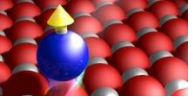
5

Bottom-up approach

Growth

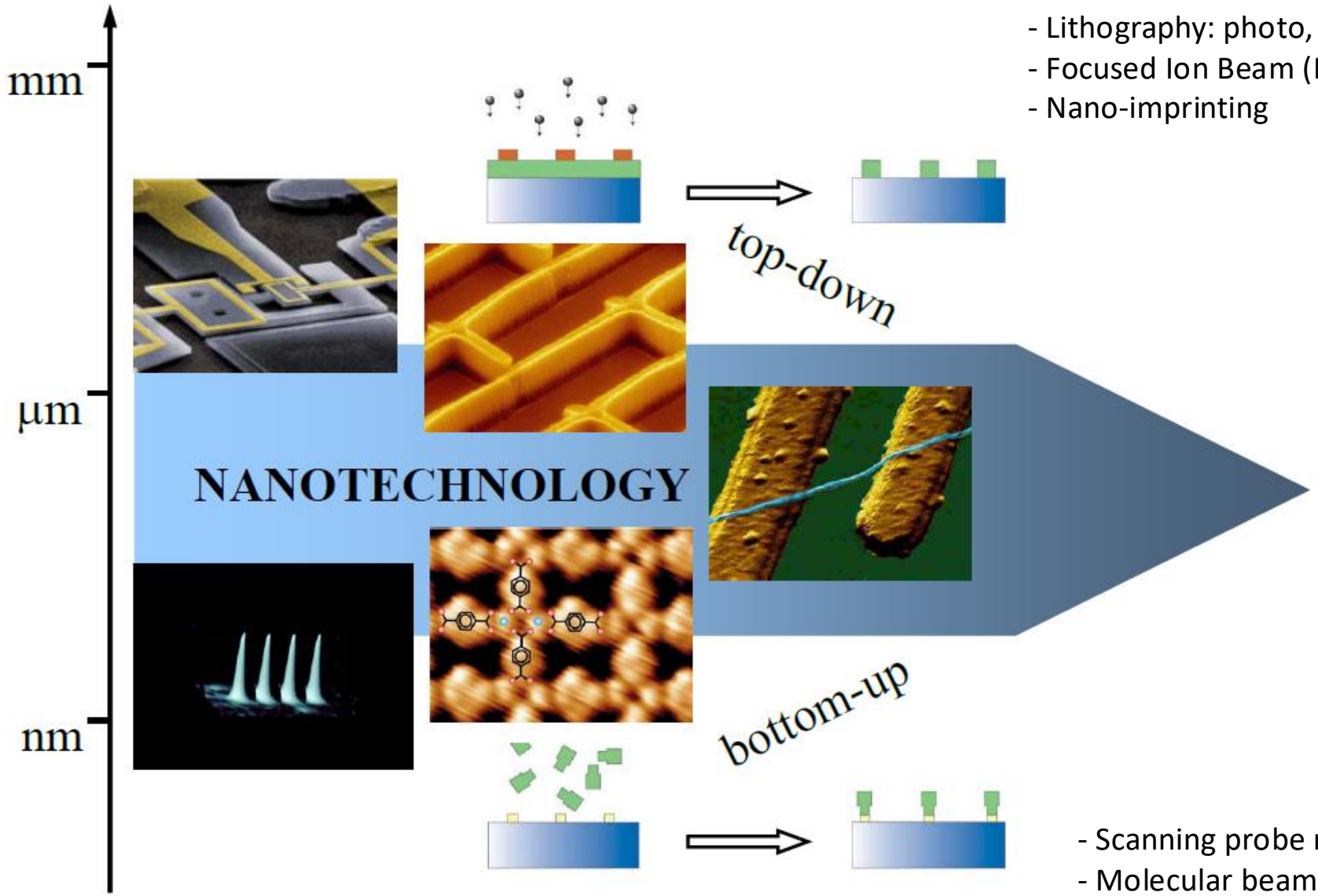


Bottom-up: Growth and self-assembly

Introduction to Surface and Thin Film Processes
J. A. Venables
Cambridge University Press

Epitaxial Growth of Thin Films
H. Brune
in: *Surface and Interface Science: Solid-Solid Interfaces and Thin Films*

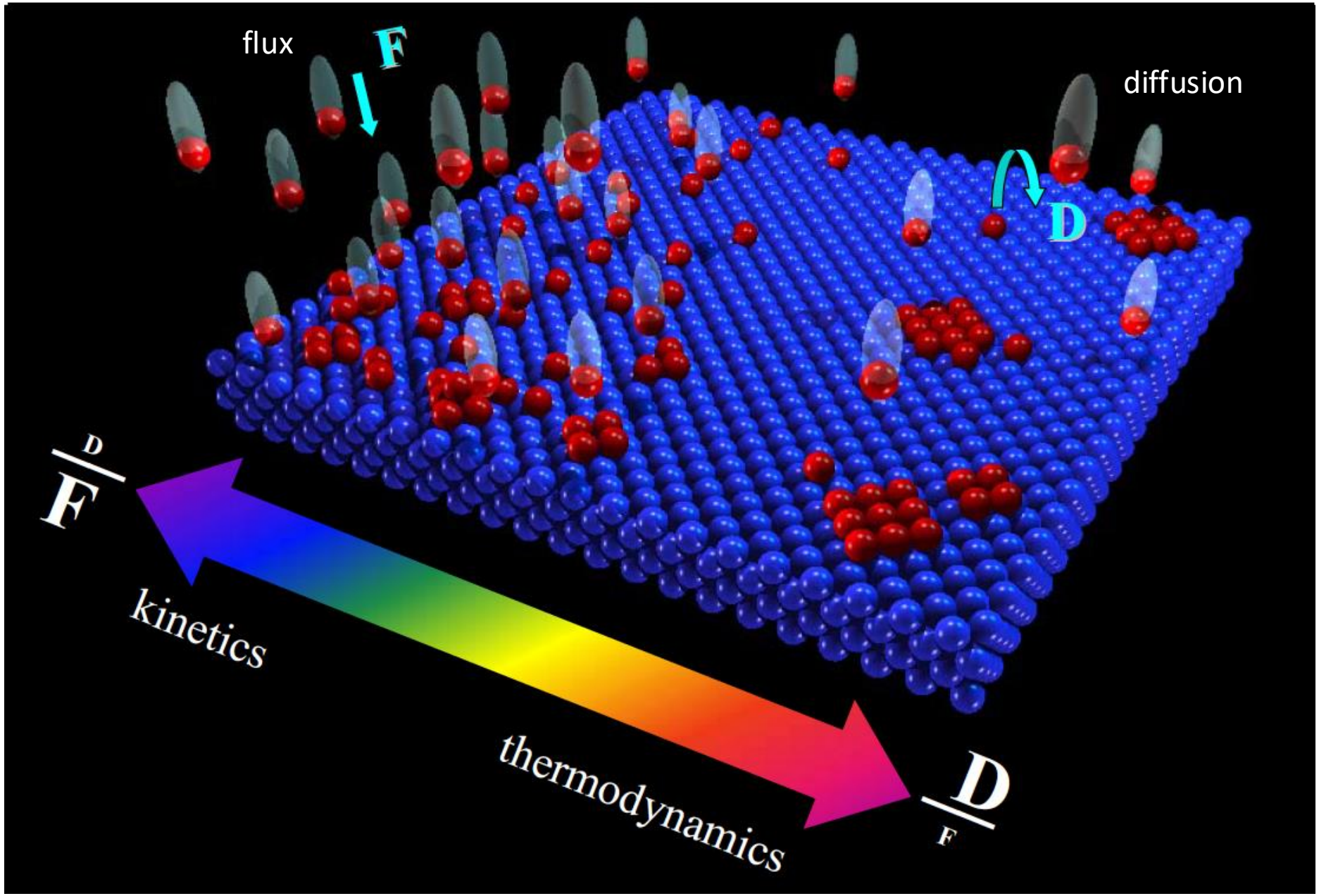
How to make the nanostructures: two approaches

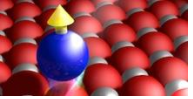


- Lithography: photo, UV, e-beam
- Focused Ion Beam (FIB)
- Nano-imprinting

- Scanning probe manipulation
- Molecular beam epitaxy
- Self-organized growth
- Self assembly

Thin film growth / Nanostructure growth





Surface tension, surface energy and equilibrium surfaces

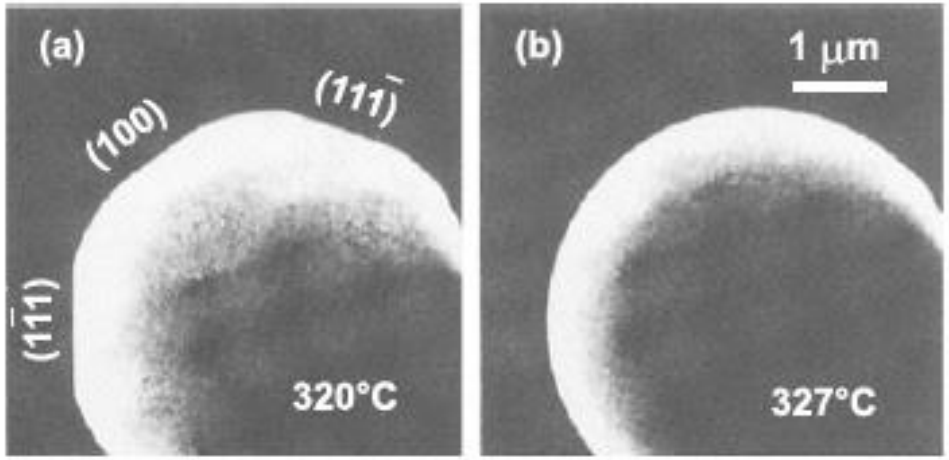
From bulk, creation of a surface (atoms that are not fully coordinated, i.e., there are broken bonds) → additional energy term γ: surface energy per unit surface (surface tension)

$\gamma > 0$ and energy = γA, with A the area of the additional surface, at constant volume

Shape of a solid at equilibrium minimizes the surface energy

in liquids γ is isotropic → spherical shape (smallest surface area)

in solids γ is different for the different surface orientations of a crystal: $\gamma(\vec{n})$

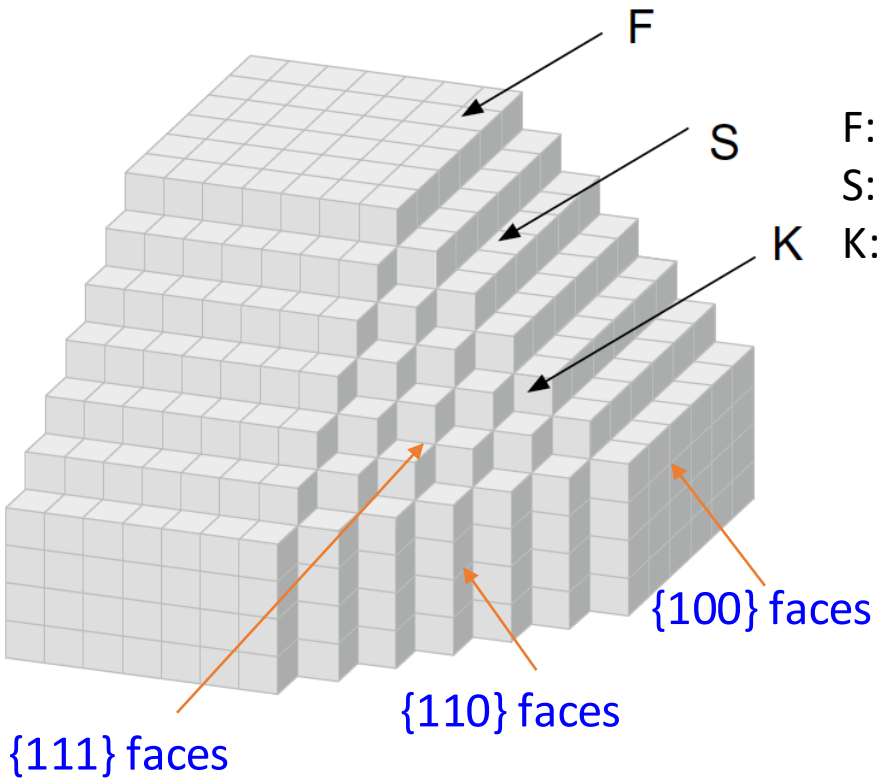


SEM photographs of the equilibrium shape of Pb crystals in the [011] azimuth; in b) Pb is liquid
J.J. Métois & J.C. Heyraud, **31**, 73 (1989)

Kossel crystal – TLK model

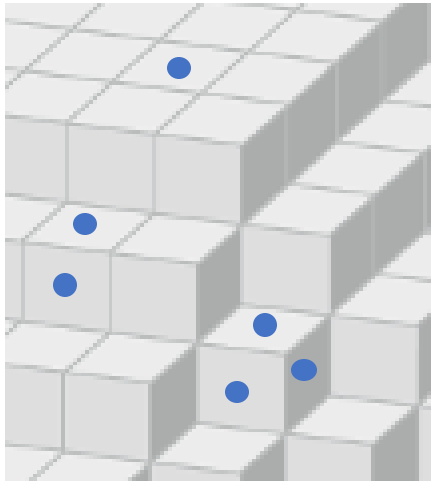
different crystal orientation → different surface energy

simplest model: Kossel crystal (simple cubic - sc)
evaluate the number of broken bonds per unit surface depending on the surface orientation



F: flat, terrace
S: step, ledge
K: kink

considering only the nearest neighbors (NN)
bulk: 6 NN → 6 bonds per atom
terrace: 5 NN → 5 bonds per atom, 1 broken bond
step: 4 NN → 4 bonds per atom, 2 broken bonds
kink: 3 NN → 3 bonds per atom, 3 broken bonds
(half-crystal site)



Surface tension for cubic crystals

EPFL

Exercises 5.1 – 5.3

Considering the number of broken bonds per unit surface, for singular (low-Miller index) surfaces:

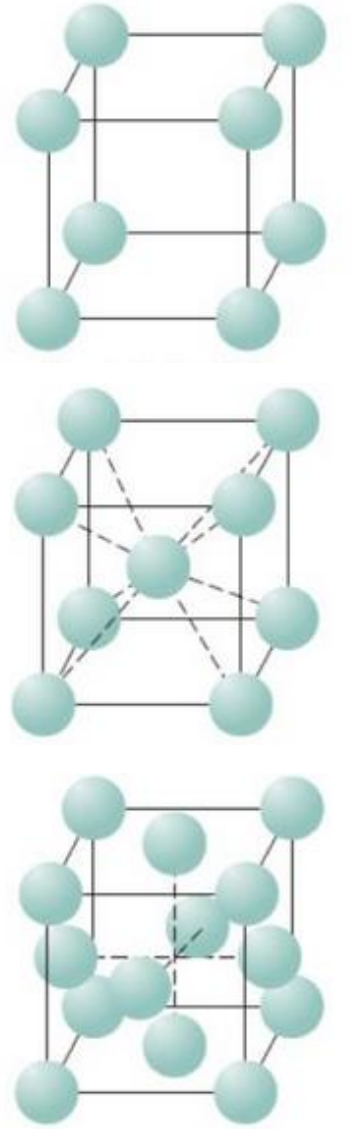
sc: $\gamma_{100} < \gamma_{110} < \gamma_{111}$

bcc: $\gamma_{110} < \gamma_{100} < \gamma_{111}$

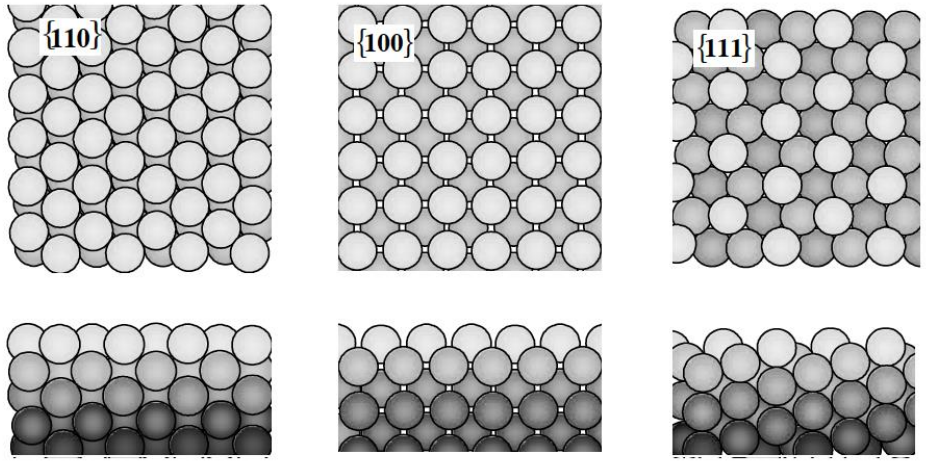
fcc: $\gamma_{111} < \gamma_{100} < \gamma_{110}$

in general, the more compact the surface, the lower the surface energy

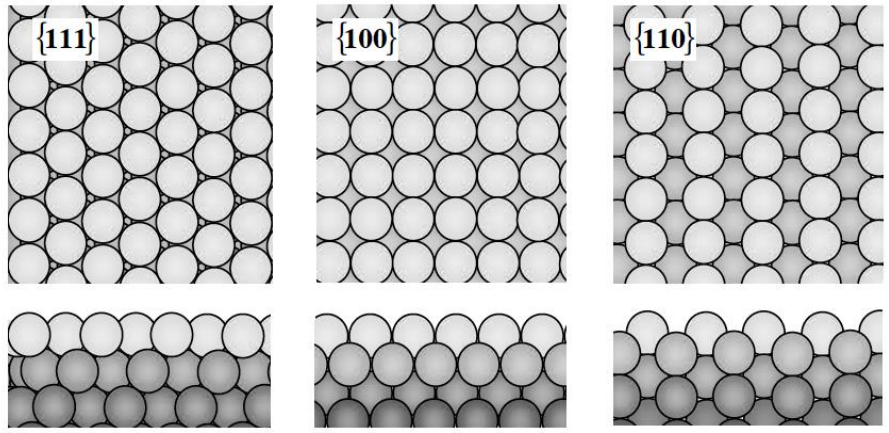
conventional unit cell



bcc

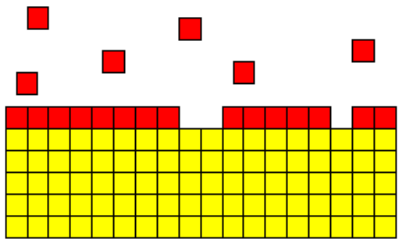


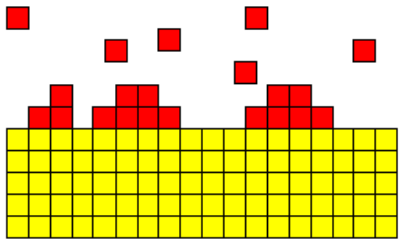
fcc

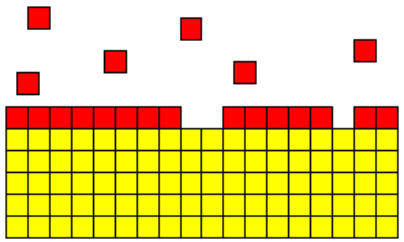


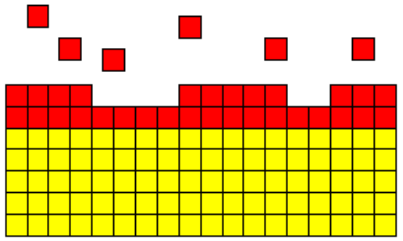
Growth modes (at thermodynamic equilibrium)

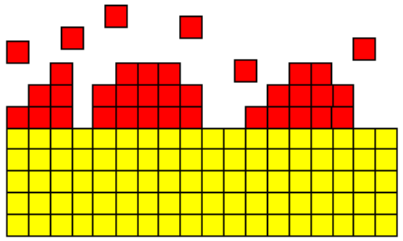
Growth of A on B

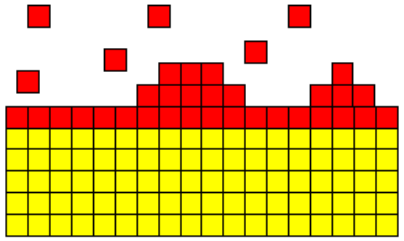












γ_A: surface energy of A (interface with vacuum)

γ_B: surface energy of B (interface with vacuum)

γ_{AB}: A-B interface energy (hybridization, lattice mismatch,...)

layer - by - layer growth (Frank - van der Merve)

$\gamma_A < \gamma_B + \gamma_{AB}$

island growth (Volmer - Weber)

$\gamma_A > \gamma_B + \gamma_{AB}$

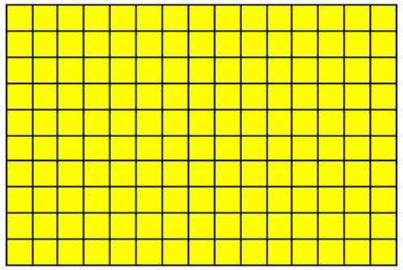
layer - by - layer + island growth (Stranski - Krastanov)

$\gamma_A > \gamma_B + \gamma_{AB}$

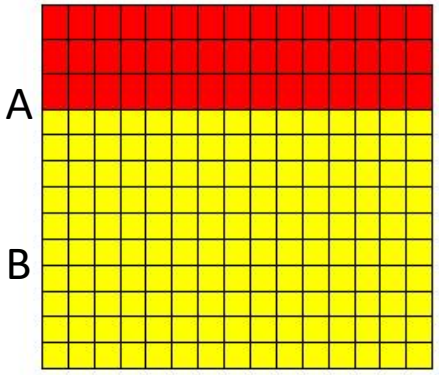
γ_{AB} increases with coverage (due to strain) → change from 2D to 3D

Stranki-Krastanov growth of semiconductor quantum dots

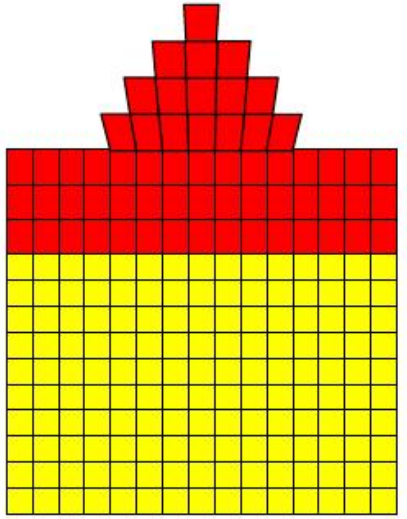
lattice constants: $a_A > a_B$



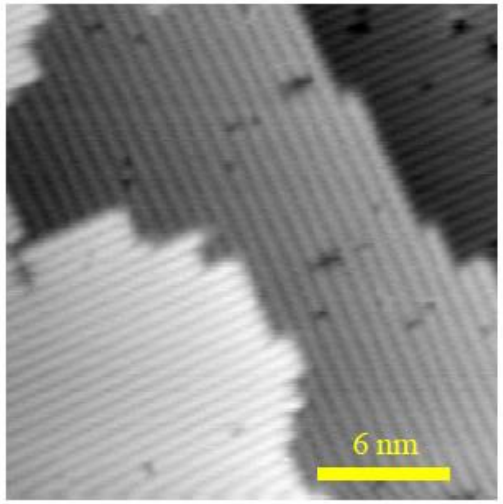
substrate



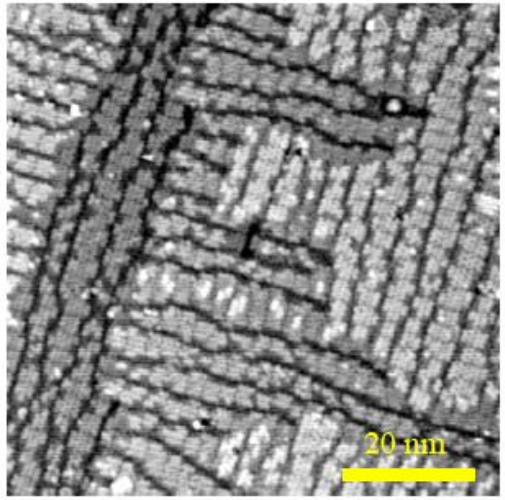
wetting layer



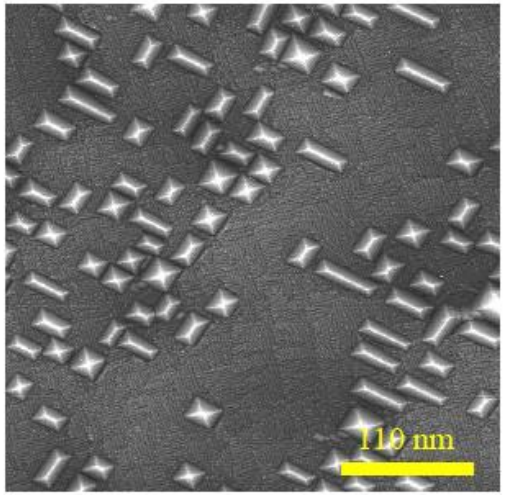
islands



Si(001)

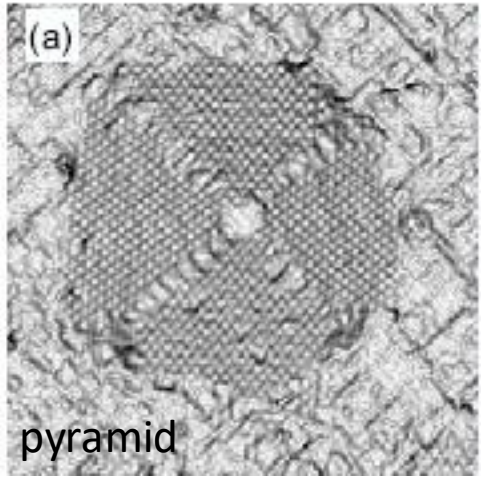


3ML Ge on Si(001)

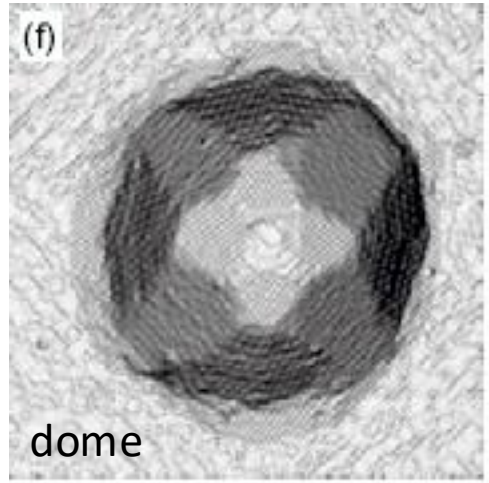


6ML Ge on Si(001)

growth parameters



pyramid



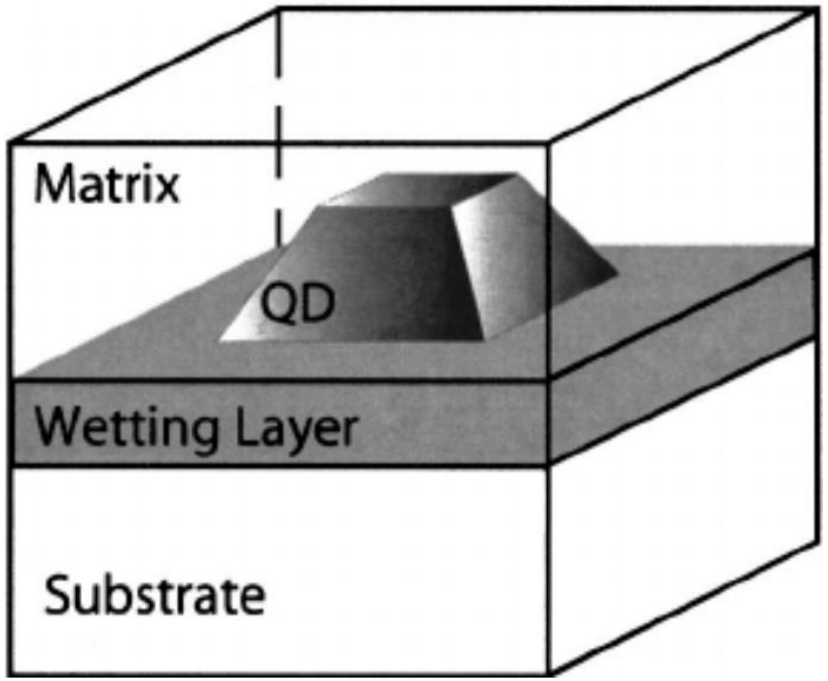
dome

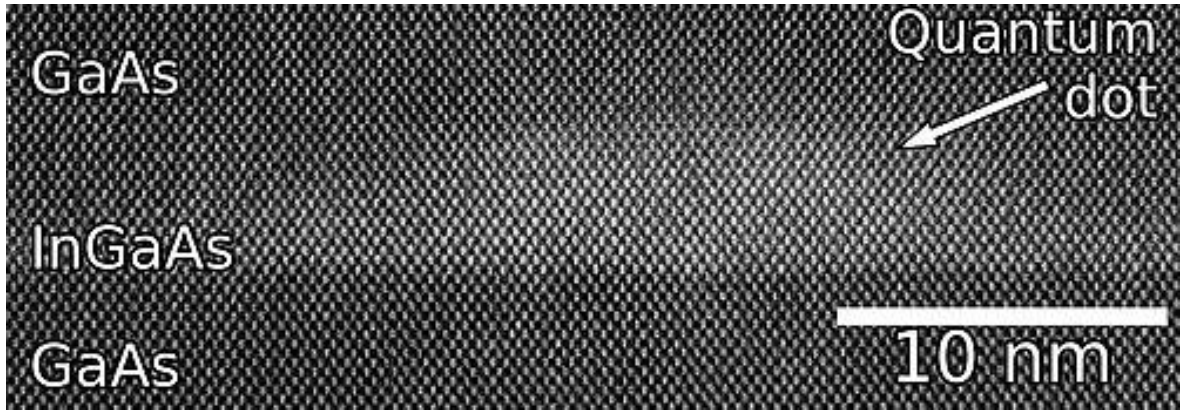
Buried quantum dot

The islands can be subsequently buried

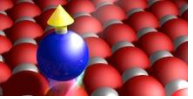
Potential applications:

- single-photon sources (quantum cryptography)
- quantum computation





TEM image



Epitaxial thin film growth - Technological relevance

Solid-state electronic devices rely on the growth of sequences of many ultrathin epitaxial layers with atomically sharp interfaces and thickness control down to the monolayer level.

Examples:

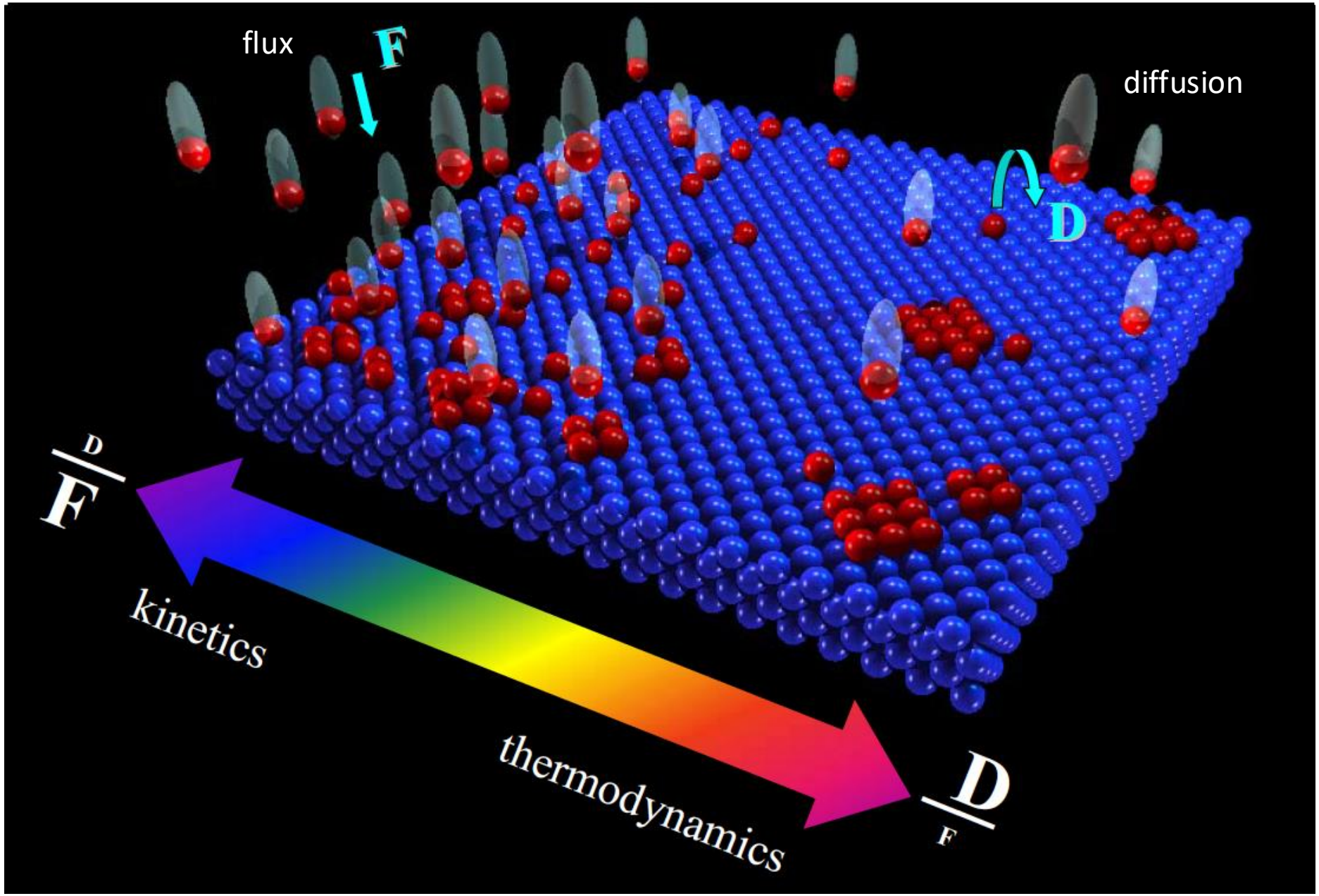
- Alternating layers of large- and small-band-gap semiconductors are grown to tailor the electronic properties by quantum confinement of charge carriers in the small-band-gap regions (quantum well structures).
  Applications: ultrafast transistors, sensors, semiconductor lasers

- Sequences of ferromagnetic layers separated by nonmagnetic spacers; metallic or insulating spacer layers.
  Applications: spin valves, magnetic hard-disk read heads, magnetic-random access memories

- …

The growth of perfectly flat 2D layers of materials A/B, and subsequently B/A, is a stringent requirement for device functionality.

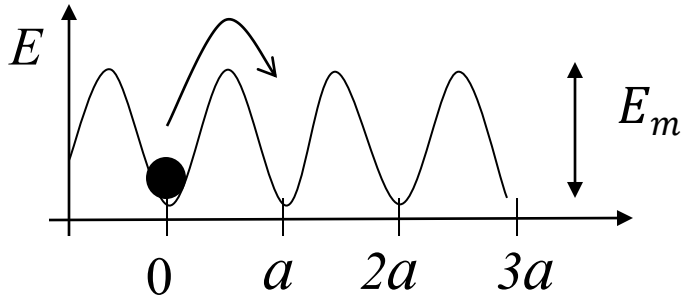
Thin film growth / Nanostructure growth



Growth as a non-equilibrium process: kinetics

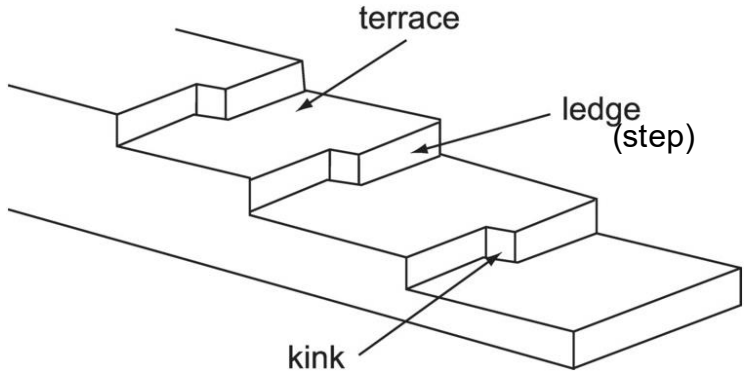
single crystal surfaces: a 2D laboratory

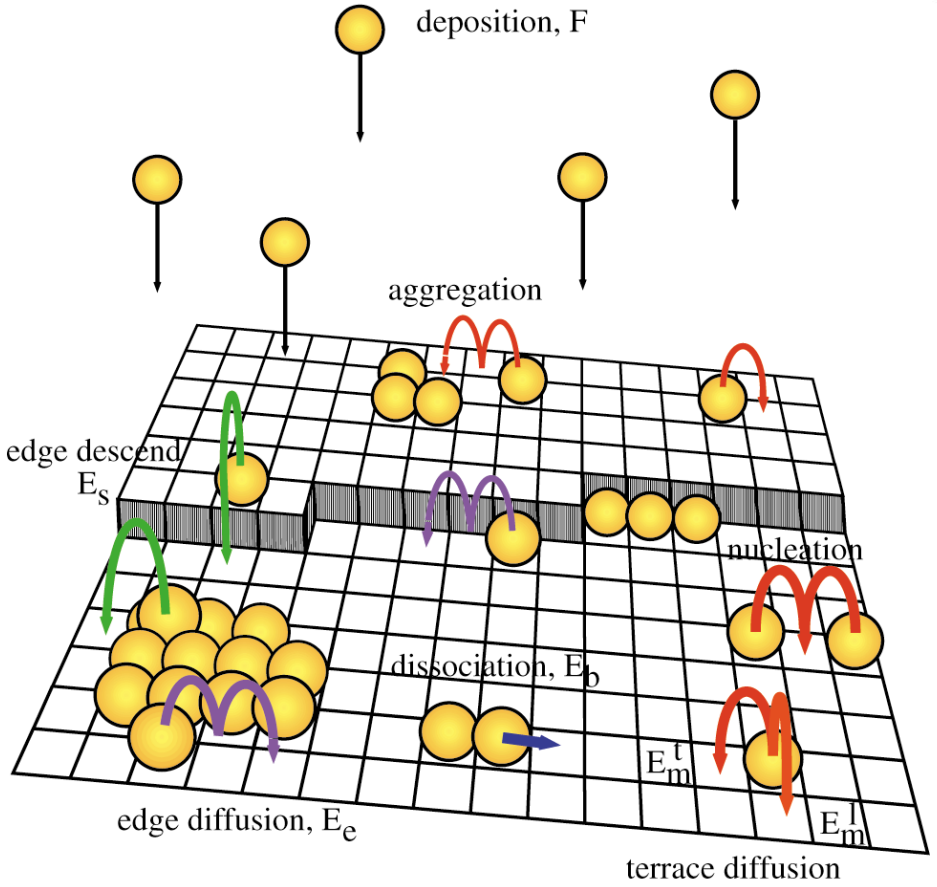
each process i has
an energy barrier E_i and a rate n



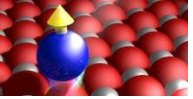
diffusion process, random walk
a lattice constant, t time
number of jumps = νt
mean squared displacement:

$$\langle \Delta r^2 \rangle = \nu a^2 t$$





H. Brune Surf. Sci. Rep. **31**, 121 (1998)



Growth as a non-equilibrium process

We aim at controlling:

- mean size
- size distribution
- density
- shape
- composition

Control parameters are:

- substrate temperature ***T***
- deposition flux ***F***
- coverage Θ
- substrate/overlayer material (strain, mixing, etc.)
- substrate symmetry or patterning

Statistical growth: T → 0 K

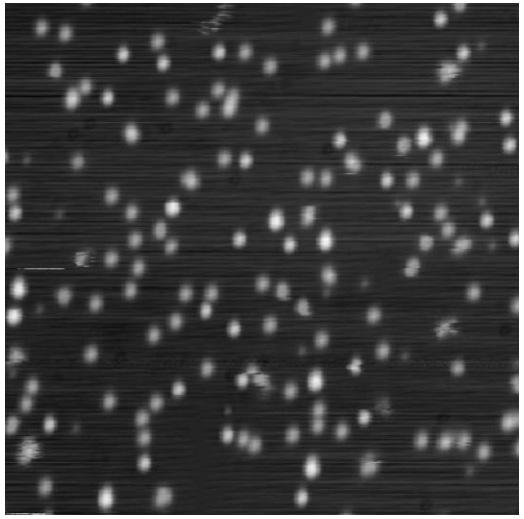
- thermally-activated diffusion is frozen

$$\nu = \nu_0 \exp(-E_1/k_B T) \rightarrow 0$$

- the coverage determines the mean island size n
- broad size distribution

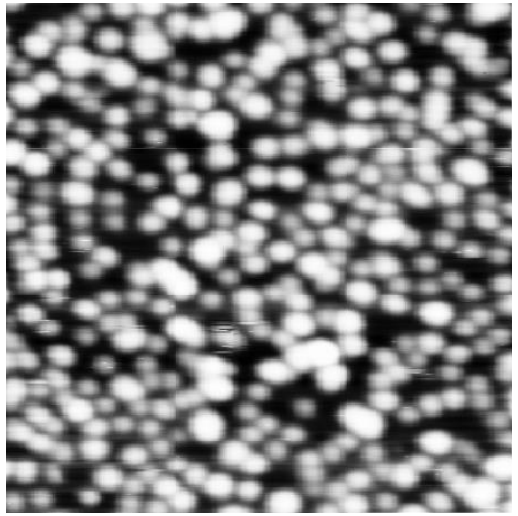
Co/Pt(111)

0.03 ML, $T = 50$ K
$n = 1.2$



50 Å

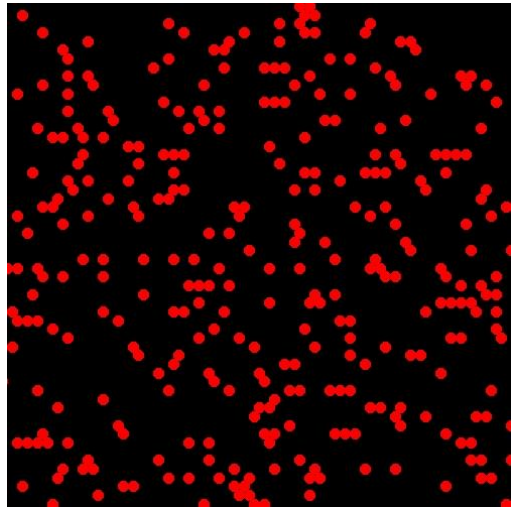
0.10 ML, $T = 50$ K
$n = 2.9$

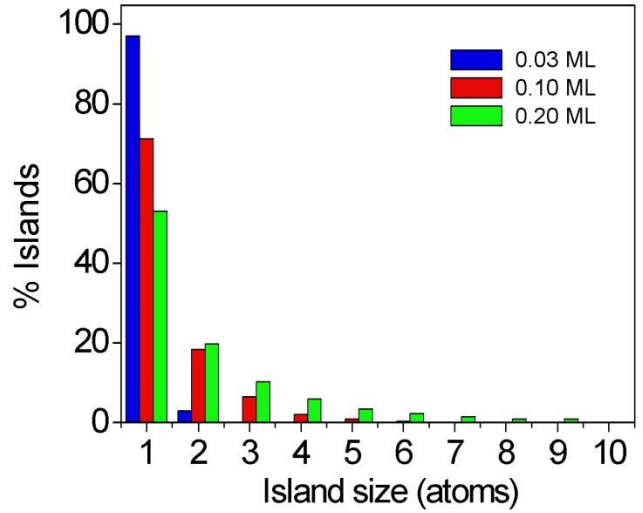


50 Å

n = mean island size = coverage / island density

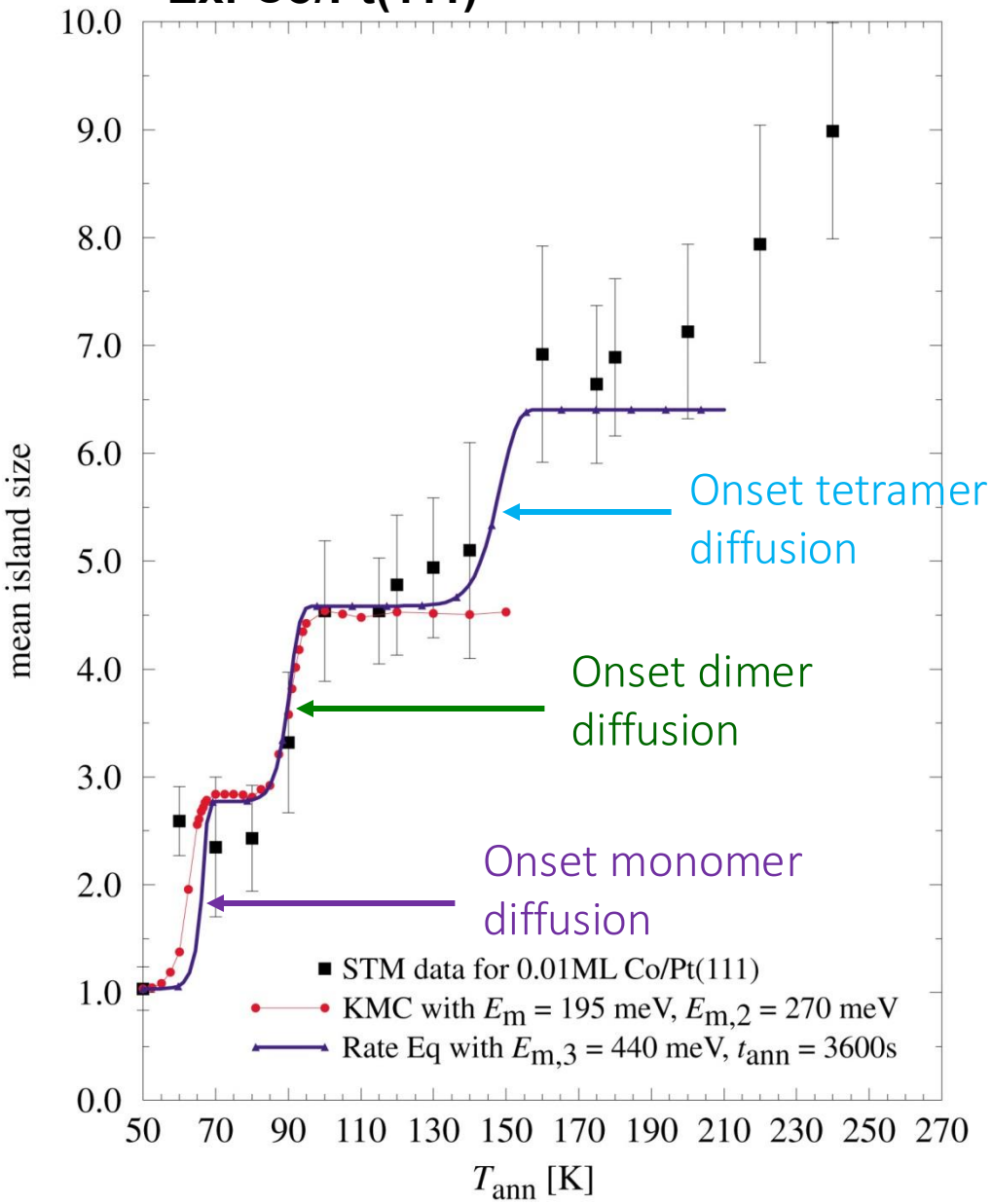
Kinetic Monte Carlo simulation



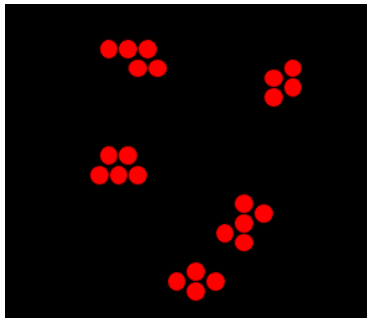


Adatom and cluster diffusion

Ex: Co/Pt(111)

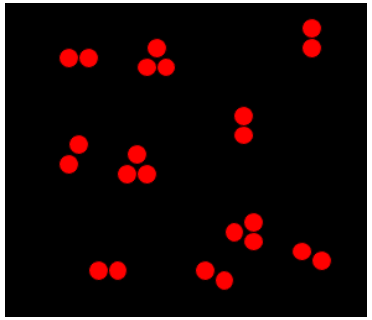


By increasing T, sequential activation of cluster diffusion results in size selection:



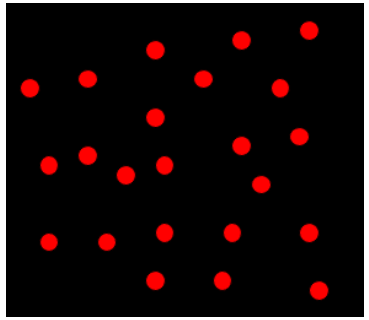
100 K < *T* < 130 K:

tetramers and pentamers



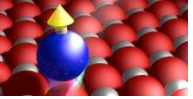
60 K < *T* < 90 K:

dimers and trimers



T < 60 K: monomers

S. Rusponi *et al.* unpublished



Rate equations: simple case of $i = 1$

Assumption: adatom can diffuse with a rate D
but
dimer is stable, i.e. when two atoms meet, they cannot detach
Critical size $i = 1$

Time evolution of average values of n_1 and n_x

n_1 adatom density

Growth flux

Dimer creation

Adatom-island attachment

$$\frac{dn_1}{dt} = F - 2\sigma_1 D n_1^2 - \sigma_x D n_1 n_x - k_x F(Ft - n_1) - 2k_1 F n_1$$

Direct impinging on an island

Direct impinging on an adatom

$$\frac{dn_x}{dt} = \sigma_1 D n_1^2 + k_1 F n_1$$

$$D = D_0 \exp(-E_1/k_B T)$$

Rate equations give the formation rate for adatoms and stable islands

Island density – Example: Ag/Pt(111)

Exercise 5.4

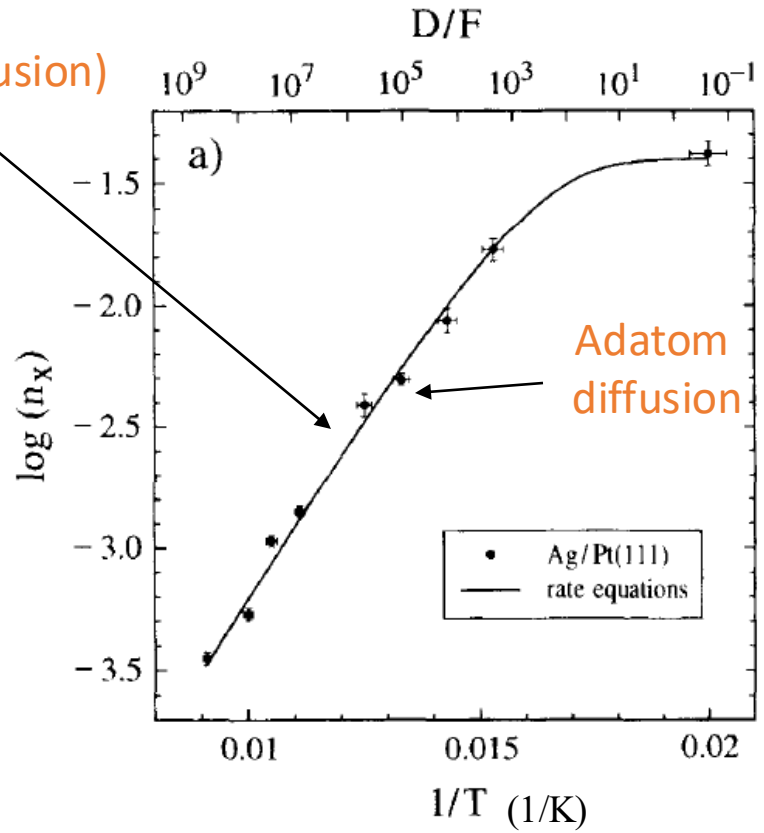
$$n_x = \eta(\theta, i)\left(\frac{D}{F}\right)^{-\chi} \exp\left(\frac{E_i^c}{(i+2)k_B T}\right) \qquad D = D_0 \exp\left(-\frac{E_1}{k_B T}\right) \qquad \chi = \frac{i}{i+2}$$

E_i^c is the dissociation energy of the island with critical size $= i$

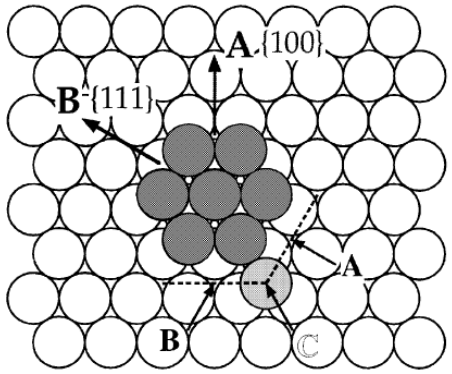
$$i = 1 \quad \rightarrow E_i^c = 0 \quad \rightarrow \quad n_x = \eta(\theta, 1)\left(\frac{D}{F}\right)^{-1/3} = \eta(\theta, 1)\left(\frac{D_0}{F}\right)^{-1/3} \exp\left(\frac{E_1}{3k_B T}\right)$$

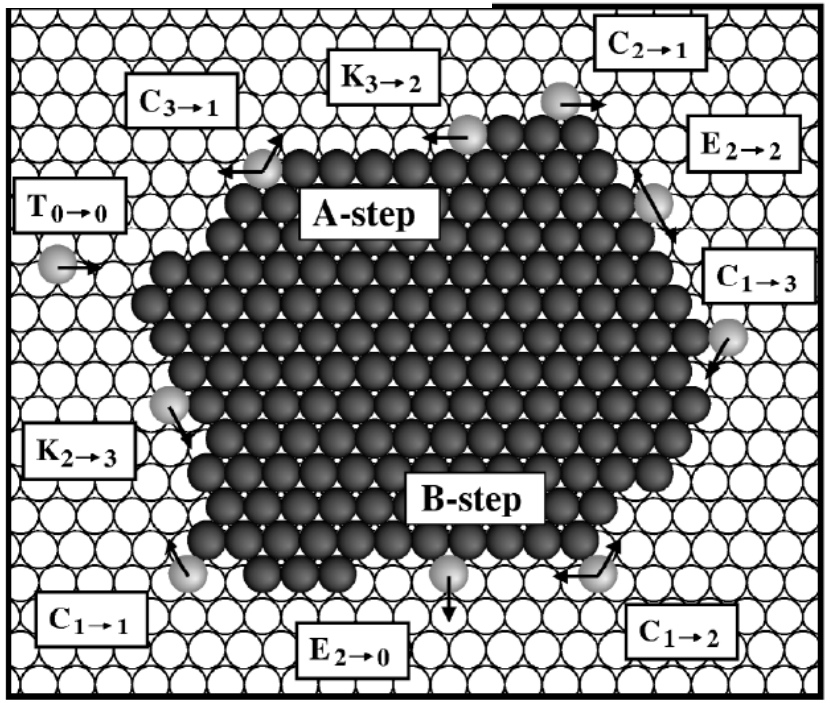
The slope gives E_1
(energy barrier for adatom (monomer) diffusion)

Arrhenius plot of saturation island densities (coverage = 0.2 ML) for the regime where dimers are stable nuclei

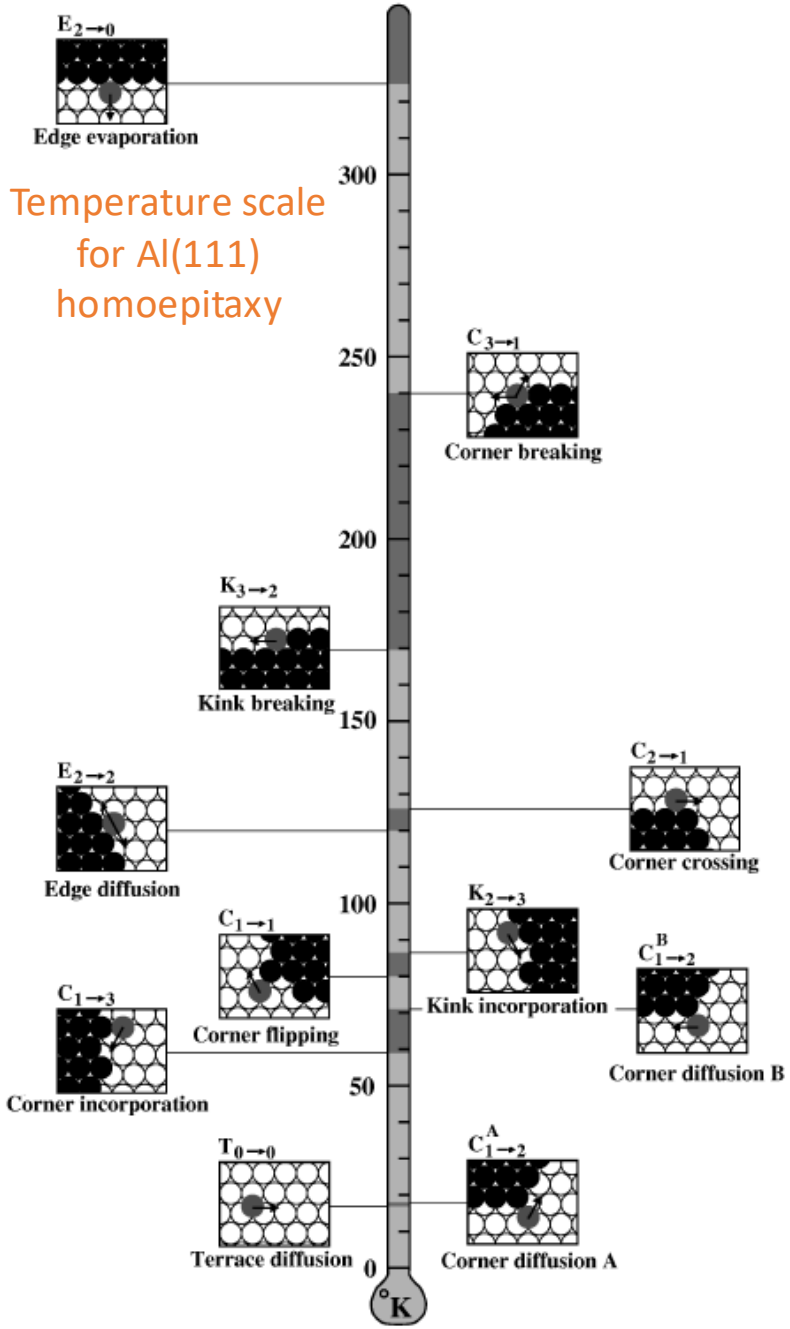


Island shape: diffusion along the edges

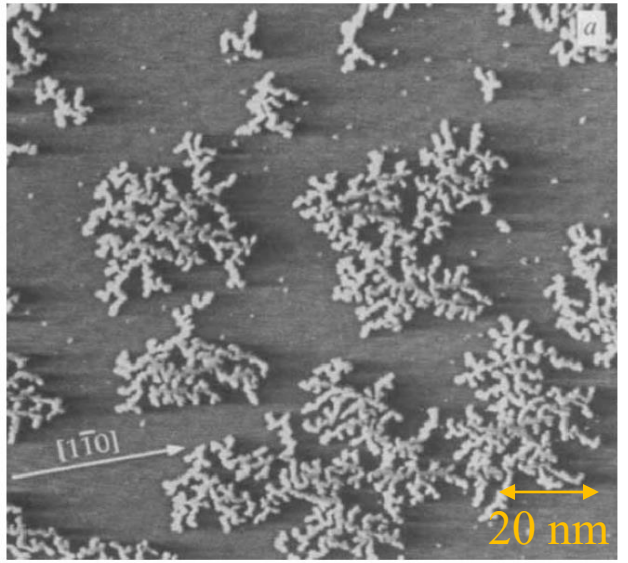


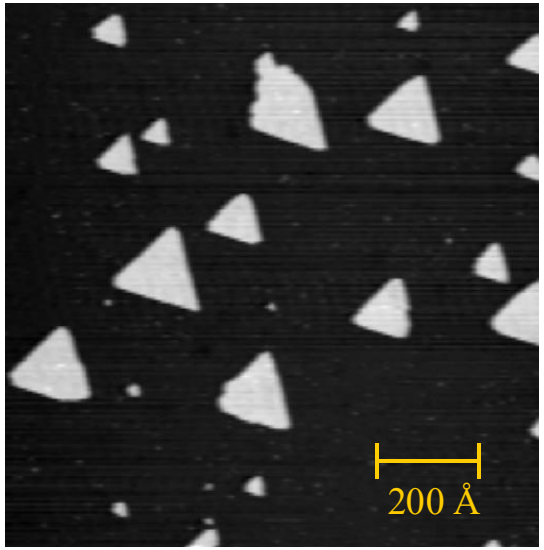


H. Brune *et al.* Nature **369**, 469 (1994);
S. Ovesson *et al.* Phys. Rev. Lett. **83**, 2608 (1999);
A. Bogicevic *et al.* Phys. Rev. Lett. **81**, 637 (1998)



Ag/Pt(111) T=110K
Adatom stick at the island edge and stop





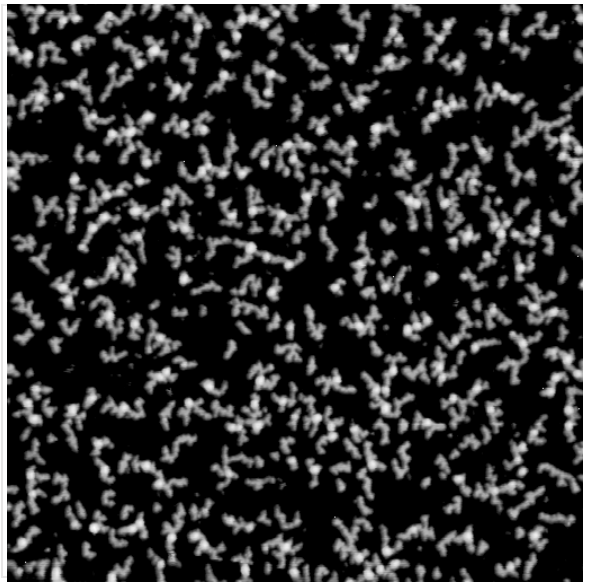
Co/Pt(111) T=270K
Activated adatom edge diffusion

Diffusion rate

Diffusion rate depends on the supporting substrate and on the deposited species

Fe

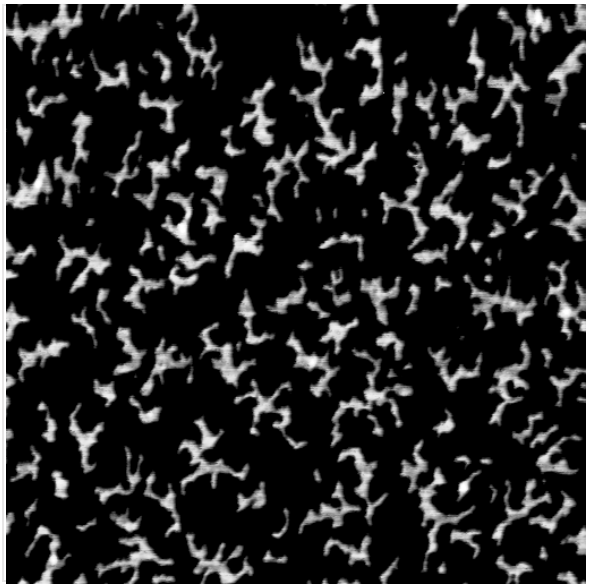
$\nu = \nu_0 \exp(-E_{Fe}/k_B T)$



Island size = 90 atoms/isl

Co

$\nu = \nu_0 \exp(-E_{Co}/k_B T)$



Island size = 390 atoms/isl

T_{dep} = 140 K

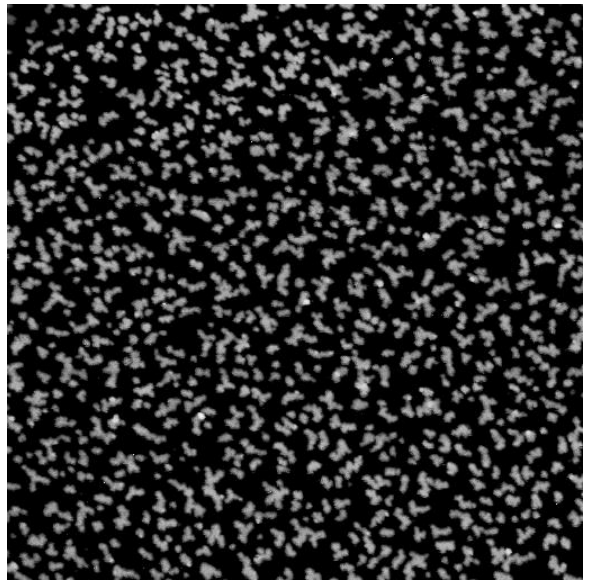
Θ = 0.25 ML

Substrate: Pt(111)

$E_{Fe} > E_{Co}$

How to form alloy clusters? How to form lattices?
With the help of patterned substrates and/or templates

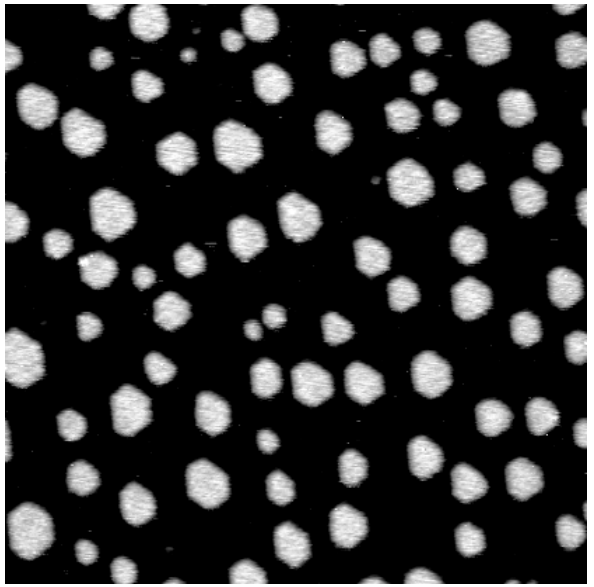
Epitaxial growth of two-dimensional alloys



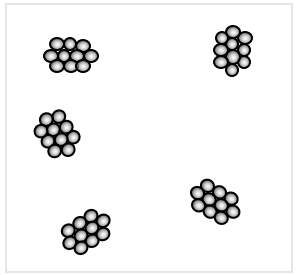
10 nm

Pt
T_{dep} = 200K
Θ = 0.2 ML

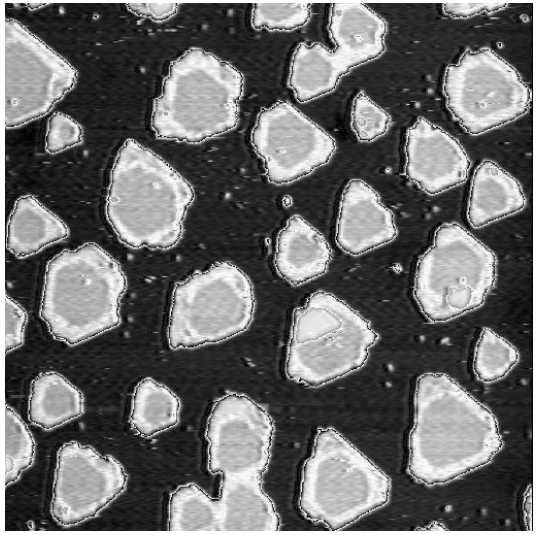
Annealing
to 800 K



10 nm



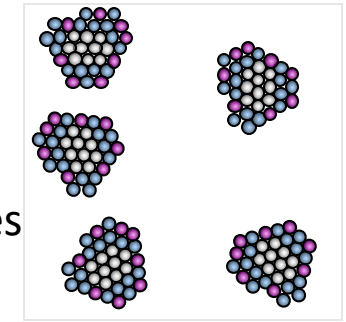
Pre-defined nucleation sites (seeds) to define the island density

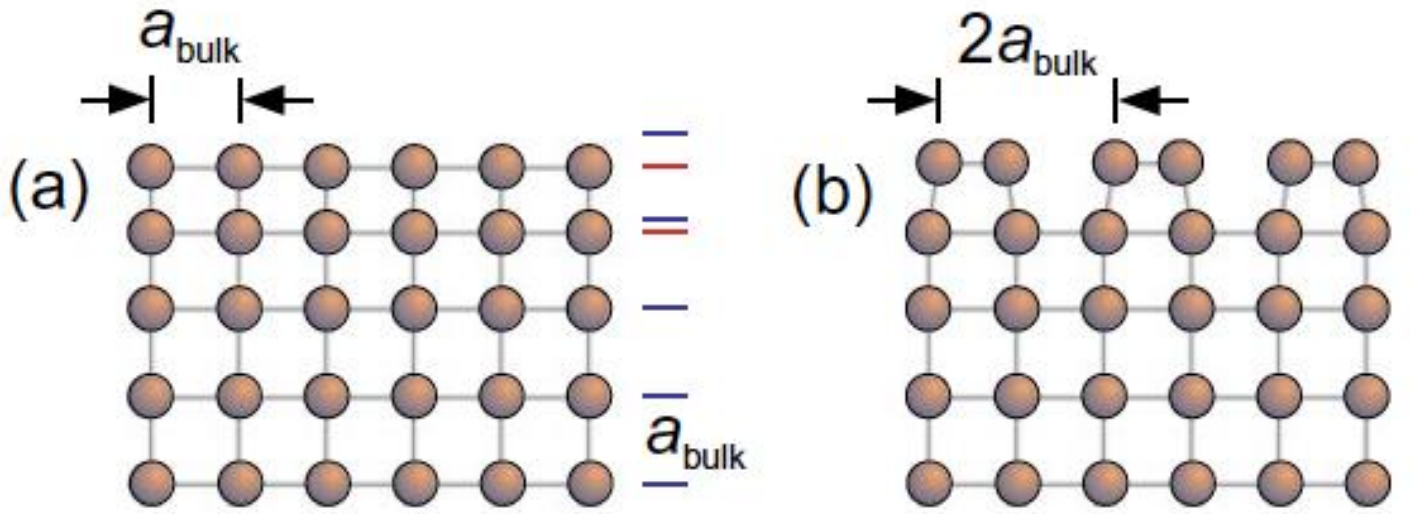


30 nm

Co_xFe_{1-x} decoration
T_{dep} = 250K
Θ = 0.2 ML

Growth of the alloyed nanostructures





rearrangements of surface (and near surface) atoms driven by the energetics of the system

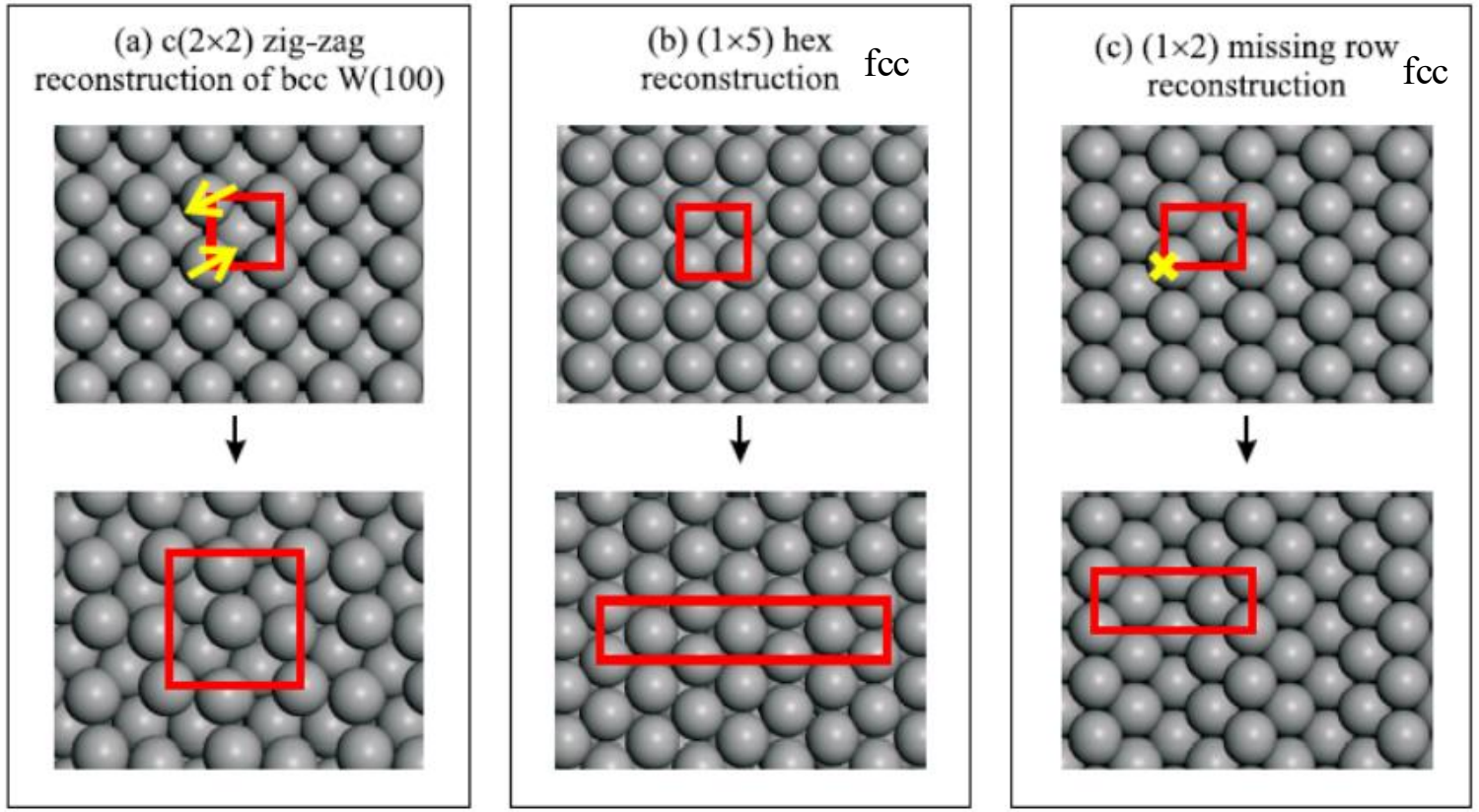
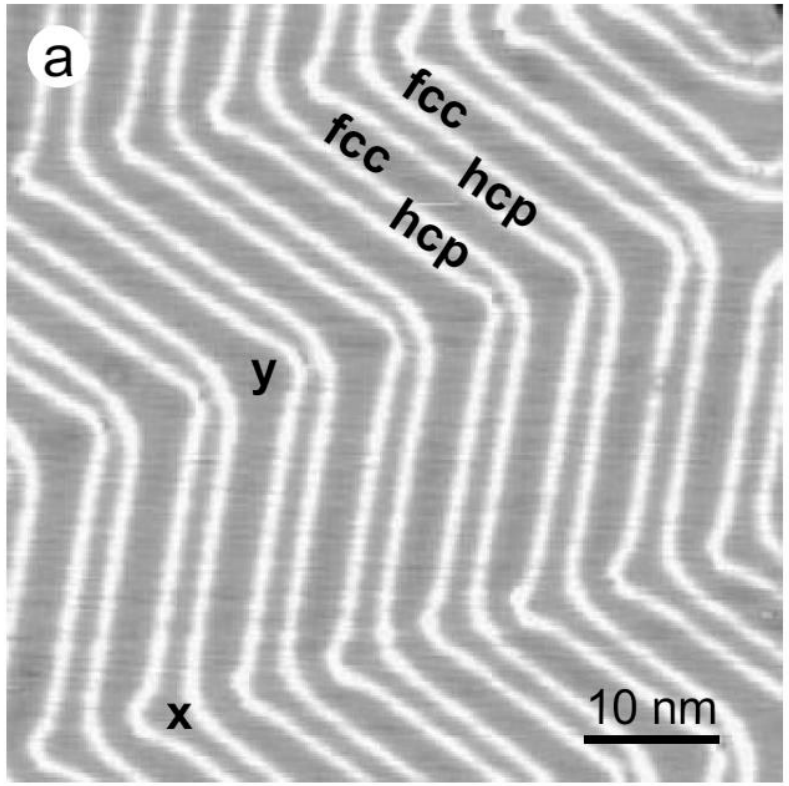
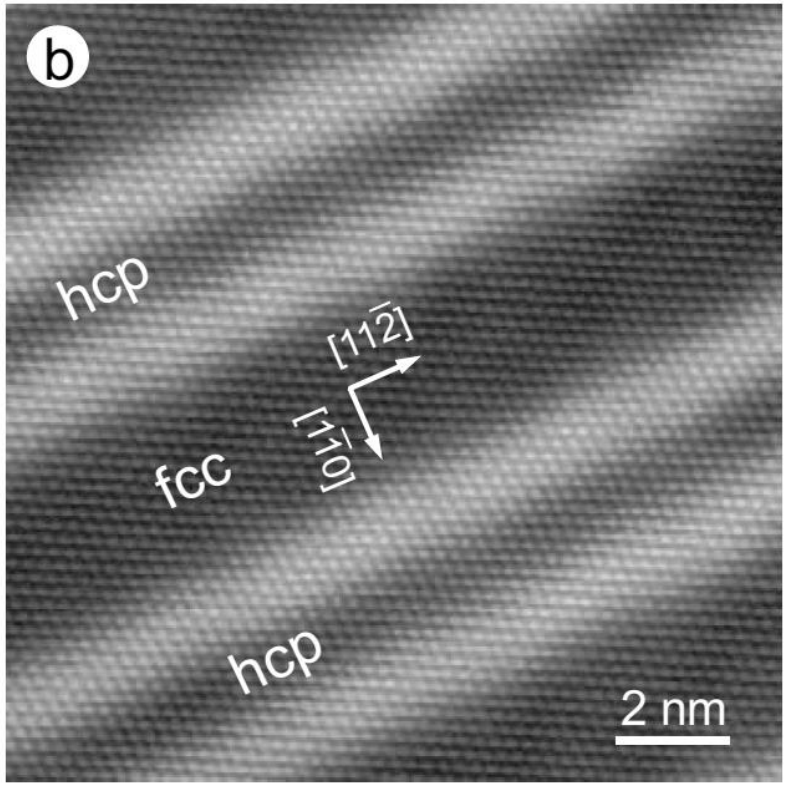


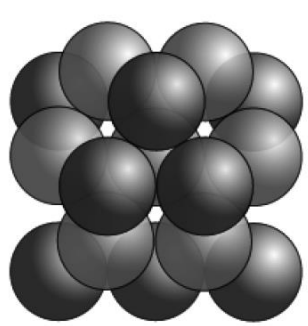
Figure 5.5. - Illustration of three bulk truncated surfaces and typical types of reconstruction that they undergo. (a) depicts the (1×1) to c(2×2) reconstruction of bcc W(100). The arrows indicate the direction in which the top layer W atoms move upon reconstruction. (b) displays an example of the "hex" reconstruction that the late 5d (fcc) transition metals undergo. The specific example is the (1 × 1) to (1 × 5) reconstruction of fcc Ir(100). (c) displays the (1 × 1) to (1 × 2) "missing row" reconstruction that occurs on the (110) surfaces of the late 5d (fcc) transition metals. The rows of atoms removed by the reconstruction are indicated by the × at the edge of the unit cell.

Michele Romeo,
PhD Thesis 2015, University of Trieste

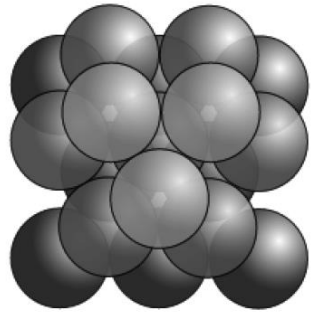
Au(111): herringbone reconstruction





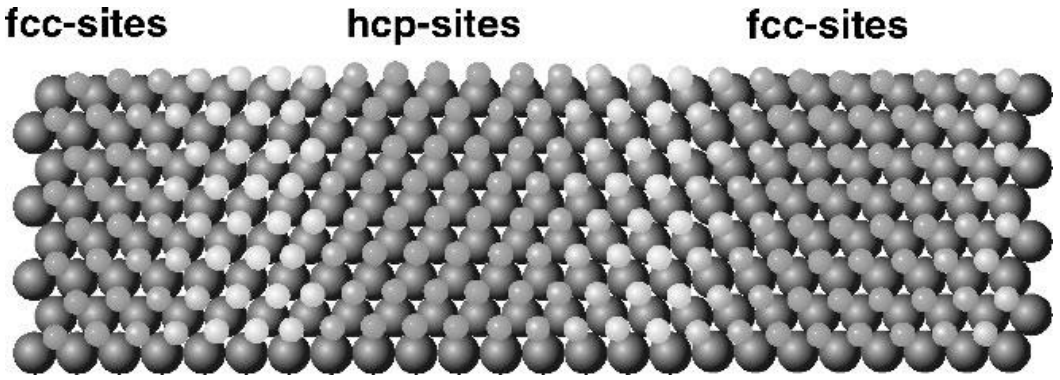


hcp: ABA



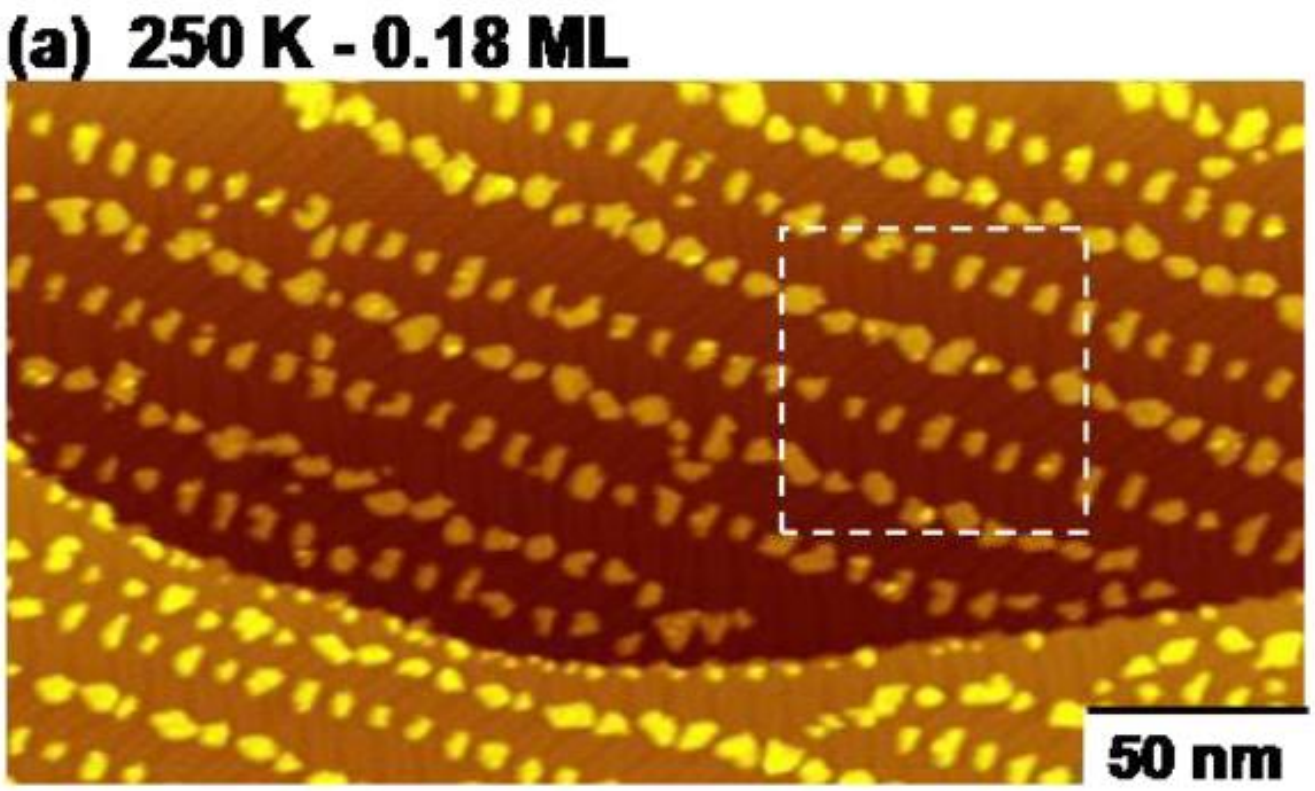
fcc: ABC

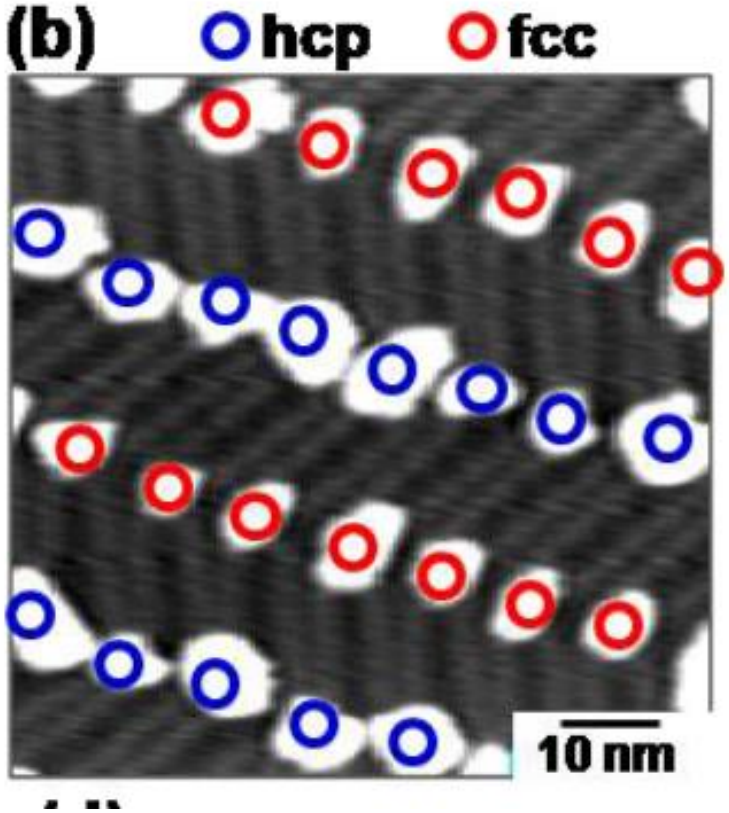
Figure 3.1: STM image showing the herringbone reconstructed Au(111) surface. a) Alternating fcc and hcp stacking domains, as well as *x*- and *y*-type elbows are visible. b) Atomically resolved STM image, revealing the slightly distorted hexagonal arrangement of the surface atoms together with the domain walls separating fcc and hcp stacking. The interatomic distances along $[11\bar{2}]$ and $[1\bar{1}0]$ are 2.88 Å and $\approx$ 2.75 Å, respectively. (Tunneling parameters: a) $V = -0.7$ V, $I = 0.2$ nA; b) $V = -0.02$ V, $I = 1.3$ nA)



M.-Ch. Blüm, PhD Thesis EPFL 2006

Au(111) herringbone reconstruction - Nucleation



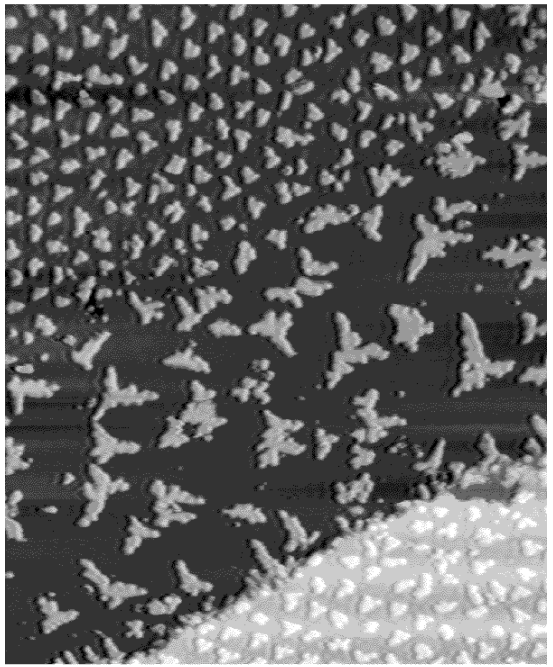


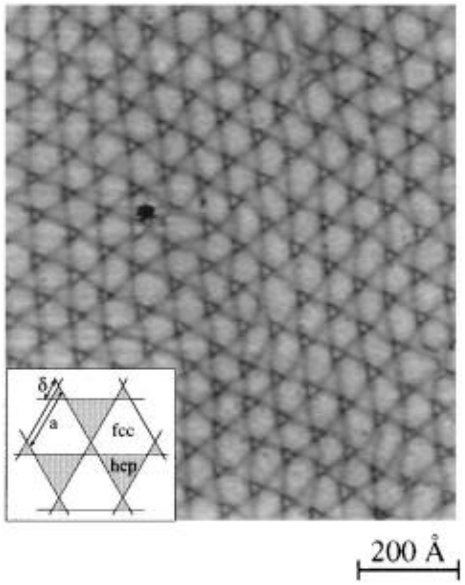
0.18 ML Fe deposited at 250 K
islands nucleate at the elbows of the reconstruction

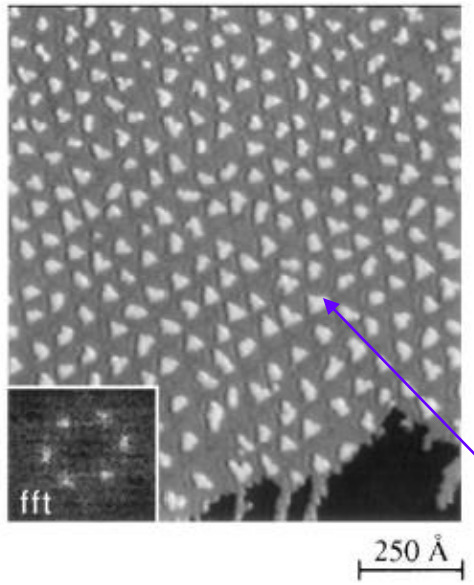
Nanotechnology **21,** 015606 (2010)

Self assembled nanostructure arrays on patterned substrate

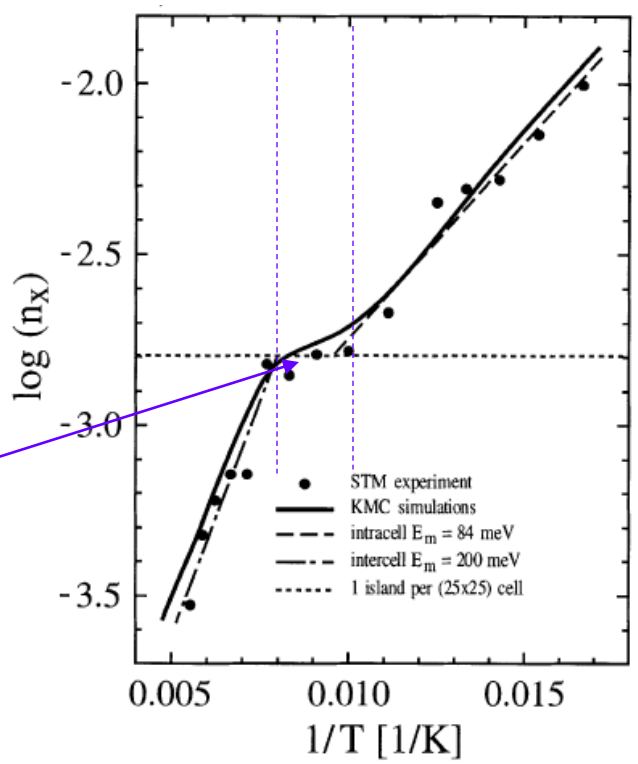
Nucleation of an Ag island superlattice (T_{dep} = 110 K) on the dislocation network formed by 2 ML of Ag on Pt(111)





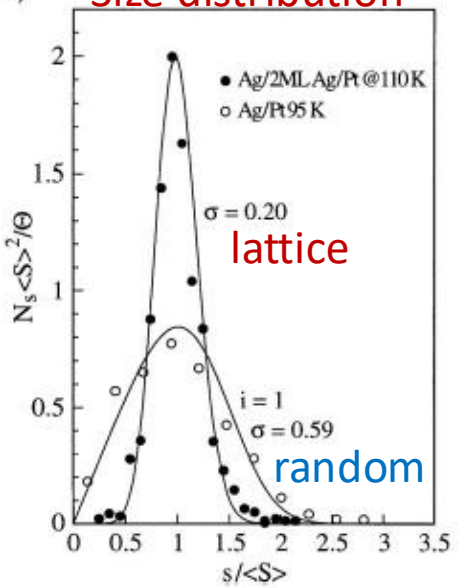


Confinement: range of T where the island density (n_x) does not change

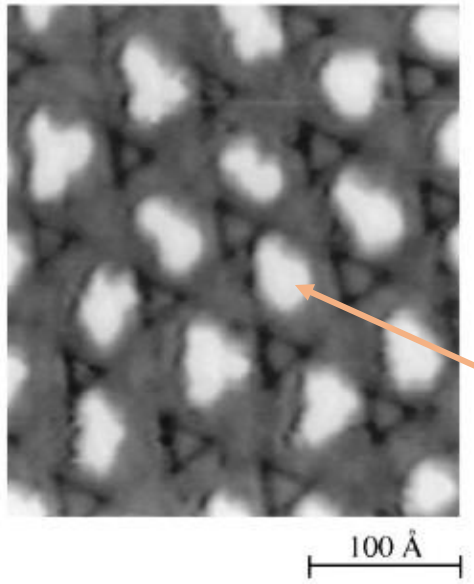


Almost monodispersed size distribution thanks to the template effect of the dislocation network

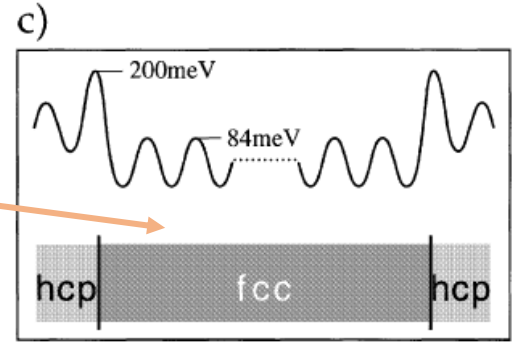
c) Size distribution



d)



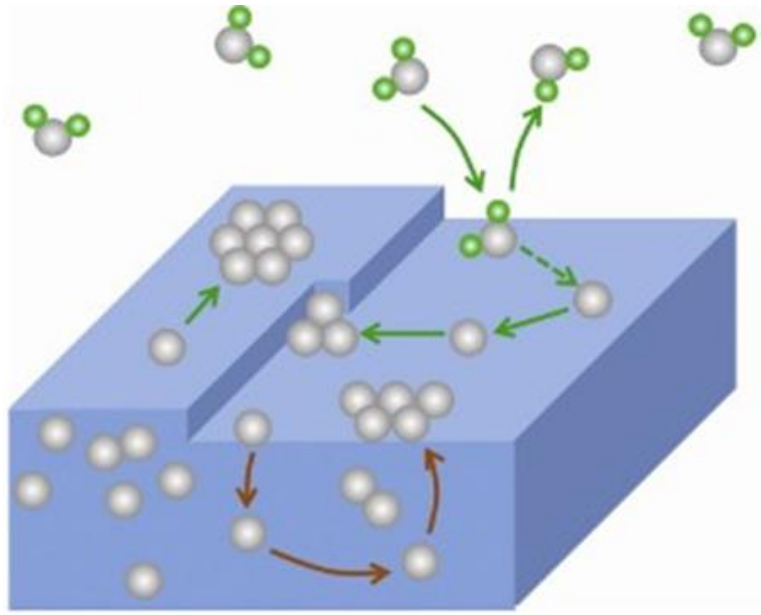
Atoms are confined in the fcc stacking areas



H. Brune *et al.* Nature **394**, 451 (1998);
H. Brune Surf. Sci. Rep. **31**, 121 (1998);

Graphene growth by CVD (chemical vapor deposition)

hydrocarbon flux



Hydrogen

Carbon

Hydrocarbon molecules dissociate on the hot surface: H atoms leave the surface while C atoms organize in the honeycomb lattice of graphene

Ex of hydrocarbons:

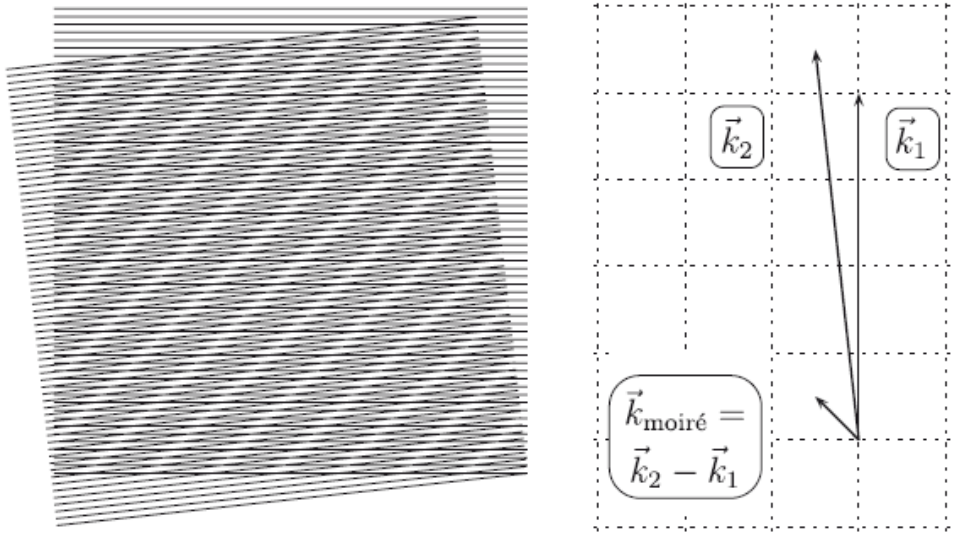
CH_2 Methylene

C_2H_4 Ethylene

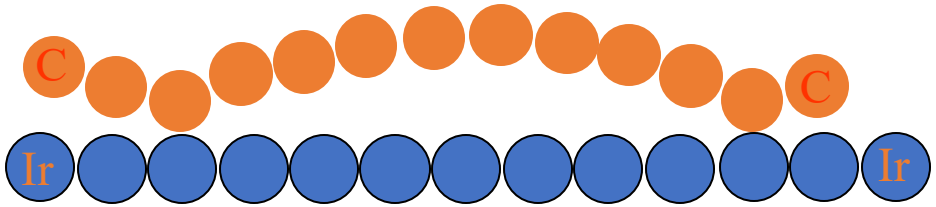
Note: C atoms dissolved in the bulk segregate to the sample surface and can contribute to form graphene

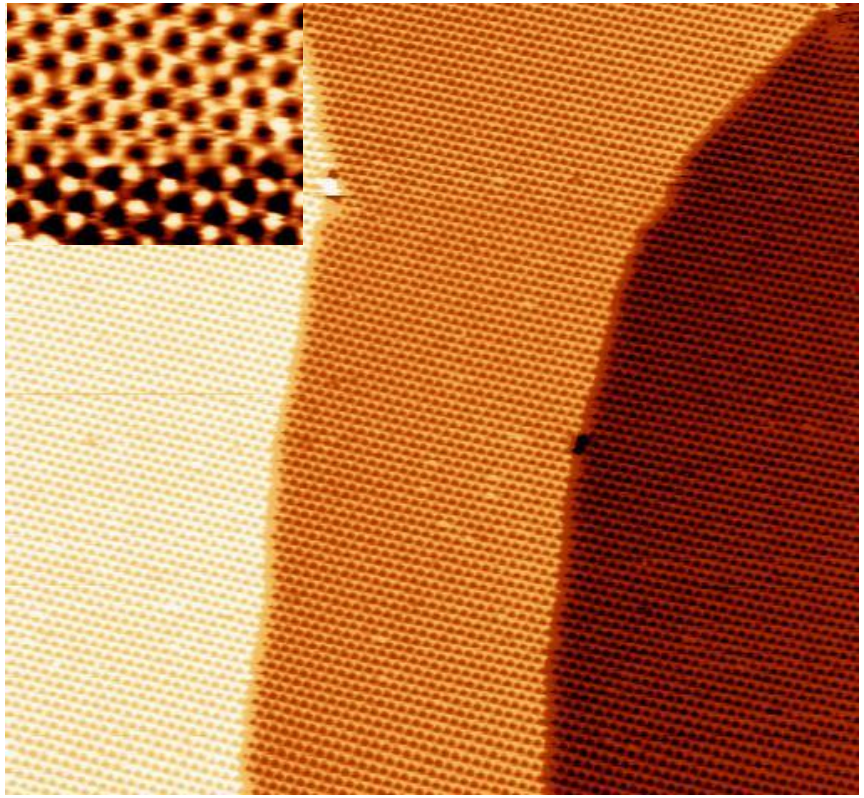
Moiré pattern due to graphene-Ir(111) lattice mismatch

A moiré is a superposition of two lattices generating a third one.



a_{Ir} = 0.27 nm
a_c = 0.245 nm





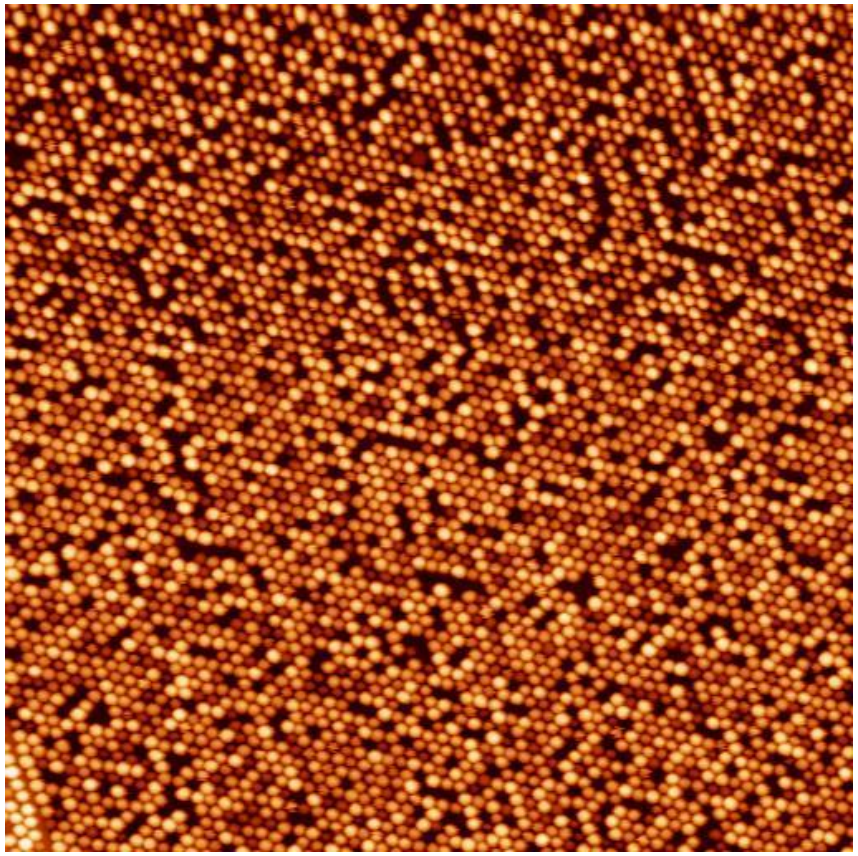
180 x 200 nm^2

Supercell with (10x10) C atoms on (9x9) Ir substrate atoms

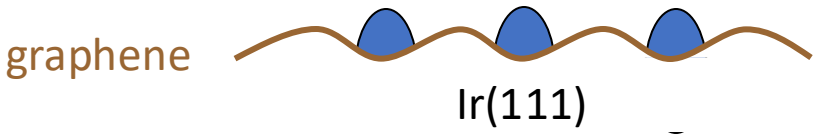
A. T. N'Diaye *et al.* New. J. Phys. **10**, 043033 (2008); A. T. N'Diaye *et al.* Phys. Rev. Lett. **97**, 215501 (2006)

Core-shell nanostructure arrays on graphene/Ir(111)

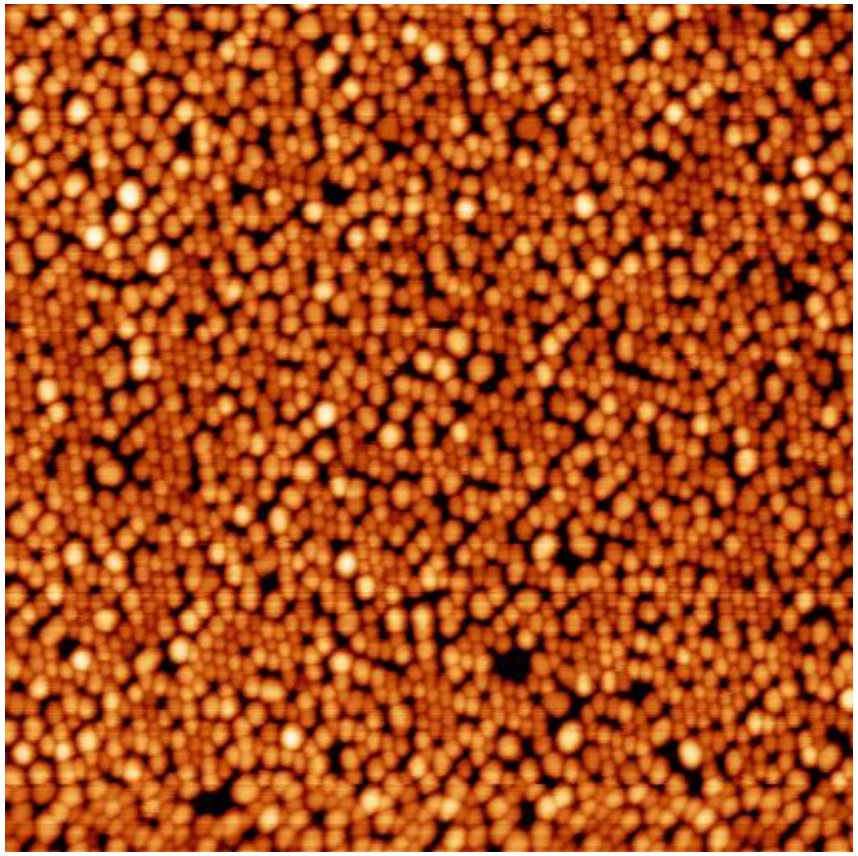
Ir island
Ir deposition: T = 375 K



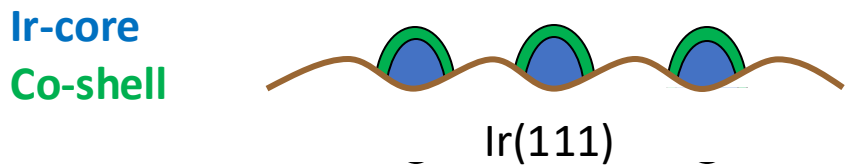
150 x 150 nm^2



Ir-core **Co**-shell islands
Ir deposition: T = 375 K
Co deposition: 1 ML, T = 300 K



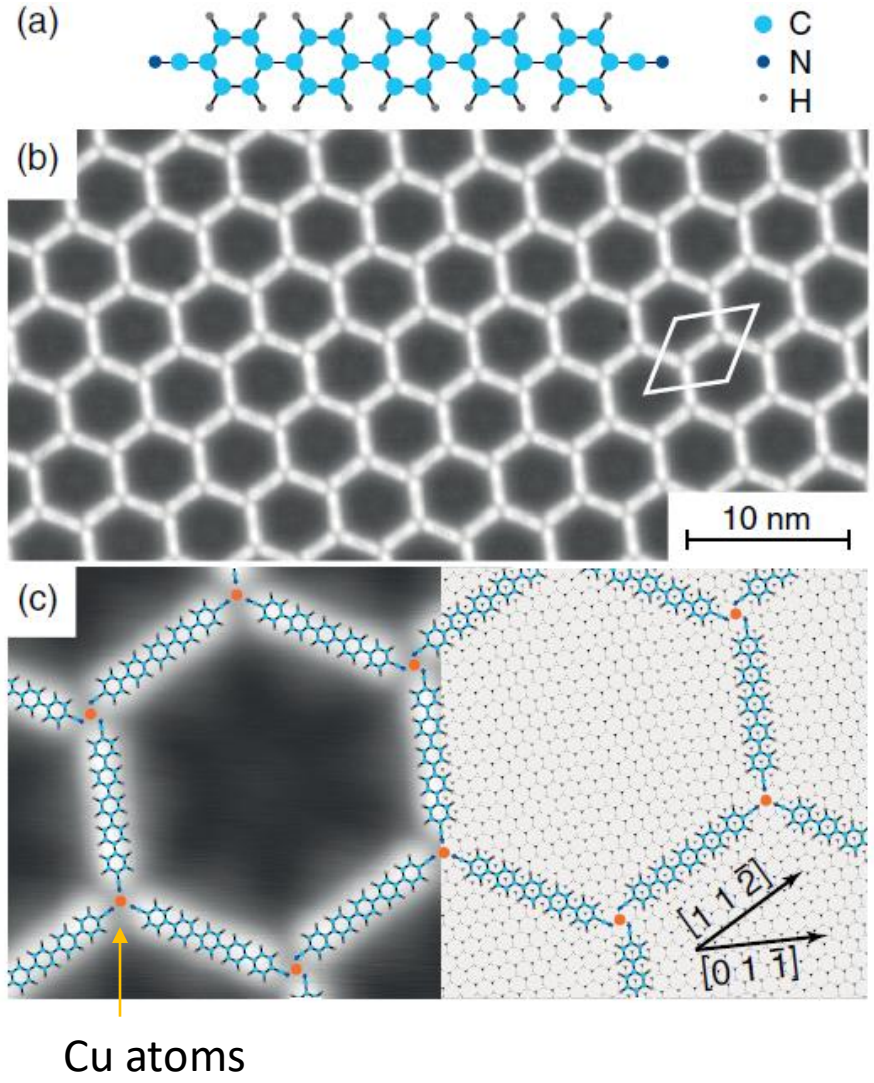
150 x 150 nm^2



S. Rusponi unpublished; A. T. N'Diaye *et al.* Phys. Rev. Lett. **97**, 215501 (2006)

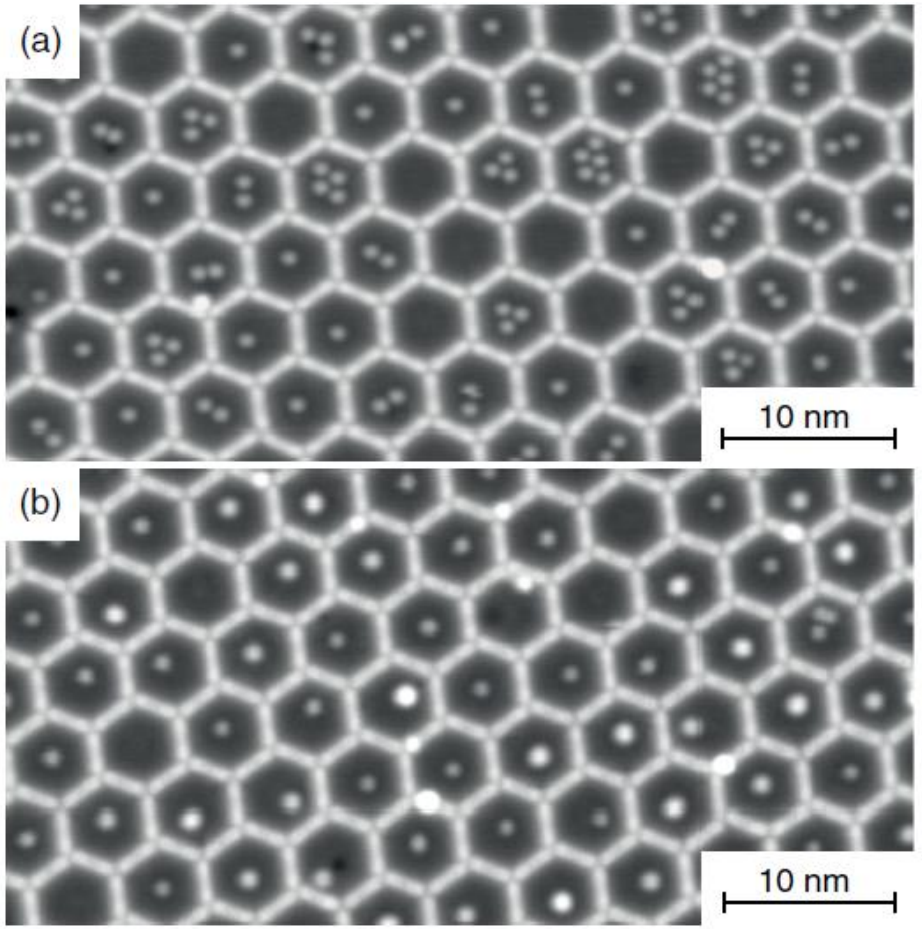
Exercise 5.5

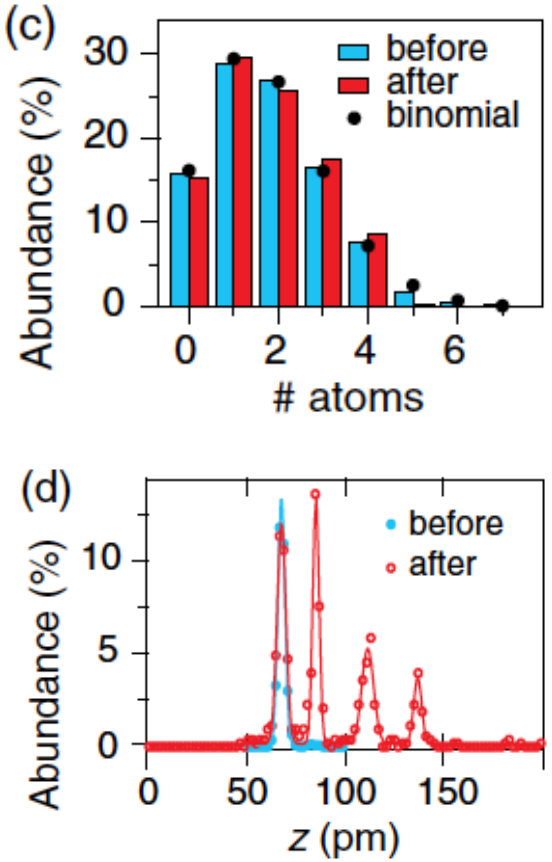
Metal organic quantum box network on Cu(111)



Cu atoms

a) Fe deposition at T = 10K





b) cluster formation after annealing to T_{ann} = 18K

Phys. Rev. Lett. **110**, 086102 (2013)