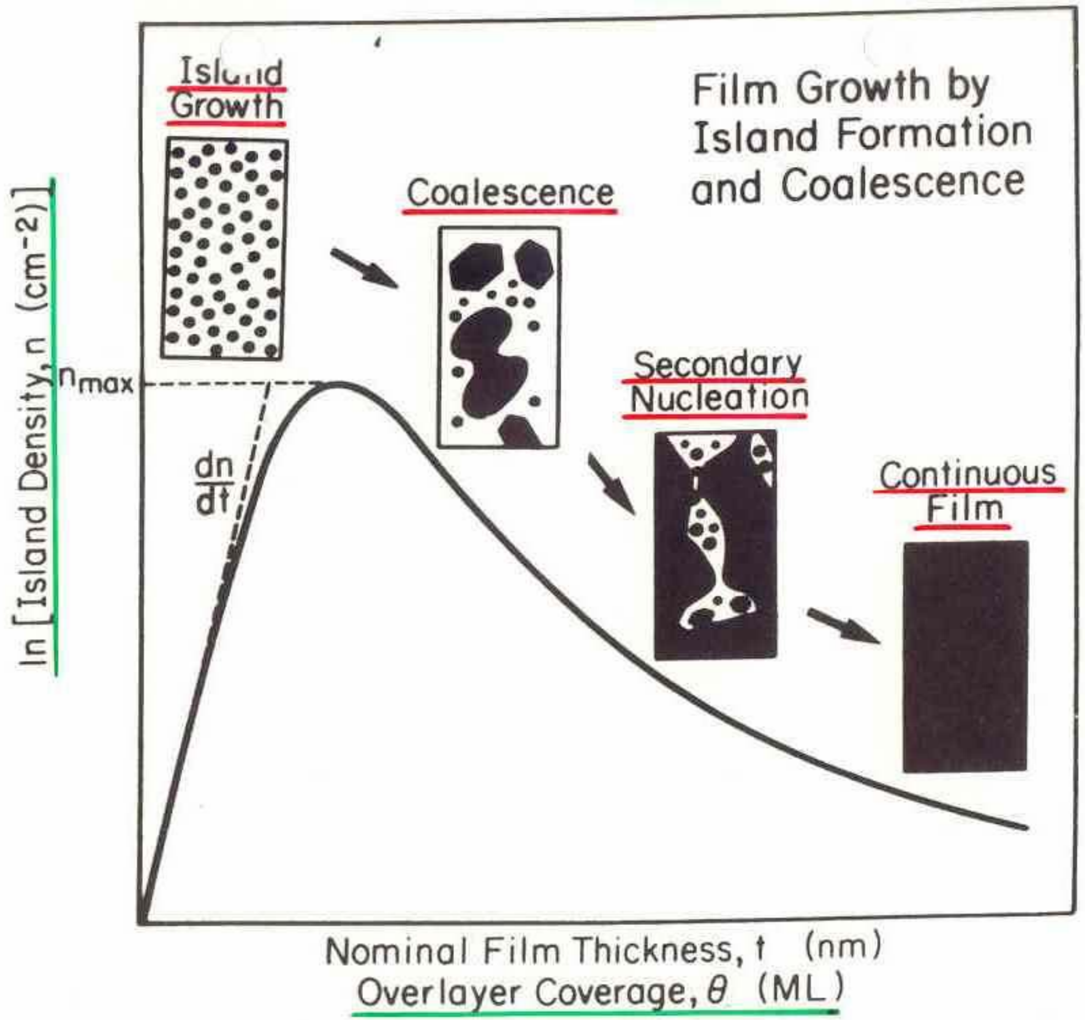


Volmer-Weber-Growth

Gold decoration of an NaCl cleavage surface

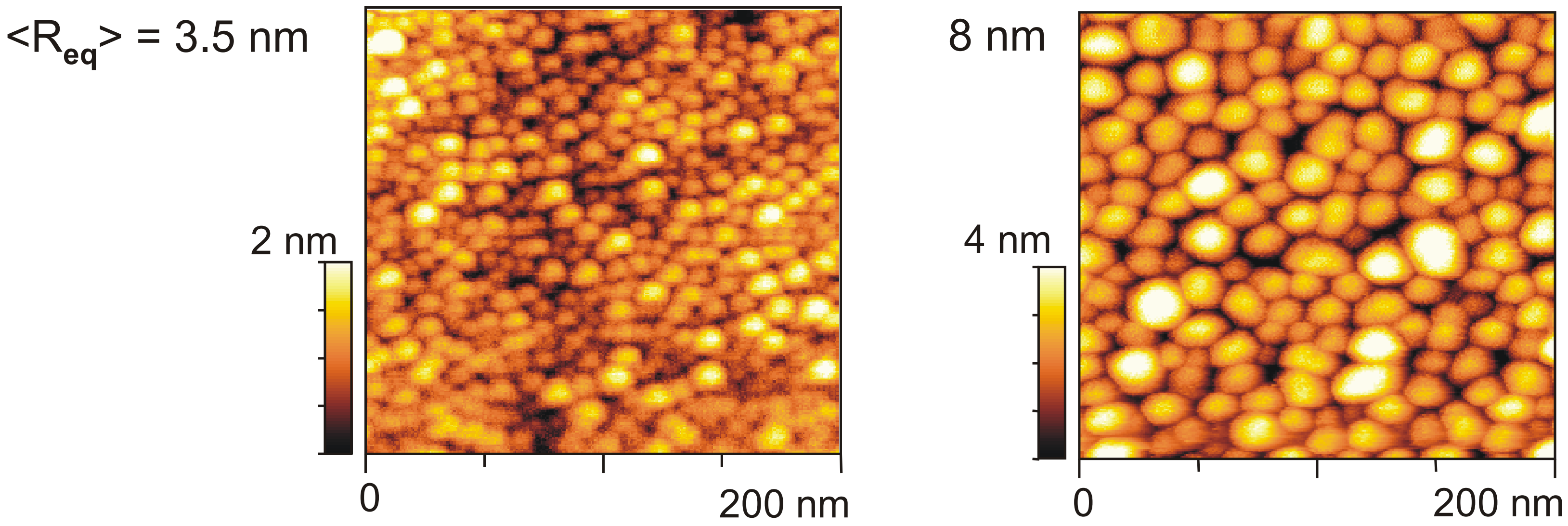


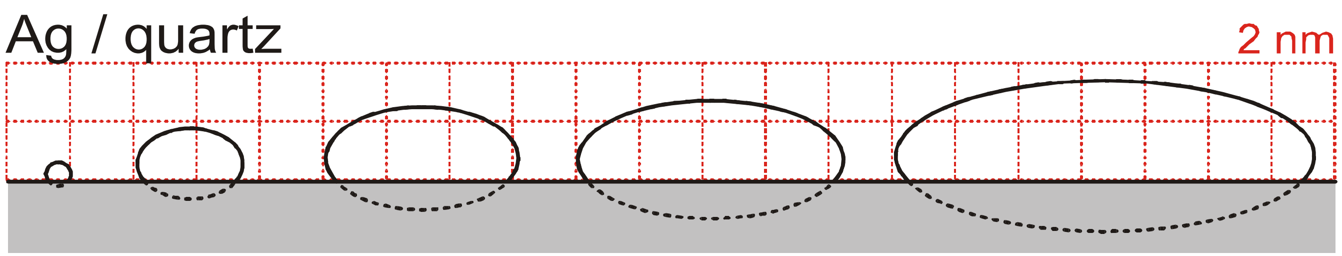
M. Krohn, Vacuum 37, 67 (1987)

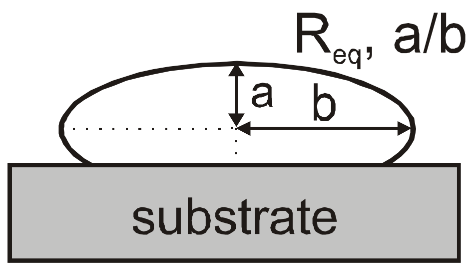


J.E. Greene, in Handbook of Crystal Growth, Vol. 1, Elsevier (1993)

Volmer-Weber-Growth

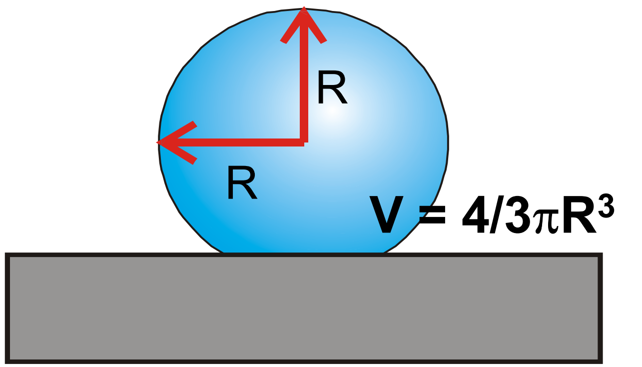




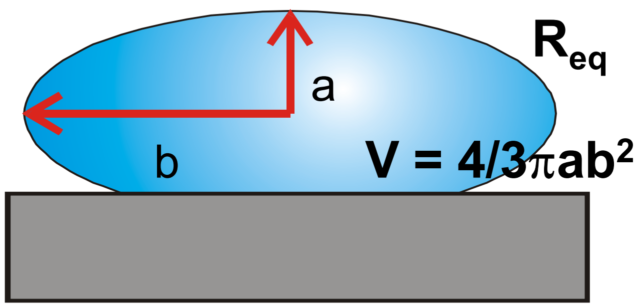


Equivalent radius of particles on surfaces

spherical particles



oblate particles
(rotational ellipsoids)



Particles are characterized by

1. equivalent radius R_{eq}
2. axial ratio a/b