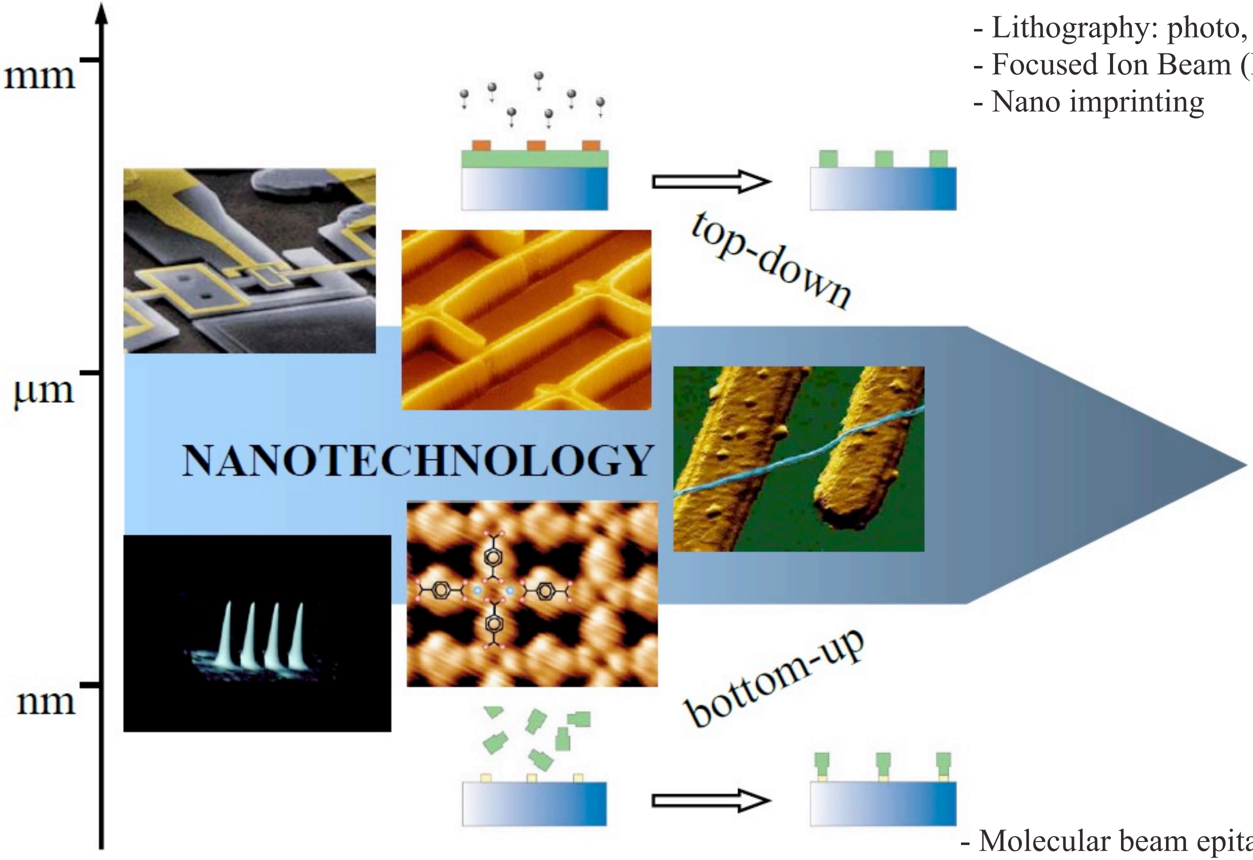
How to make the nanostructures: two approaches

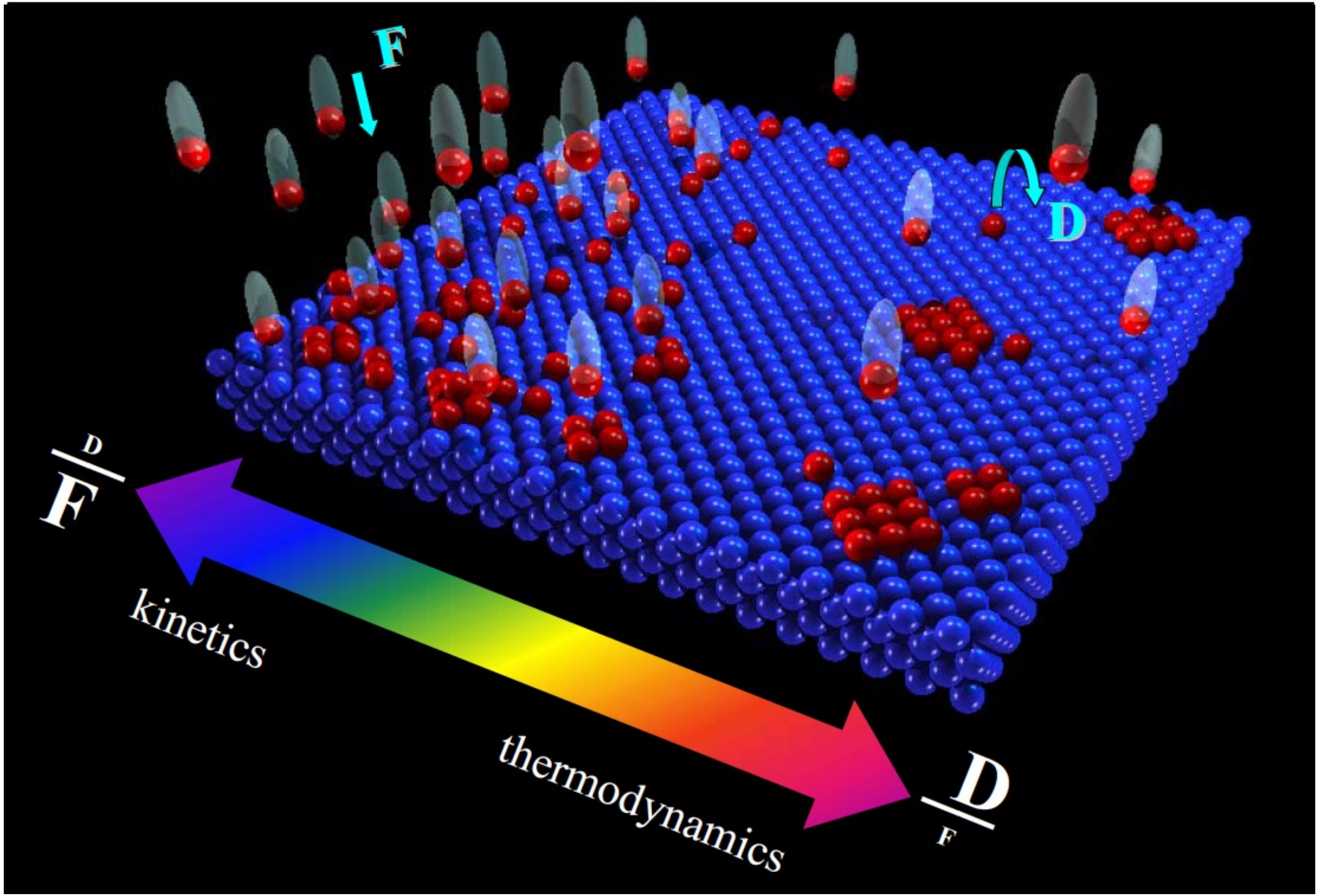
- Lithography: photo, UV, e-beam
- Focused Ion Beam (FIB)
- Nano imprinting



- Molecular beam epitaxy (MBE)
- Self assembly
- Chemical vapor deposition (CVD)
- Atomic manipulation (STM)

K. Kern courtesy

Thin film growth / Nanostructure growth



K. Kern courtesy

Surface tension, surface energy and equilibrium surfaces

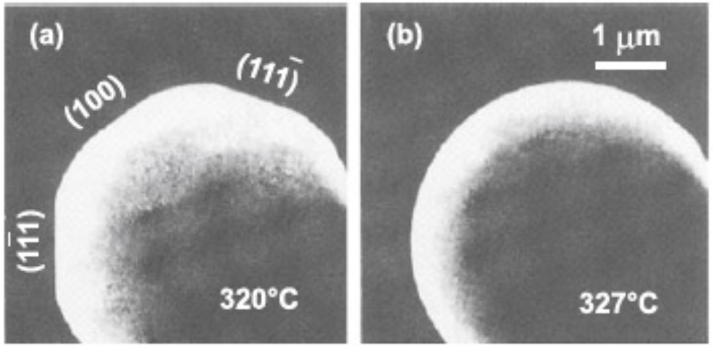
from bulk, creation of a surface (atoms that are not fully coordinated, i.e. broken bonds) → additional energy term γ: surface energy per unit surface (surface tension)

$\gamma > 0$ 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: $\gamma(\vec{n})$

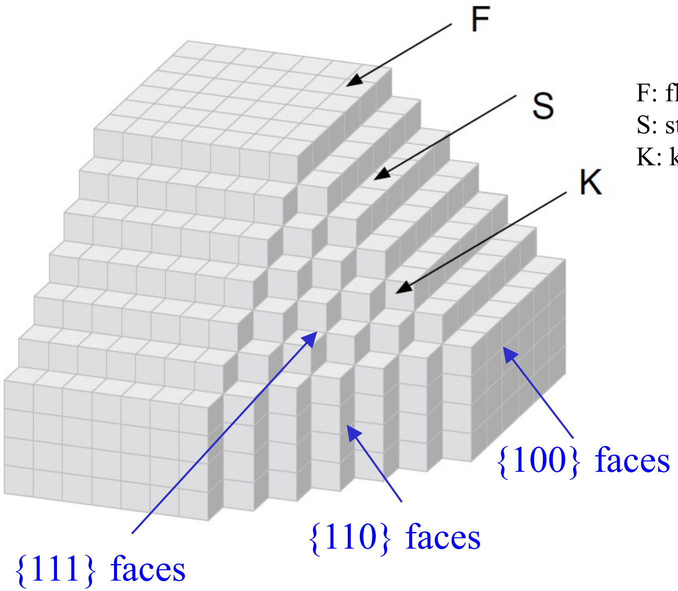


SEM photographs of the equilibrium shape of Pb crystals in the [011] azimuth; in b) Pb is liquid
J.J. Métois & J.C. Heyraud, **31**, 73 (1989)

Kossel crystal – TLK model

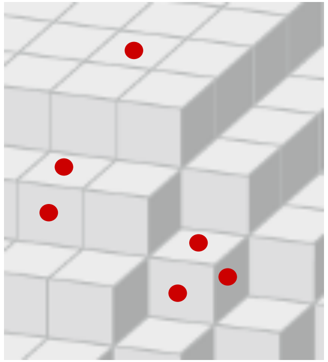
different crystal orientation → different surface energy

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

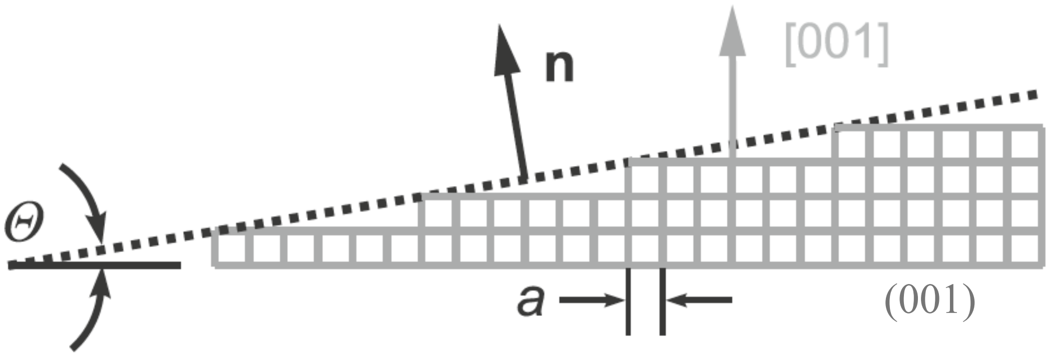


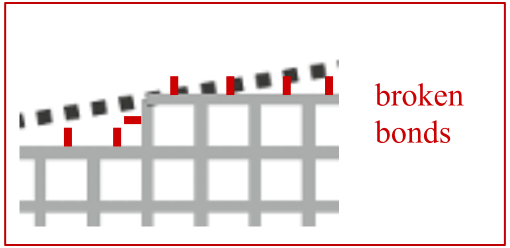
F: flat, terrace
S: step, ledge
K: kink

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)



Vicinal surfaces (stepped)

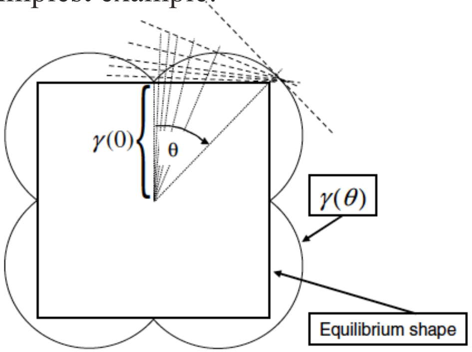




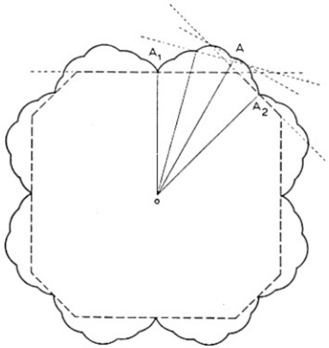
Wulff construction / γ plot

- The surface energy of a vicinal surface always exceeds that of the corresponding singular surface
- From $\gamma(\theta)$ → equilibrium crystal shape
- Experimentally: from crystal shape → surface energy

simplest example:



more realistic:

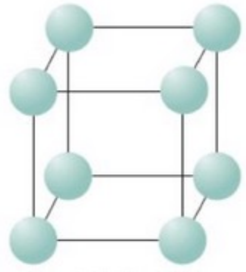


Surface tension for cubic crystals

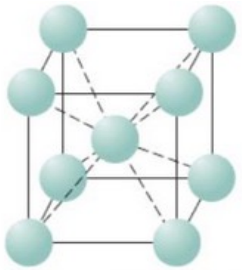
considering the number of broken bonds per unit surface, for singular (low-Miller index) surfaces:

conventional unit cell

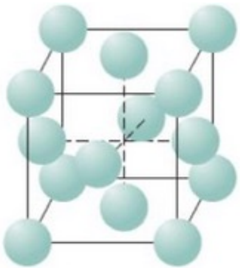
sc: $\gamma_{100} < \gamma_{110} < \gamma_{111}$



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

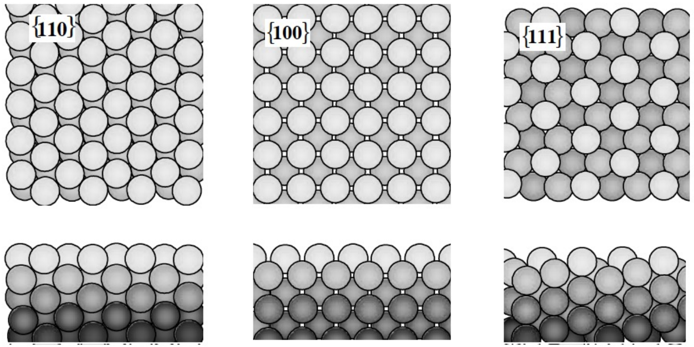


fcc: $\gamma_{111} < \gamma_{100} < \gamma_{110}$

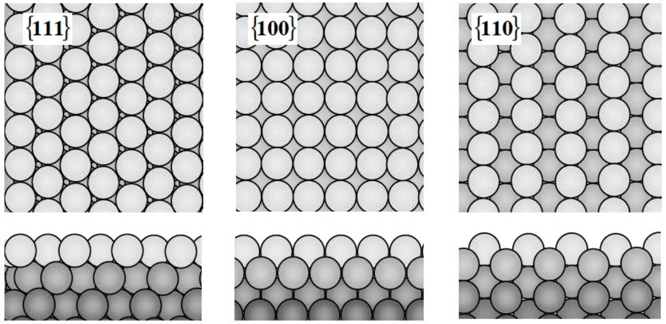


in general, the more compact the surface, the lower the energy

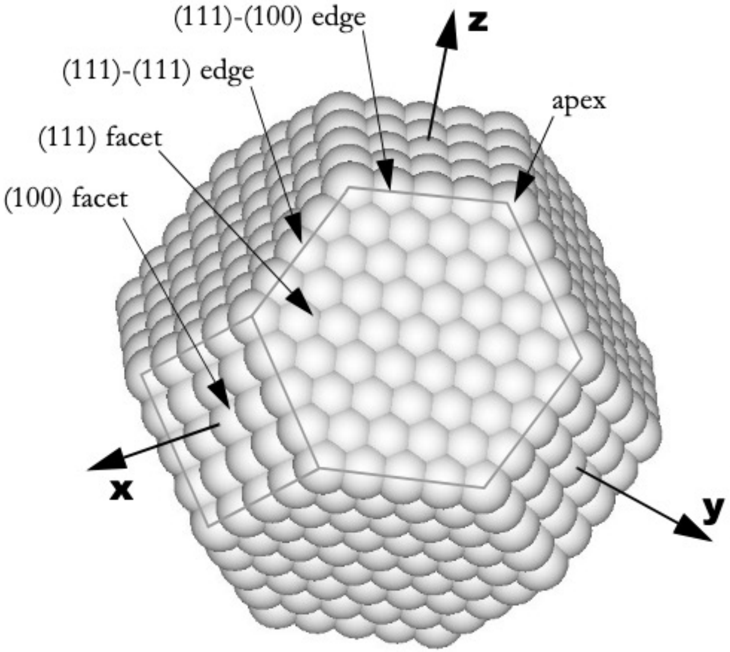
bcc



fcc



Equilibrium crystal shape



1289 atoms, truncated octahedron
surface:volume ratio = 482:807

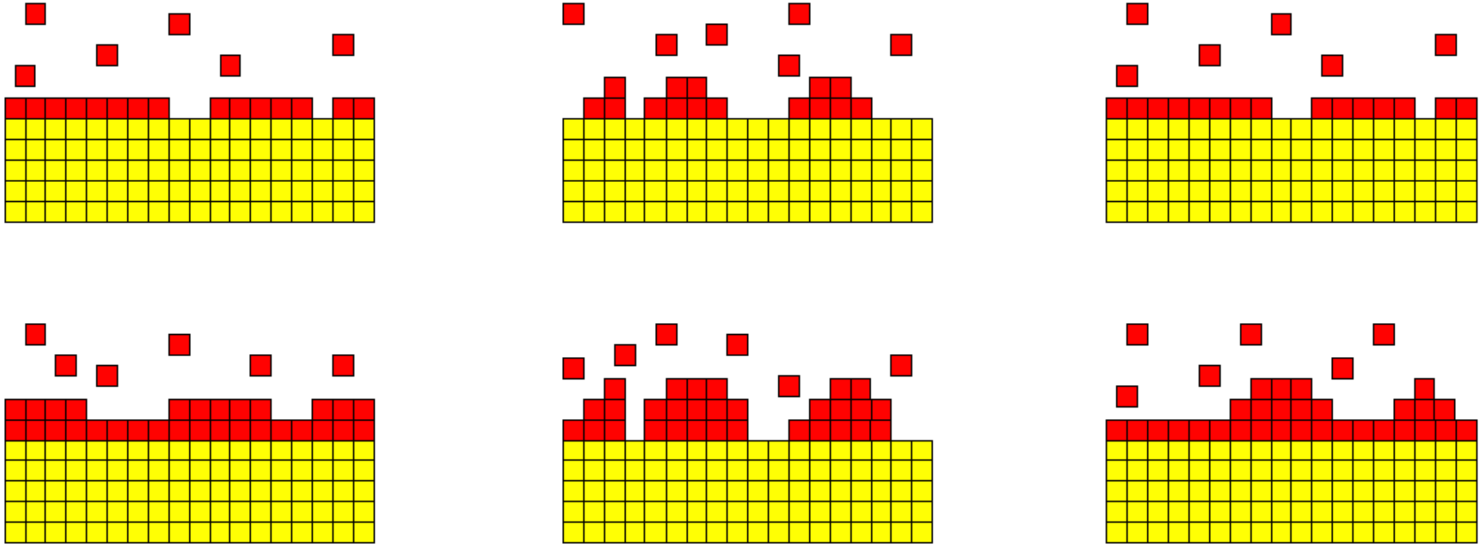
Facts and Figures:

- 482 surface atoms
- 8 (111)-facets
- 6 (100)-facets
- 24 apex positions
- 54 atoms on a (100)-surface (excluding edges)
- 296 atoms on a (111)-surface (excluding edges)
- 36 atoms form a (111)-(111) edge
- 72 atoms form a (100)-(111) edge

Warning: the broken bond model for surface energy neglects the relaxation in positions of the atoms near the surface of a crystal (discussed later)

Growth modes (at thermodynamic equilibrium)

Growth of B on A



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

island growth
(Volmer - Weber)

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

surface energy

surface energy & strain

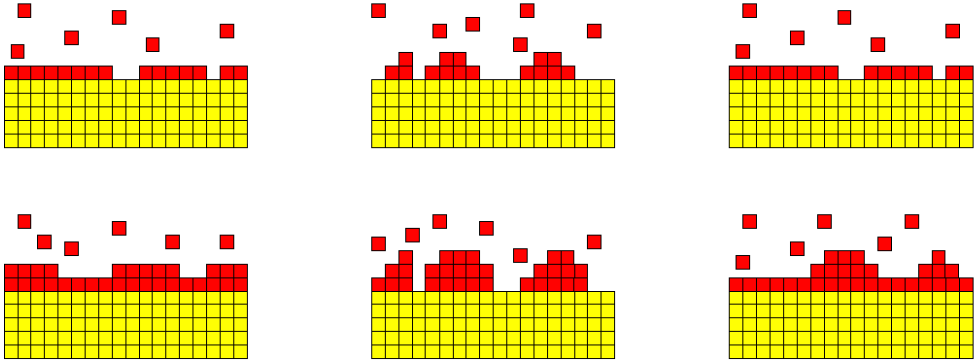
Growth modes (at thermodynamic equilibrium)

Growth of B on A

γ_A: surface energy of A (interface with vacuum)

γ_B: surface energy of B (interface with vacuum)

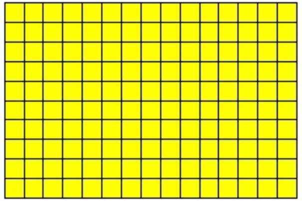
γ_{AB}: A-B interface energy (hybridization, lattice mismatch,...)



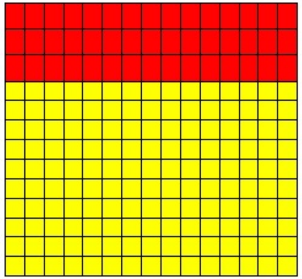
layer - by - layer growth (Frank - van der Merve)	island growth (Volmer - Weber)	layer - by - layer + island growth (Stranski - Krastanov)
$\gamma_B + \gamma_{AB} \leq \gamma_A$	$\gamma_A < \gamma_B + \gamma_{AB}$	$\gamma_B + \gamma_{AB} < \gamma_A$ at the beginning, but γ_{AB} increases with coverage (typically due to strain) $\rightarrow$ change from 2D to 3D

Stranki-Krastanov growth of semiconductor quantum dots

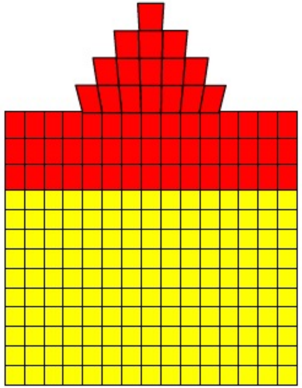
lattice parameters don’t match $a_B > a_A$



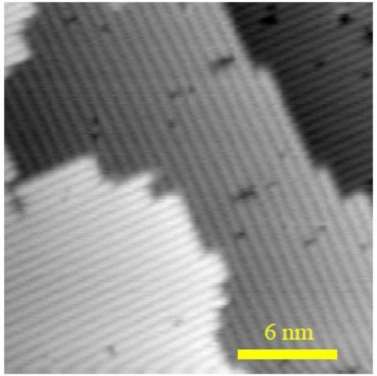
substrate



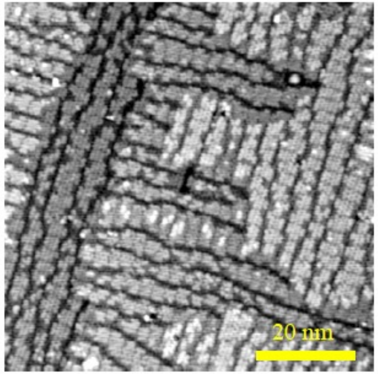
wetting layer



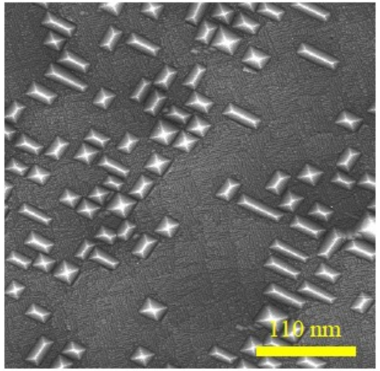
islands



Si(001)



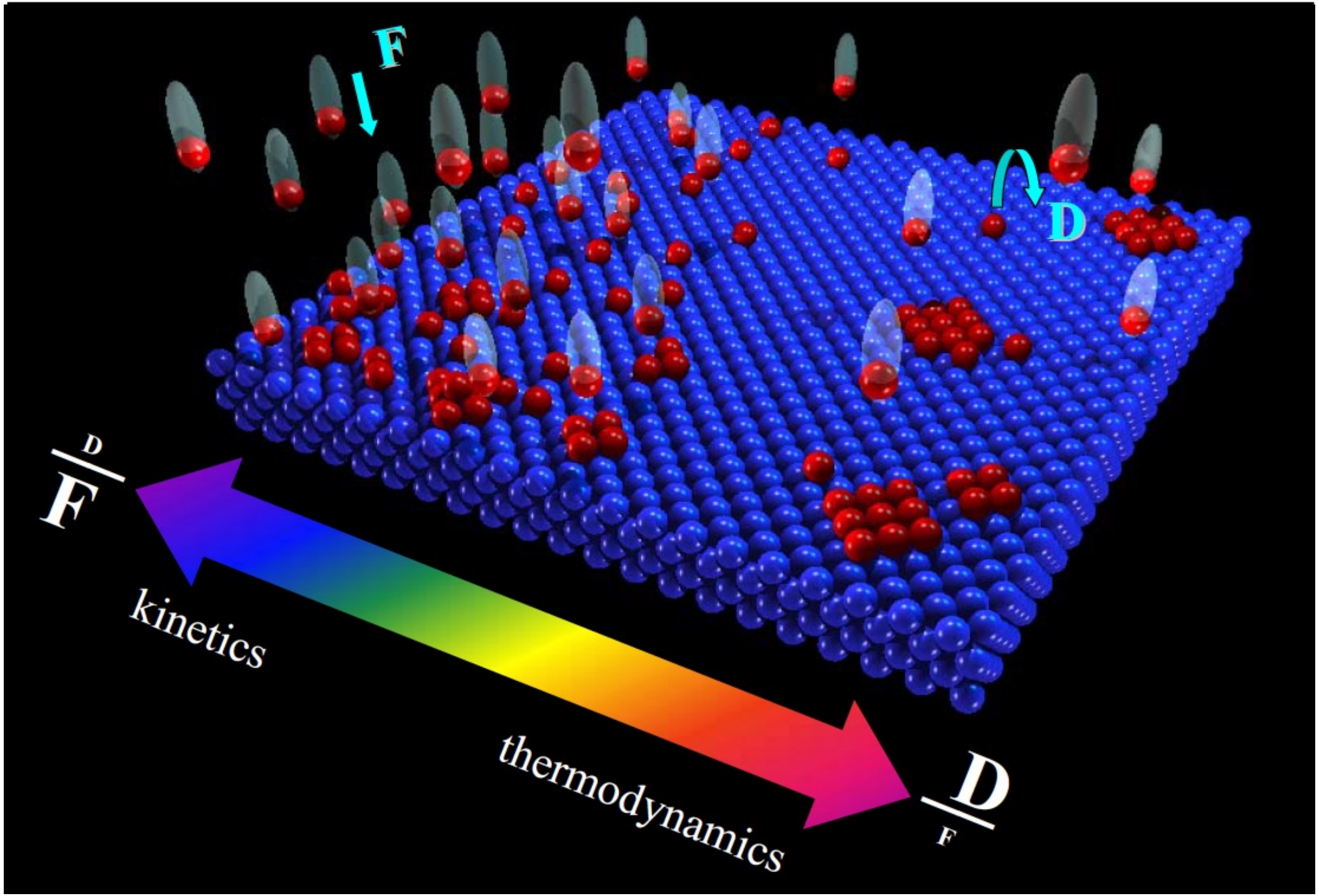
3ML Ge on Si(001)



6ML Ge on Si(001)

exact shape: balance between surface energy, strain energy, and volume

Thin film growth / Nanostructure growth



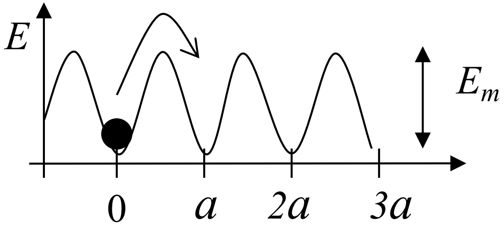
K. Kern courtesy

Growth as a non-equilibrium process: kinetics

single crystal surfaces: a 2D laboratory

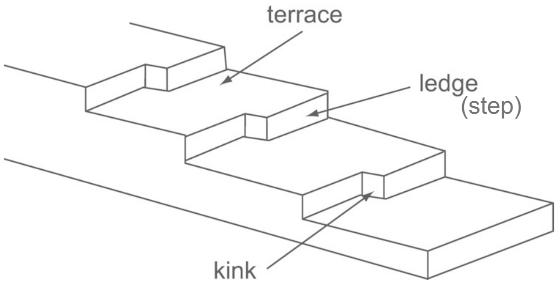
each process i has
an energy barrier E_i and a rate ν

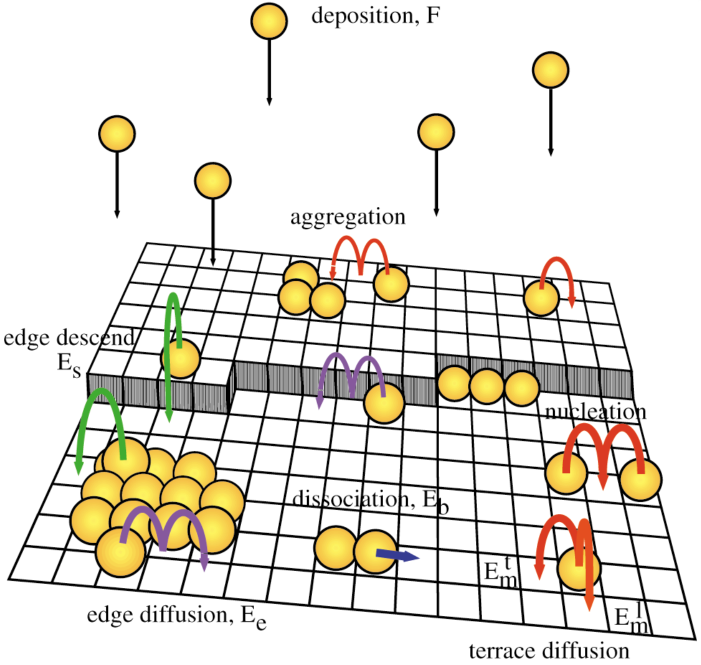
$$\nu = \nu_0 \exp(-E_i/k_B T)$$



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

Aim: controlling

- mean size (size distribution)
- density
- shape
- composition

Control parameters:

- substrate temperature $\boldsymbol{T}$
- deposition flux $\boldsymbol{F}$
- surface coverage $\boldsymbol{\Theta}$
- substrate/overlayer material (strain, mixing, etc.)
- substrate symmetry or patterning

Statistical growth: $T \rightarrow 0$ K

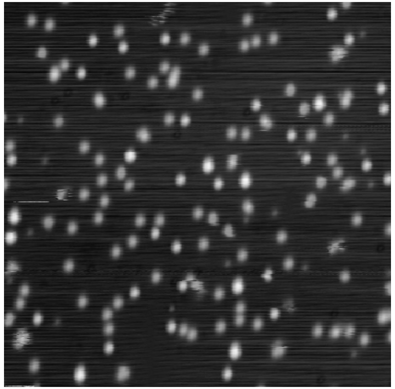
- thermally-activated diffusion is frozen

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

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

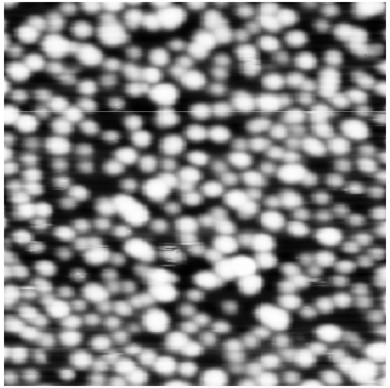
Co/Pt(111)

0.03 ML, T = 50 K:
n = 1.2



50 Å

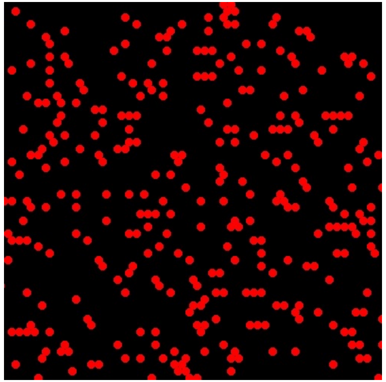
0.10 ML, T = 50 K:
n = 2.9

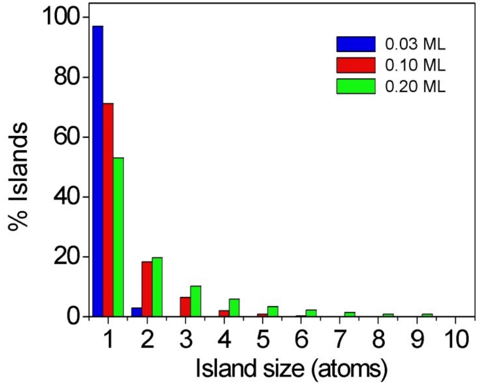


50 Å

n = mean island size = coverage/island density

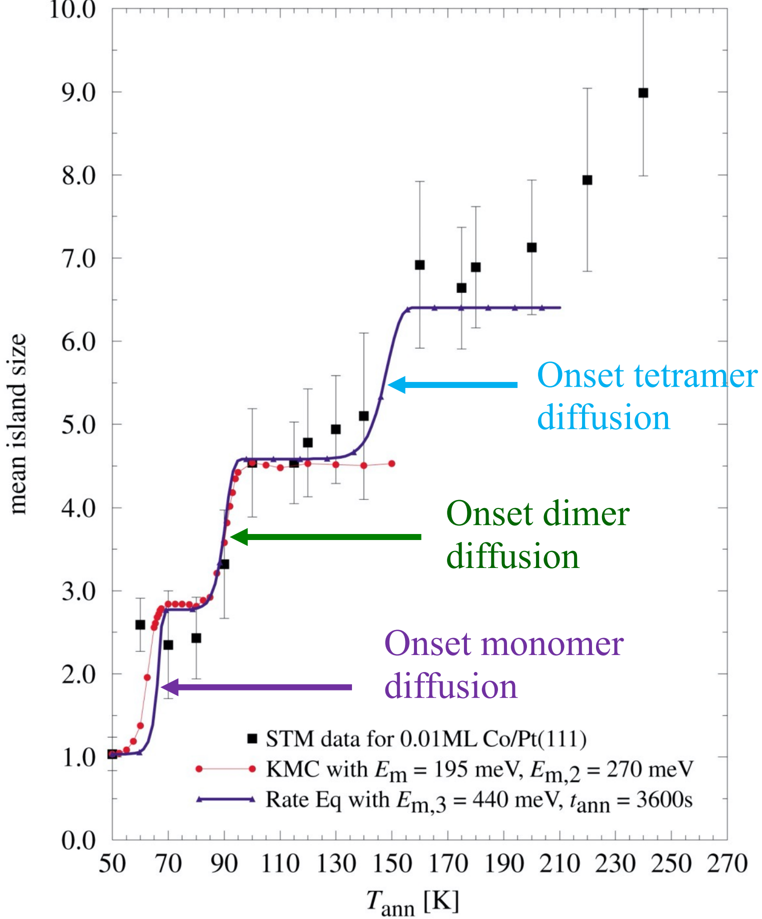
Kinetic Monte Carlo simulation



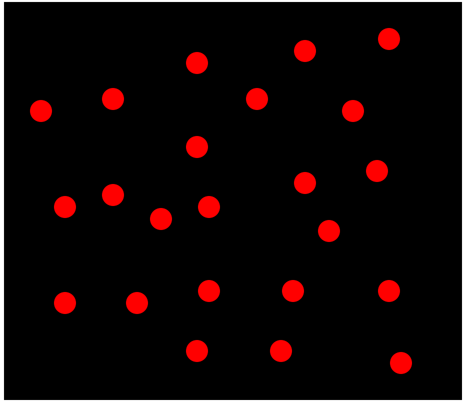


Adatom and cluster diffusion

Ex: Co/Pt(111)



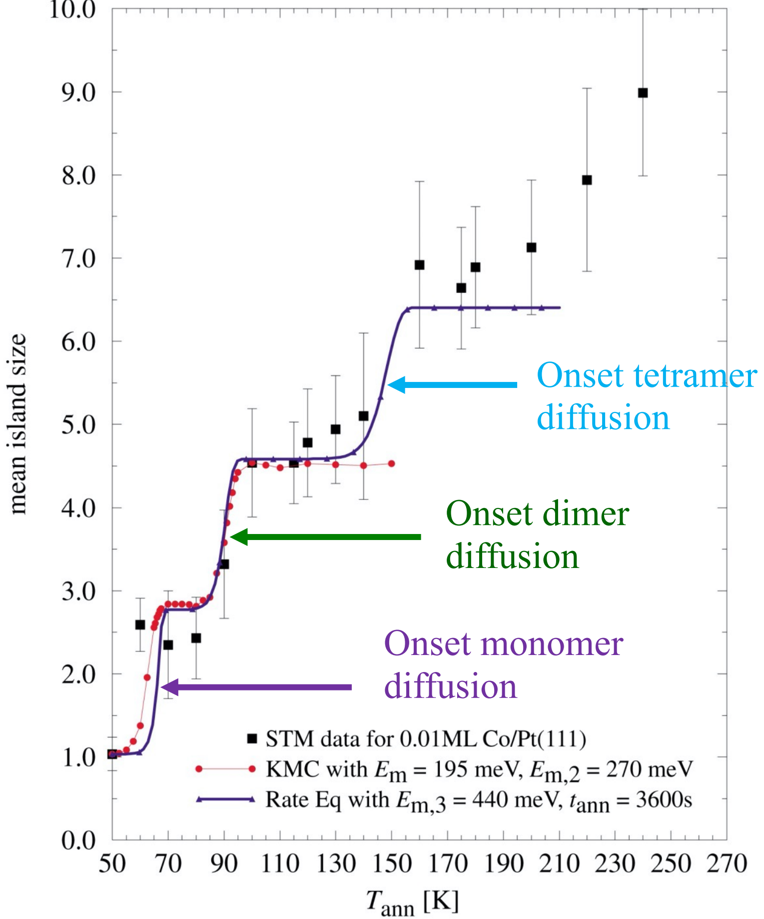
T < 60 K: monomers



S. Rusponi *et al.* unpublished

Adatom and cluster diffusion

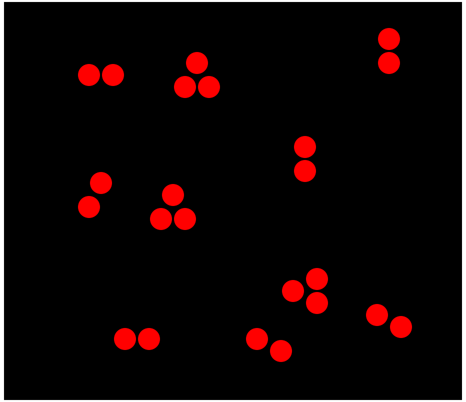
Ex: Co/Pt(111)



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

$T < 60$ K: monomers

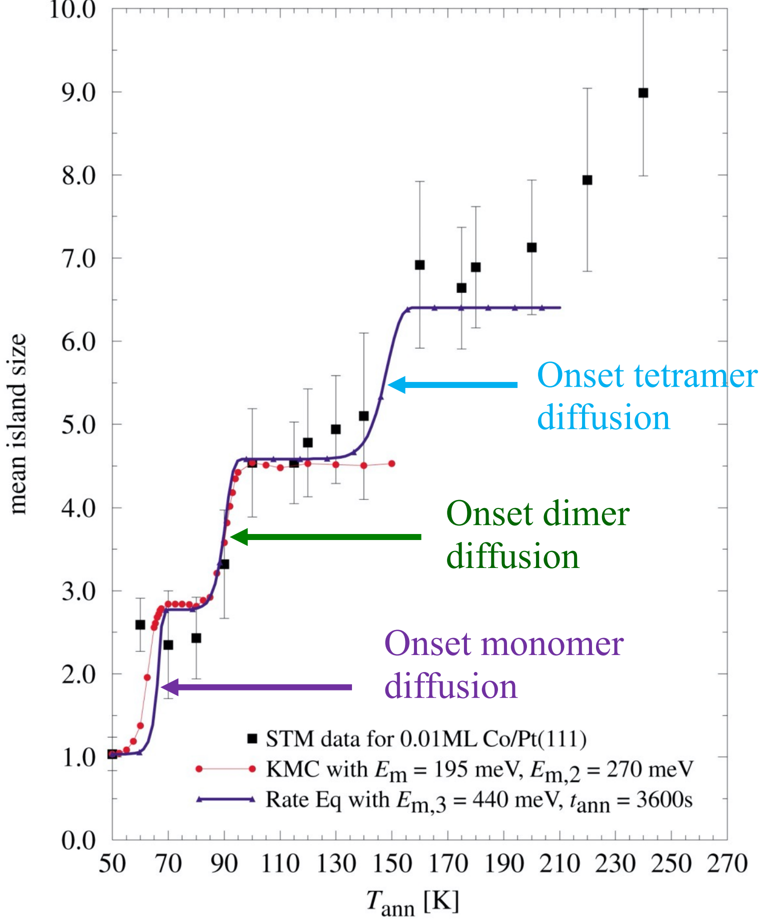
60 K $< T <$ 90 K: dimers and trimers



S. Rusponi *et al.* unpublished

Adatom and cluster diffusion

Ex: Co/Pt(111)

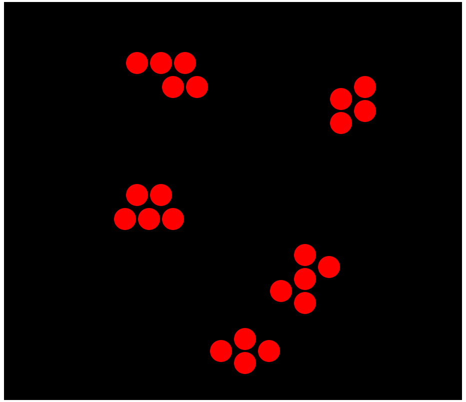


By increasing T, sequential activation of cluster diffusion results in size selection:

$T < 60$ K: monomers

60 K $< T <$ 90 K: dimers and trimers

100 K$< T <$ 130 K: tetramers and pentamers



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

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

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

σ_1 and σ_x capture rates

E_1 is the diffusion energy barrier of a monomer (i=1)

Rate equations give the formation rate for adatoms and stable islands

Island density

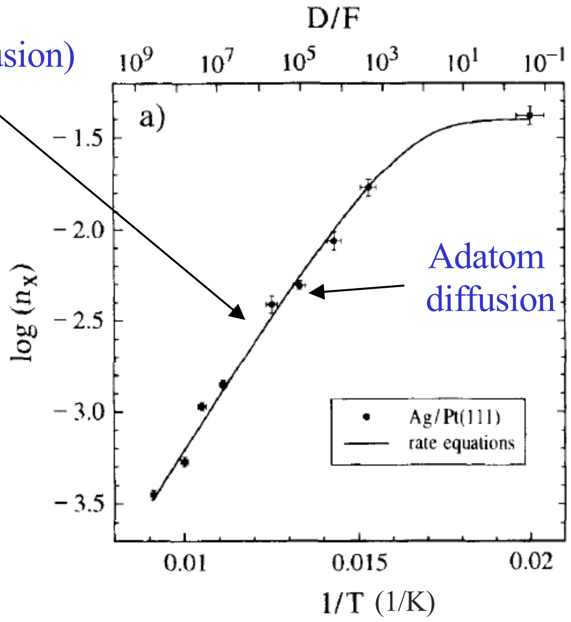
$$n_x = \eta(\theta, i)\left(\frac{D}{F}\right)^{-\chi} \exp\left(\frac{E_i^c}{(i+2)k_BT}\right) \qquad D = D_0 \exp\left(-\frac{E_1}{k_BT}\right) \qquad \chi = \frac{i}{i+2}$$

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

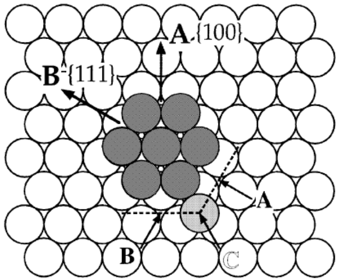
$$i = 1 \quad \rightarrow E_i^c = 0 \quad \rightarrow \quad n_x = \eta(\theta, 1)\left(\frac{D}{F}\right)^{-1/3} = \eta(\theta, 1)\left(\frac{D_0}{F}\right)^{-1/3} \exp\left(\frac{E_1}{3k_BT}\right)$$

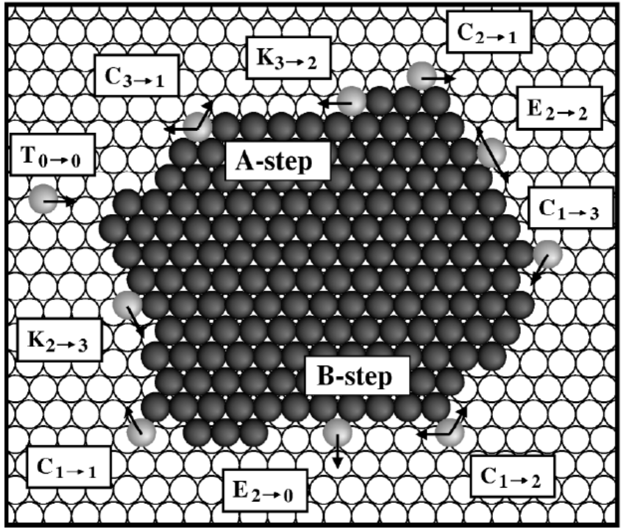
The slope gives E_1
(energy barrier for adatom (monomer) diffusion)

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

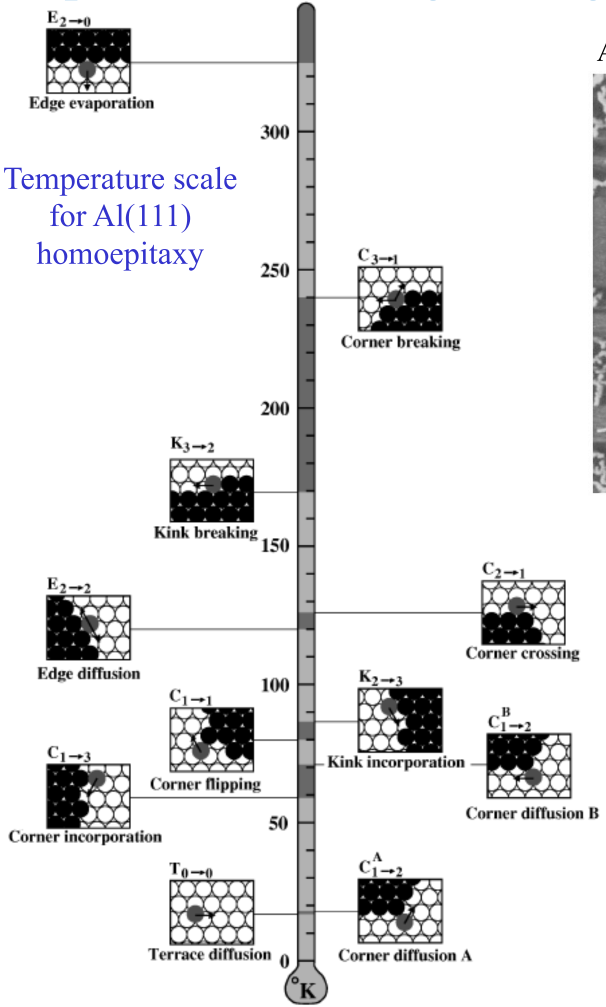


Island shape: diffusion along the edges

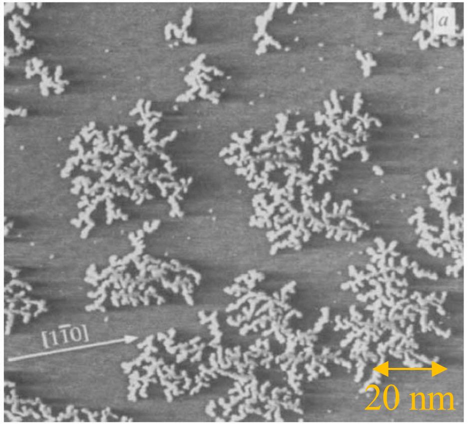


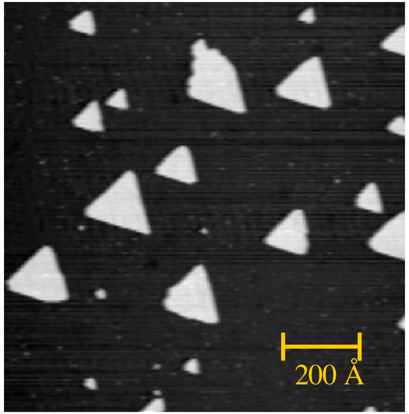


Temperature scale
for Al(111)
homoepitaxy



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





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

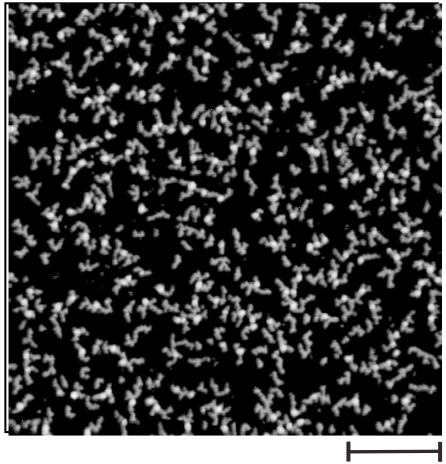
H. Brune *et al.* Nature **369**, 469 (1994);
S. Ovesson *et al.* Phys. Rev. Lett. **83**, 2608 (1999);
A. Bogicevic *et al.* **81**, 637 (1998)

Diffusion rate

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

Fe

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



27 nm

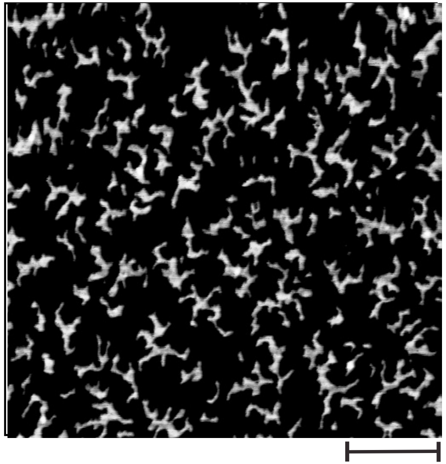
Island size = 90 atoms/isl

$T_{dep} = 140$ K
$\Theta = 0.25$ ML

Substrate: Pt(111)

Co

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



30 nm

Island size = 390 atoms/isl

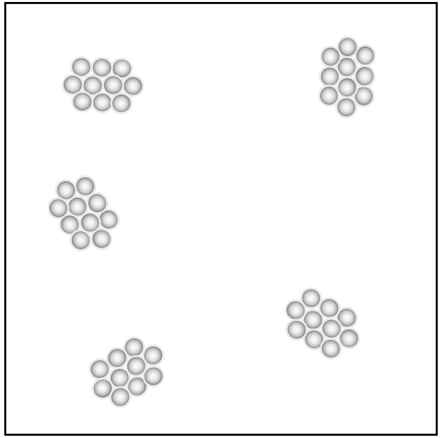
$E_{Fe} > E_{Co}$

How to form alloy clusters?
How to form lattices?

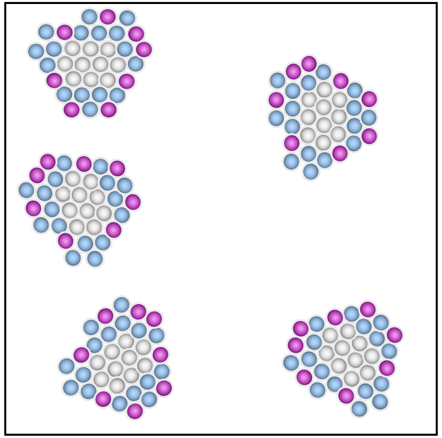
→ Patterned substrate

Epitaxial growth of two-dimensional alloys

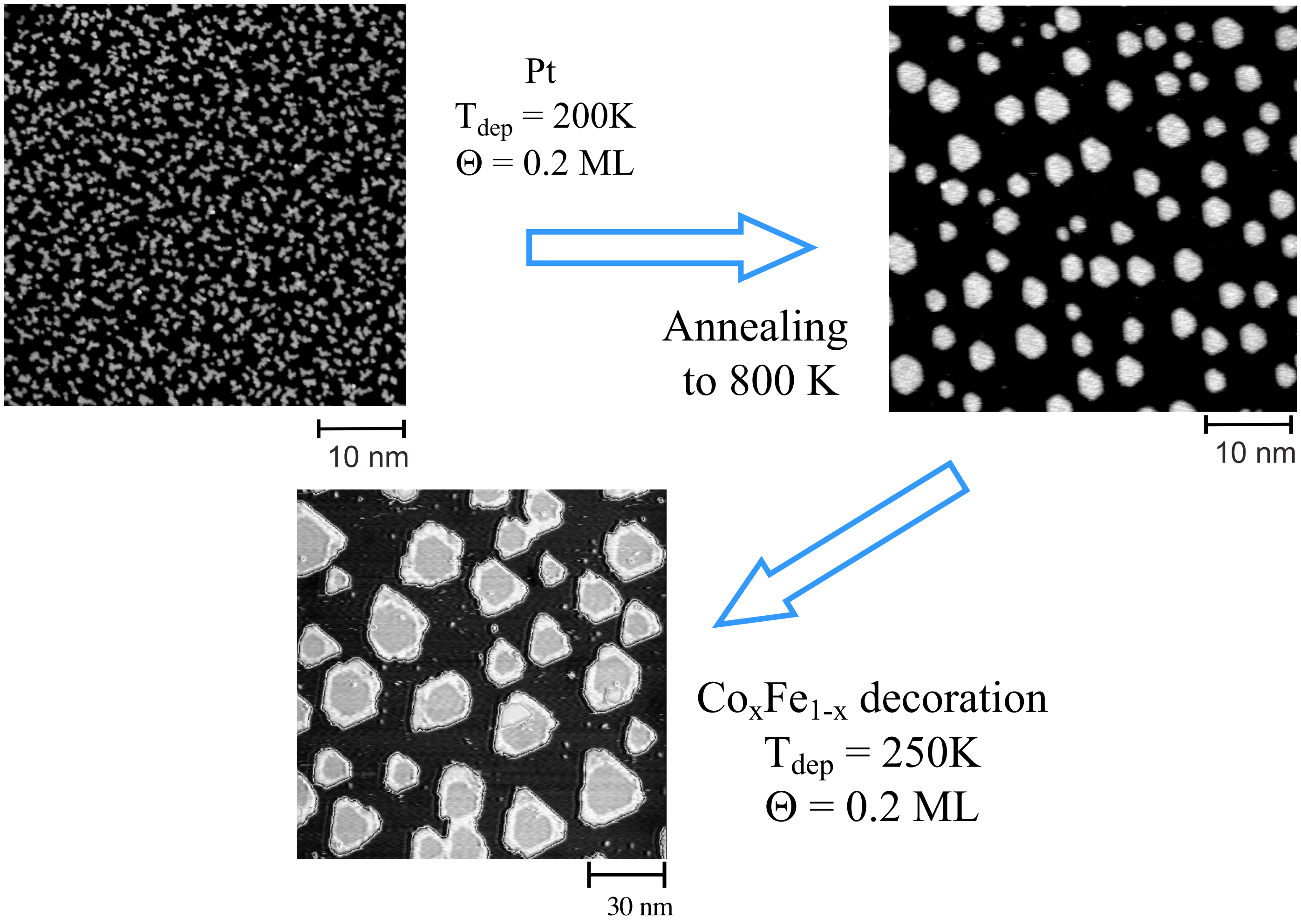
Pre-defined nucleation sites (seeds) to define the island density: template



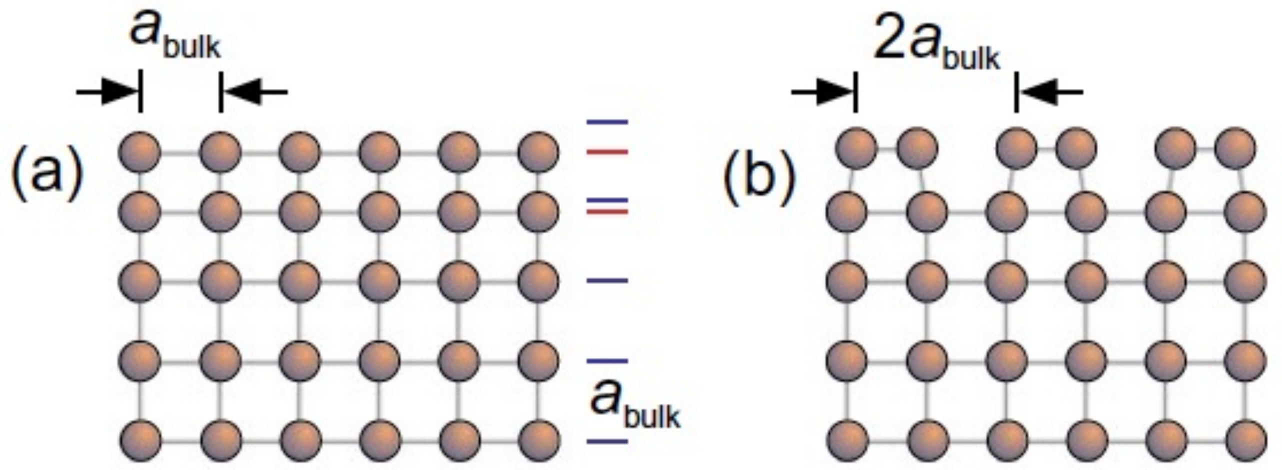
Growth of the alloyed nanostructures on the template substrate



Epitaxial growth of two-dimensional alloys



Surface relaxation and surface reconstruction



Surface reconstructions

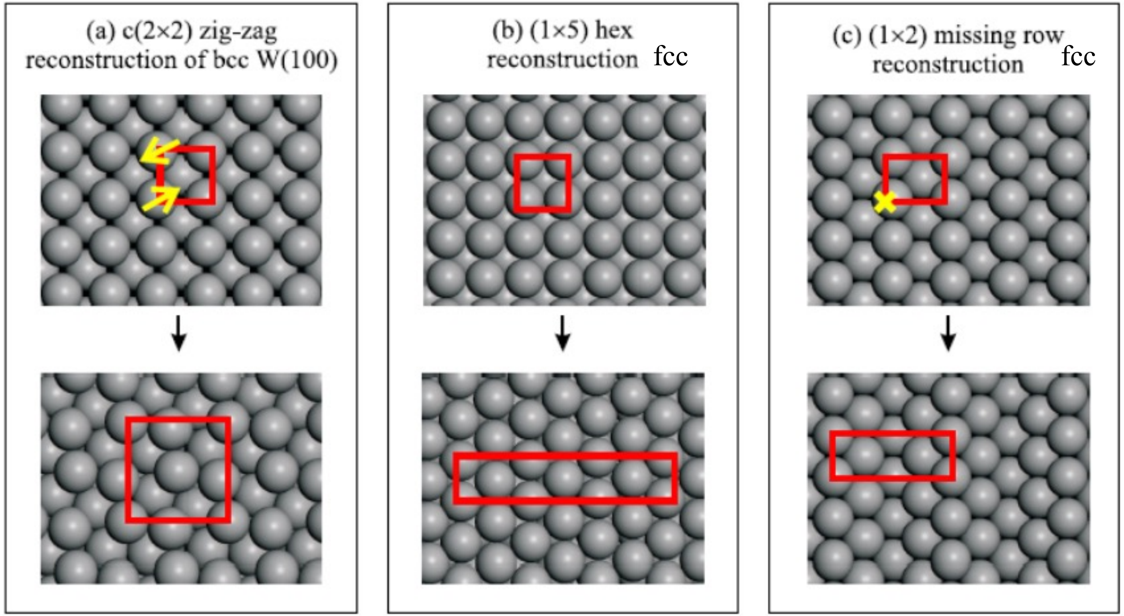


Figure 5.5. - Illustration of three bulk truncated surfaces and typical types of reconstruction that they undergo. (a) depicts the (1×1) to c(2×2) reconstruction of bcc W(100). The arrows indicate the direction in which the top layer W atoms move upon reconstruction. (b) displays an example of the "hex" 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,
Università di Trieste

Au(111): herringbone reconstruction

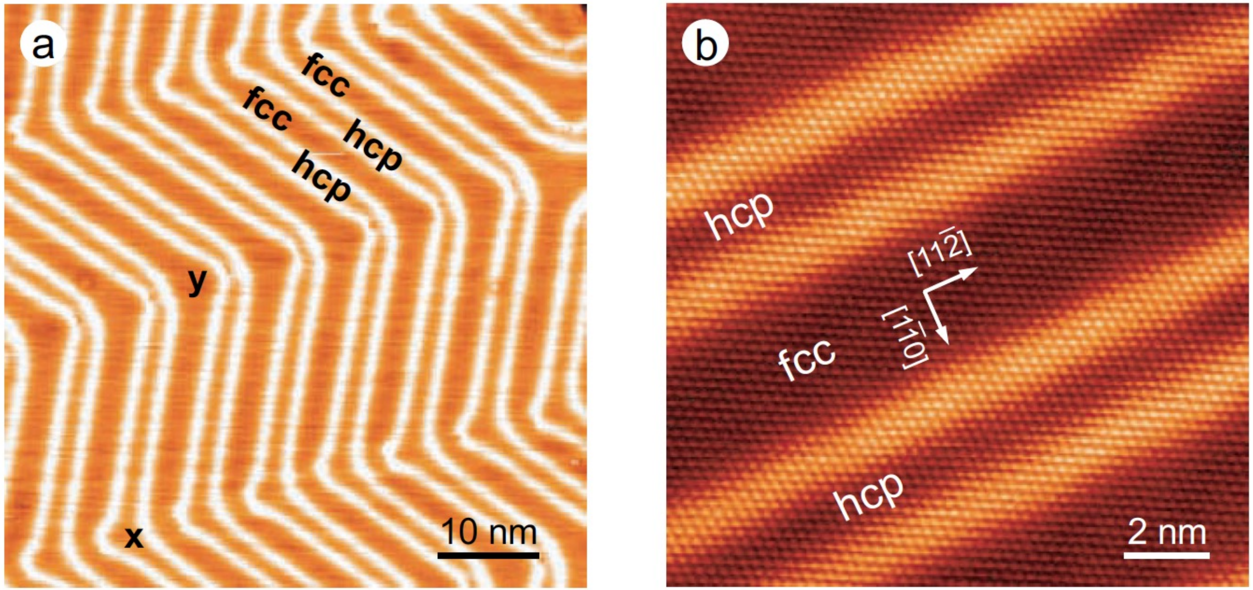
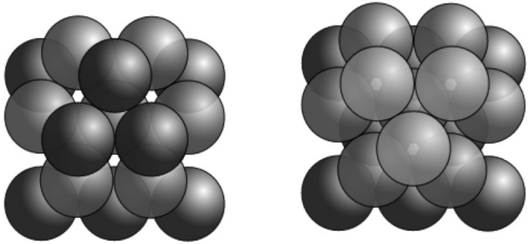
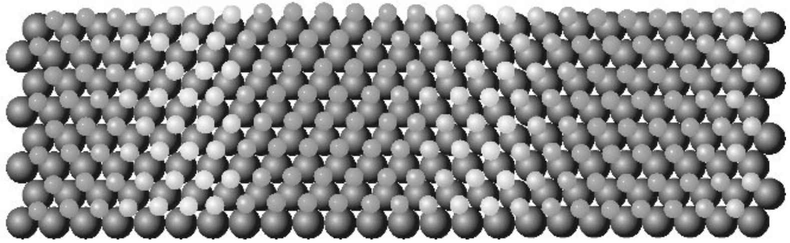


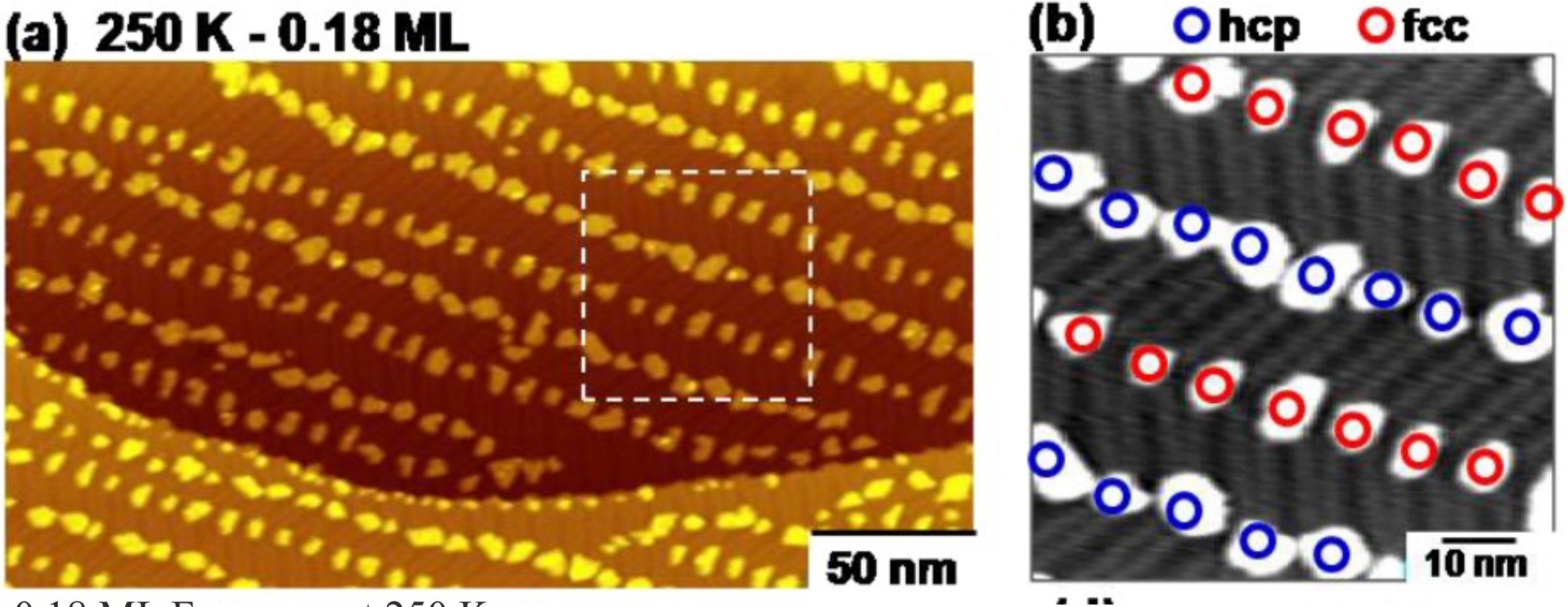
Figure 3.1: STM image showing the herringbone reconstructed Au(111) surface. a) Alternating fcc and hcp stacking domains, as well as *x*- and *y*-type elbows are visible. b) Atomically resolved STM image, revealing the slightly distorted hexagonal arrangement of the surface atoms together with the domain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

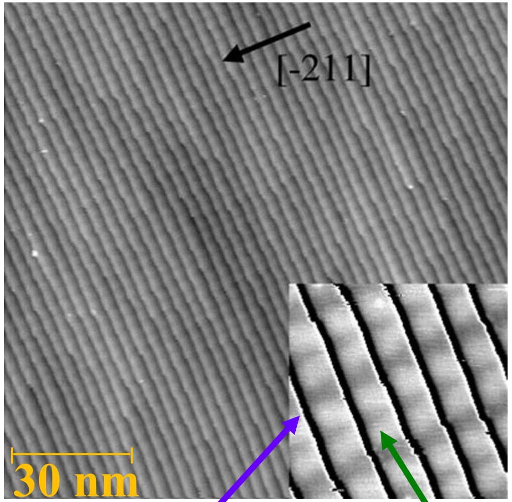
Au(111) herringbone reconstruction - Nucleation

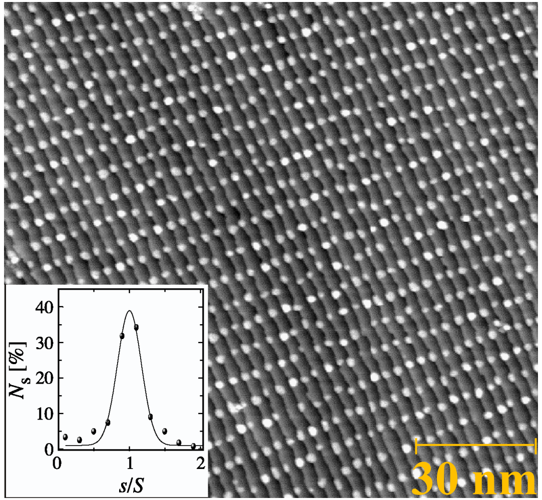


0.18 ML Fe grown at 250 K
islands nucleate at elbows

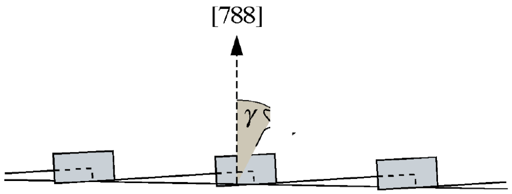
Nanotechnology **21,** 015606 (2010)

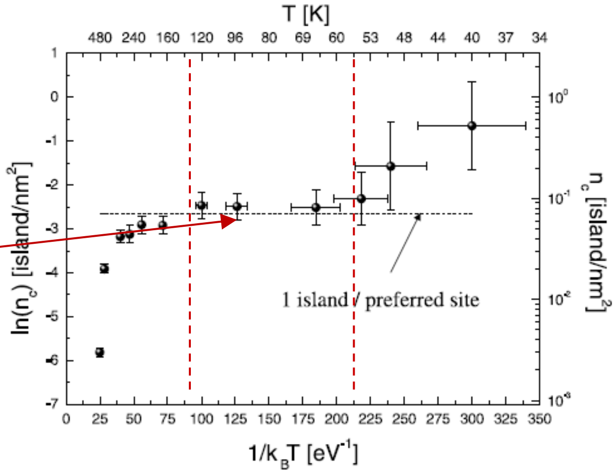
Vicinal Au surfaces: Au(7,8,8)





0.2 ML Co
T_{dep} = 130 K
T_{ann} = 400 K





the step edges and the terrace reconstruction lines

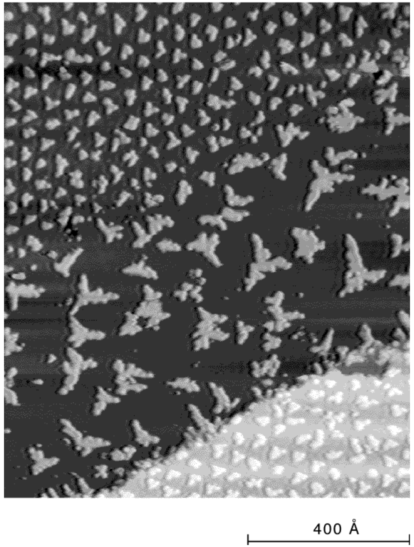
confine the Co adatoms

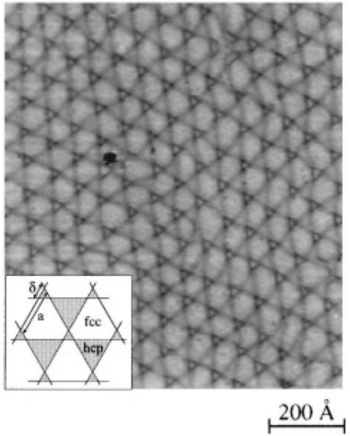
range of T where the island density (n_x) does not change

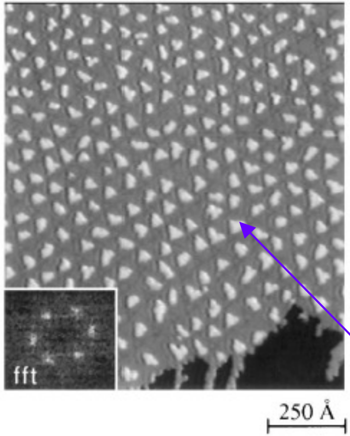
S. Rohart *et al.* Surf. Sci. **559**, 47 (2004);
N. Weiss et al. Phys. Rev. Lett. **95**, 157204 (2005)

Self assembled nanostructure arrays on patterned substrate

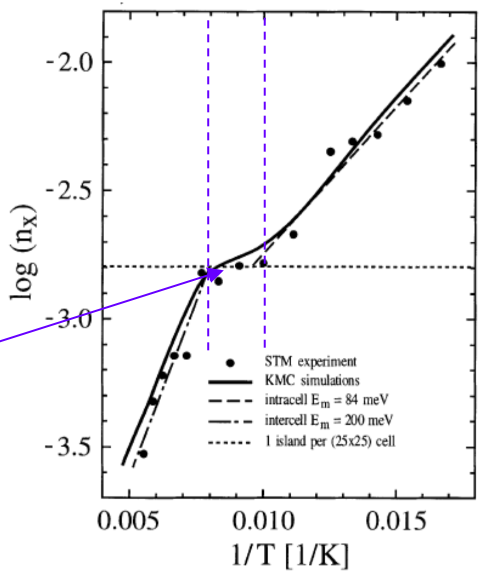
Nucleation of an Ag island superlattice (T_{dep} = 110 K) on the dislocation network formed by 2 ML of Ag on Pt(111)



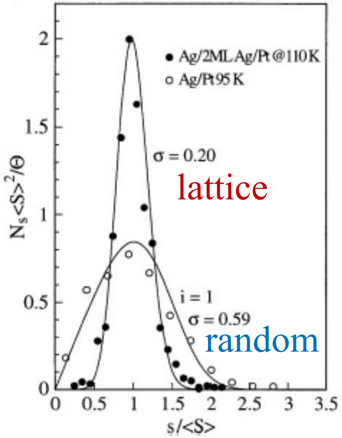




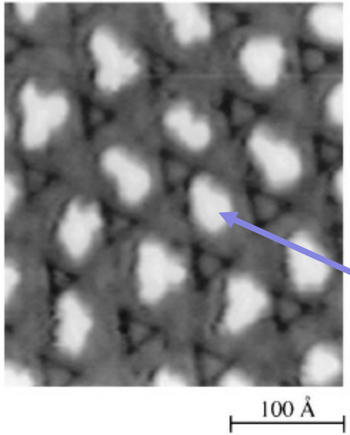
Confinement: range of T where the island density (n_x) does not change



c) Size distribution



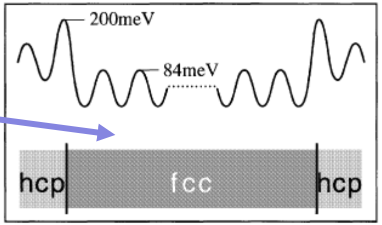
d)



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

Atoms are confined in the fcc stacking areas

c)

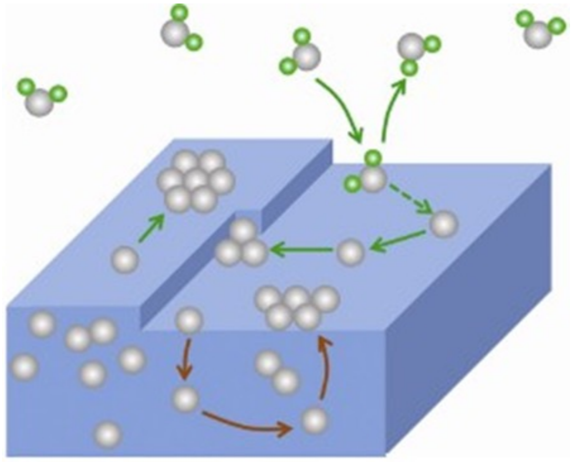


H. Brune *et al.* Nature **394**, 451 (1998);
H. Brune Surf. Sci. Rep. **31**, 121 (1998);

Self assembled nanostructures on graphene

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 network of graphene

Ex of hydrocarbons:

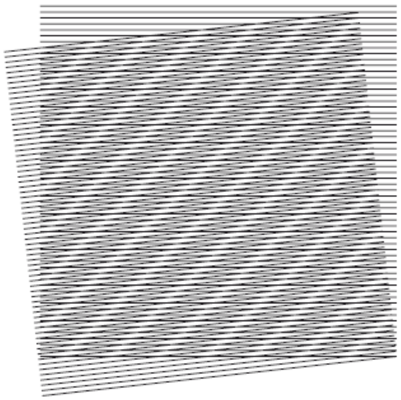
CH_2 → Methylene

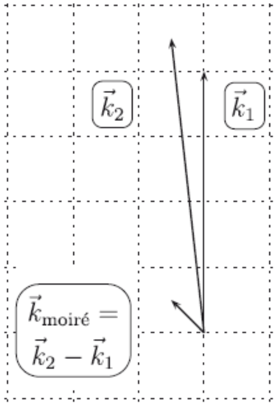
C_2H_4 → Ethylene

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

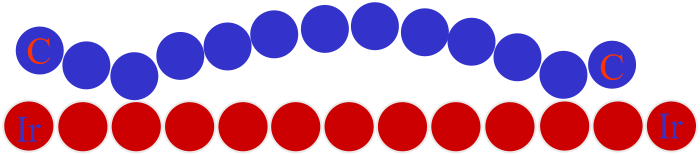
Moiré pattern due to graphene-Ir(111) lattice mismatch

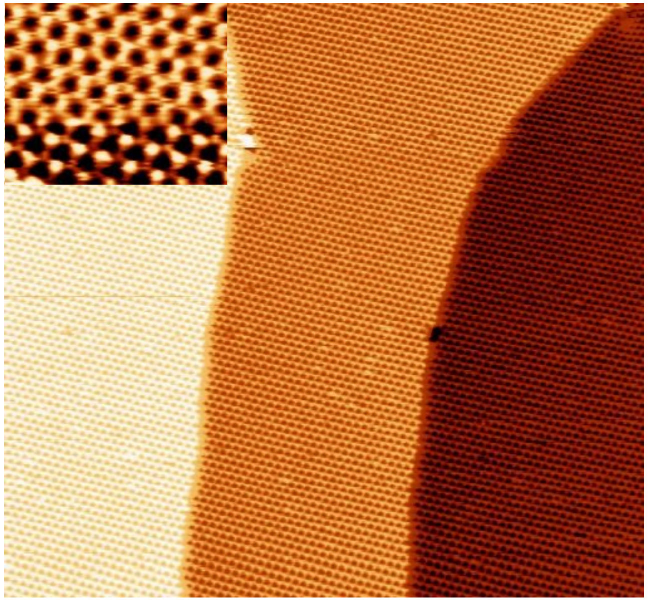
A moiré is a superposition of two lattices
generating a third one.





$a_{Ir} = 0.27$ nm
$a_c = 0.245$ nm





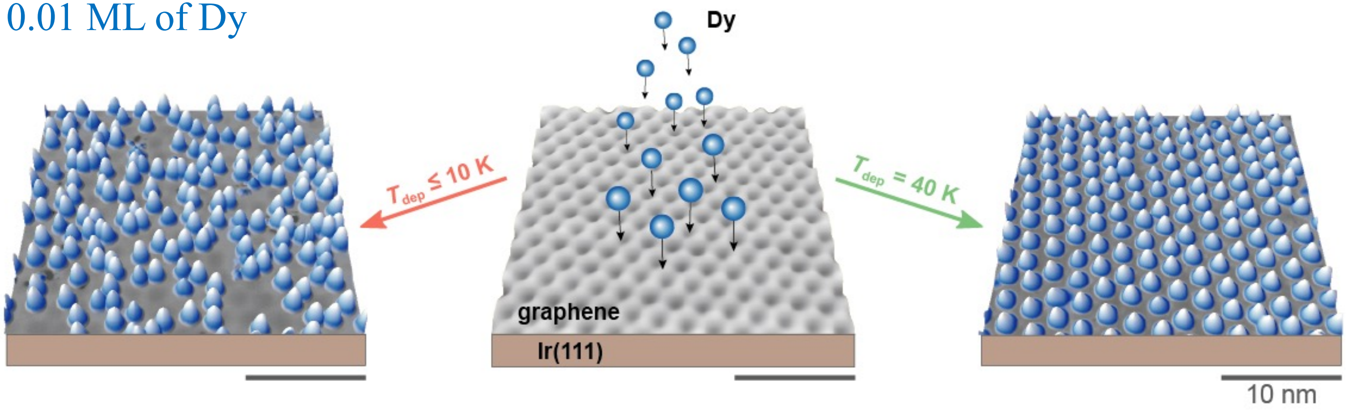
180 x 200 nm^2

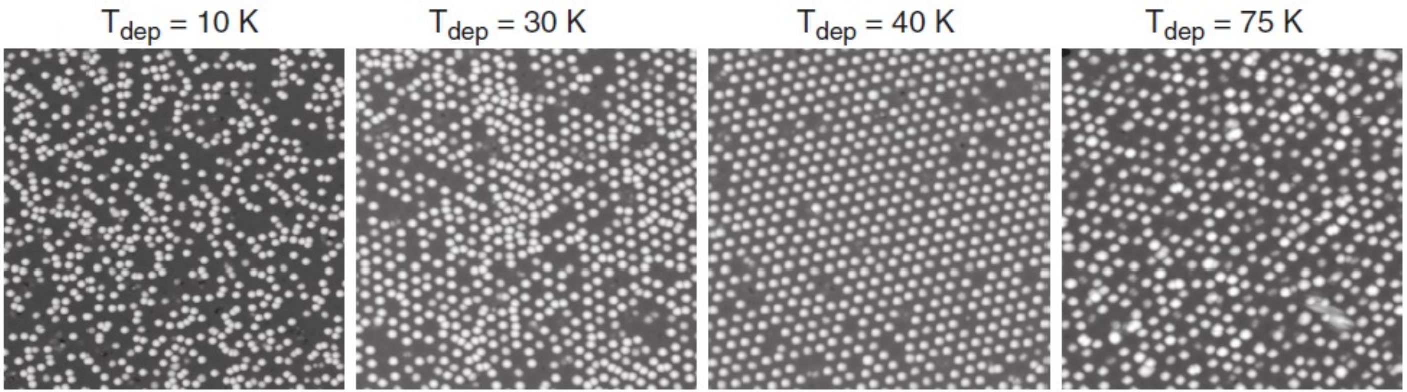
Supercell with (10x10) C atoms
on (9x9) Ir substrate atoms

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

Superlattice of single atom magnets on graphene

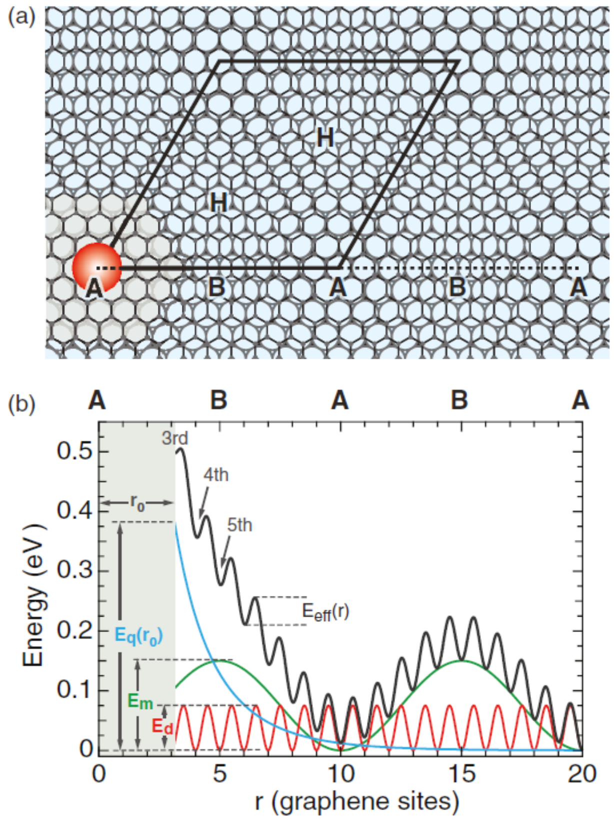
Dy atoms on graphene/Ir(111)
0.01 ML of Dy





R. Baltic *et al.*, Nano Letters **16**, 7610 (2016); M. Pivetta *et al.*, Phys. Rev. B **98**, 115417 (2018)

Diffusion energy landscape



Moiré with (10 × 10) graphene unit cells on (9 × 9) Ir(111) atoms.

Stacking areas: (A) atop, (B) bridge, and (H) hollow.

Rare-earth atom (red) together with its direct impingement area (gray).

1D diffusion energy profile for a second rare-earth atom resulting from the superposition of:

1) atomic corrugation E_d
2) moiré corrugation E_m of graphene
3) Coulomb repulsion E_q

$$E_q(r) = \frac{1}{4\pi\epsilon_0}\frac{q^2}{r}\exp\left(-\frac{r}{r_0}\right)$$

q is the charge transferred from the rare-earth to graphene

M. Pivetta *et al.*, Phys. Rev. B **98**, 115417 (2018)

Self assembled core-shell nanostructure arrays on graphene/Ir(111)

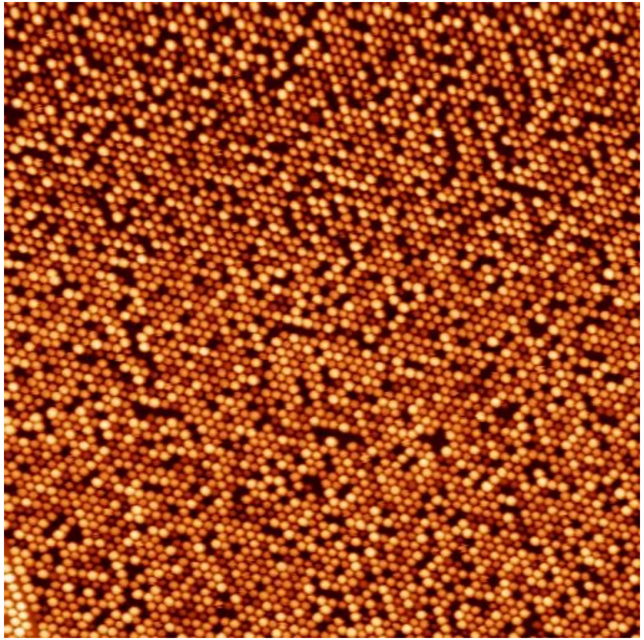
Ir island

Ir deposition: T=375 K

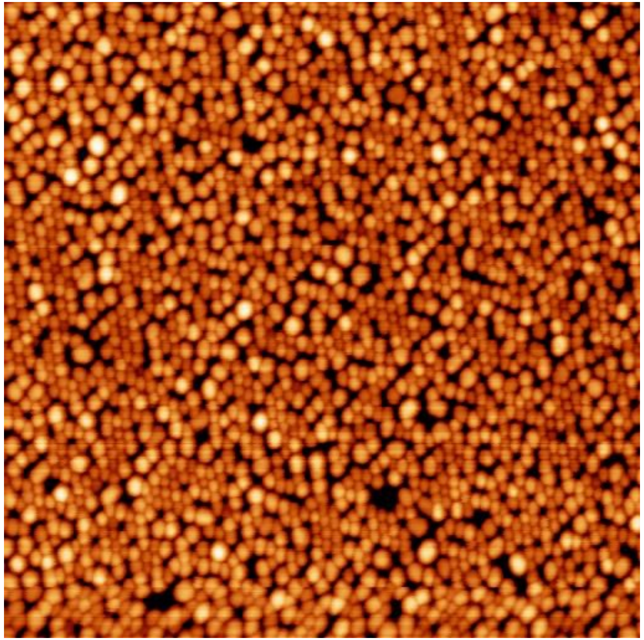
Ir-core Co-shell islands

Ir deposition: T=375 K

Co deposition:1 ML,   T=300 K



150 x 150 nm2



150 x 150 nm2

graphene

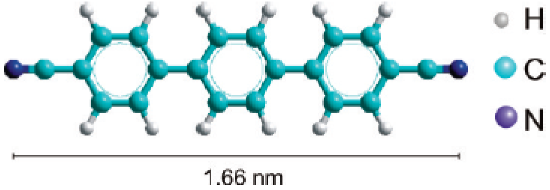
Ir-core

Co-shell

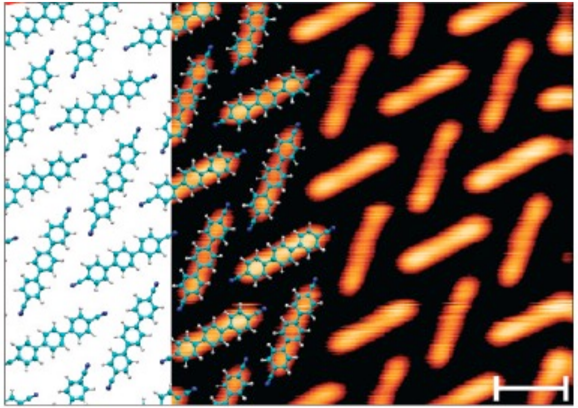
S. Rusponi unpublished; A. T. N'Diaye *et al.* Phys. Rev. Lett. **97**, 215501 (2006)

Molecular and metal-organic networks

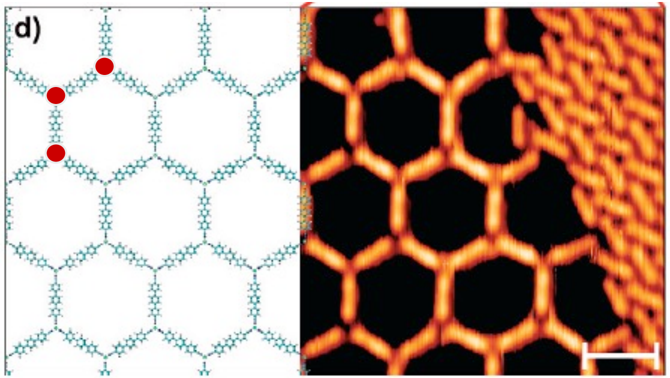
NC-Ph$_3$-CN



On Ag(111)



Cobalt

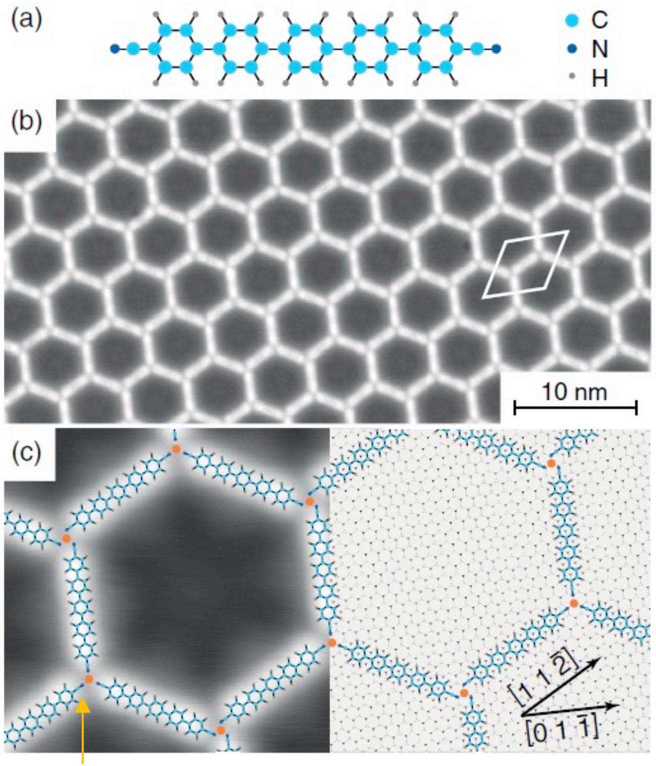


Co atoms added at room temperature coordinate the molecules in a 3-fold coordinated motif

U. Schlickum *et al.* J. Phys. Chem. C **114**, 15602 (2010)

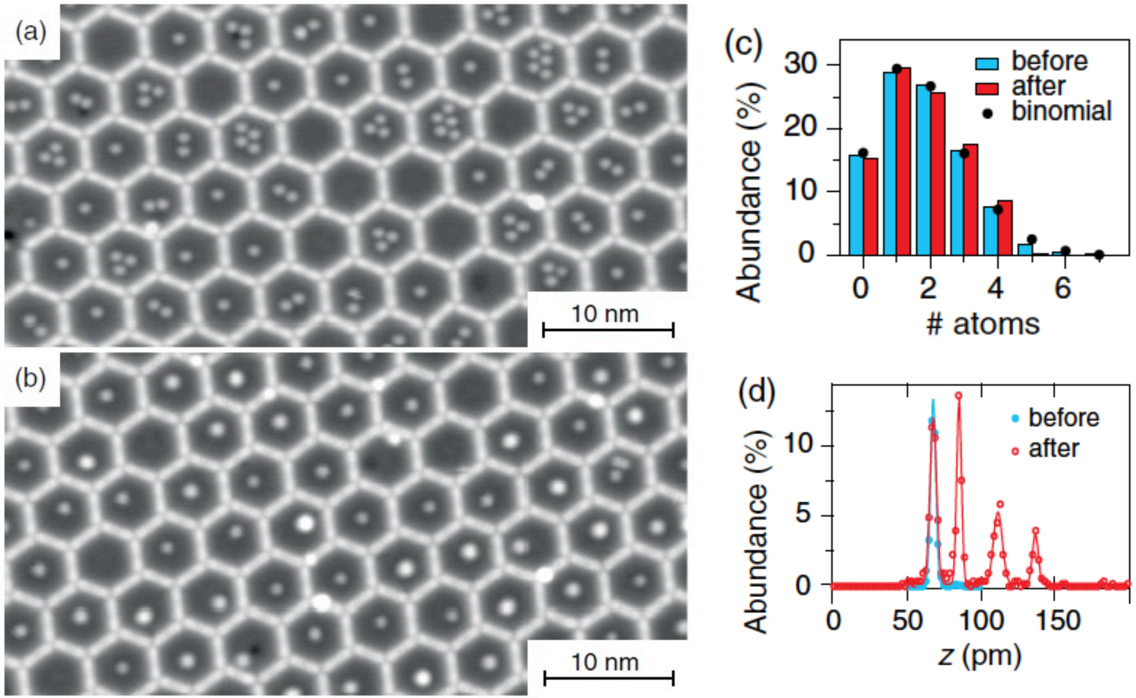
Cluster superlattice in a metal-organic quantum box network

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

M. Pivetta *et al.* Phys. Rev. Lett. **110**, 086102 (2013)

Superlattices: density *vs* blocking T

System	density	T_b
Co/Au(11,12,12)	15 T_{dot}/in^2	75 K
Fe/Co/Au(11,12,12)	15 T_{dot}/in^2	105 K
Co/Au(788)	26 T_{dot}/in^2	50 K
Co/$GdAu_2$/Au(111)	52 T_{dot}/in^2	< 90 K
Fe/NC-Ph_3-CN/Cu(111)	90 T_{dot}/in^2	?
Fe/Al_2O_3/Ni_3Al(111)	92 T_{dot}/in^2	?
Co/Ir/graphene/Ir(111)	116 T_{dot}/in^2	< 50 K