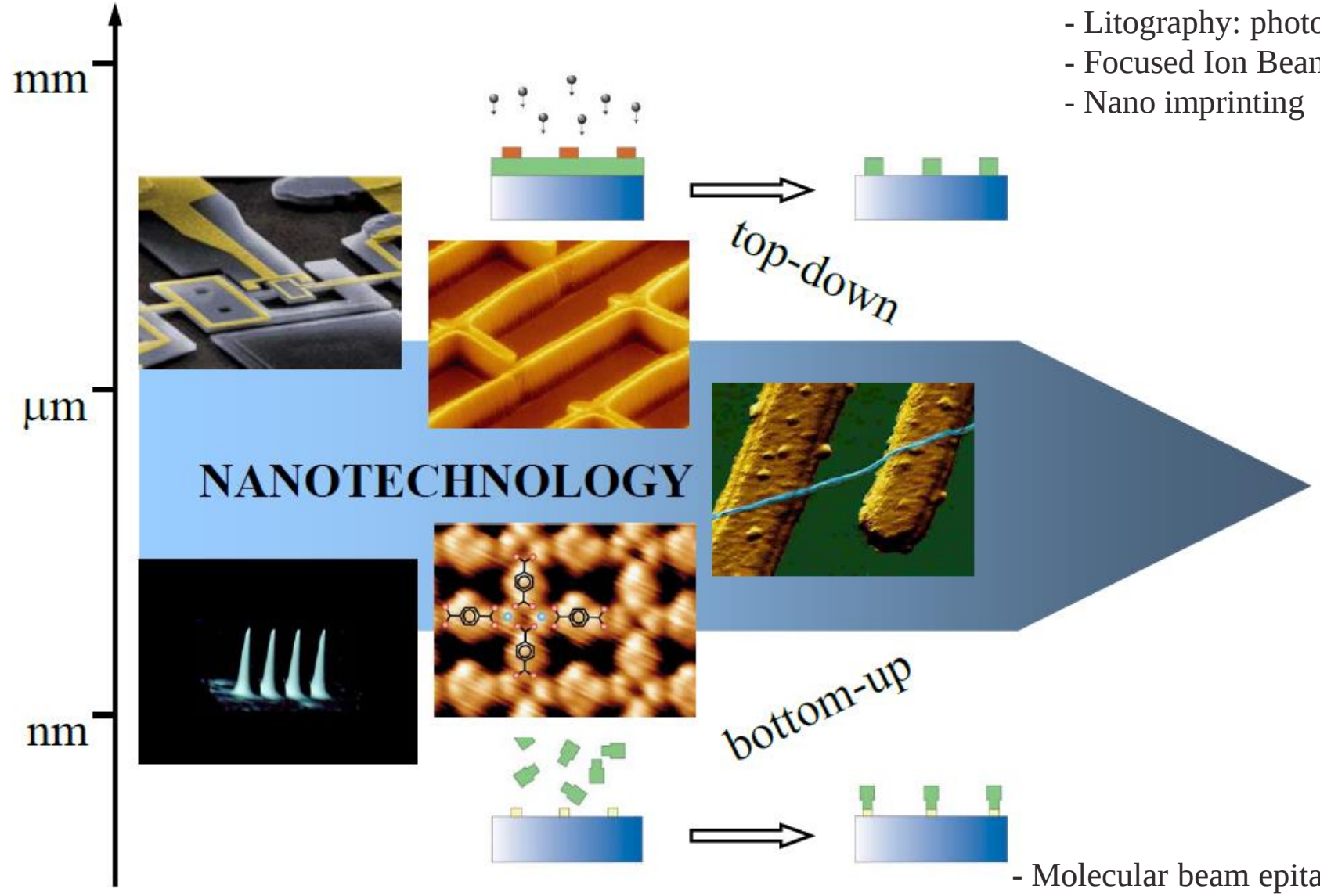
Nanostructures growth: two approaches

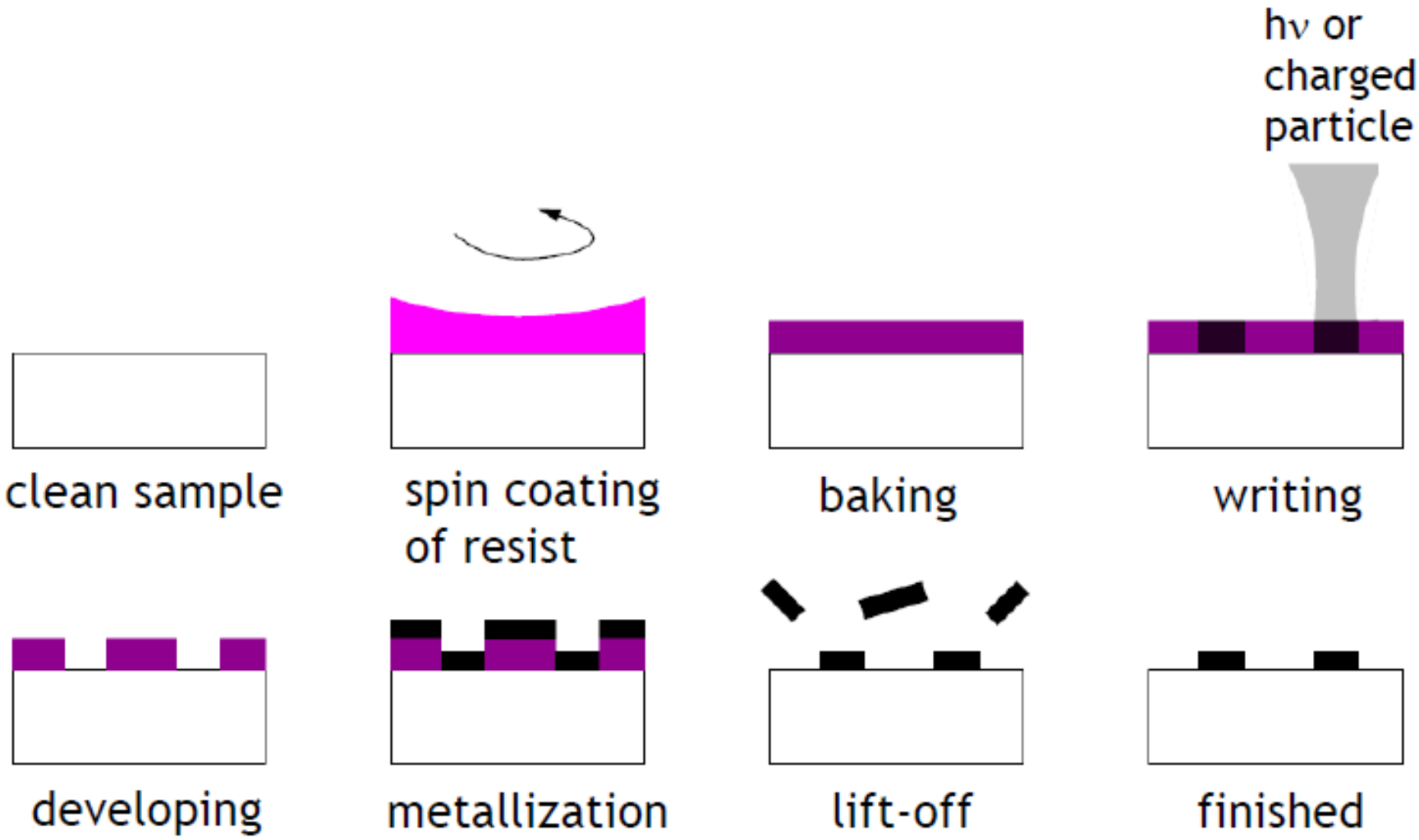
- Litography: photo, e-beam
- Focused Ion Beam (FIB)
- Nano imprinting



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

K. Kern courtesy

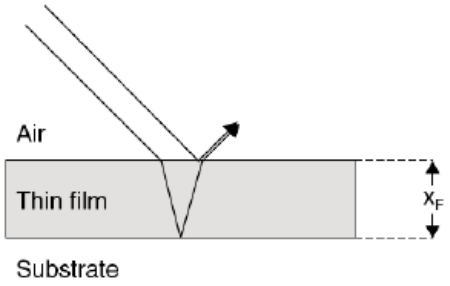
Lithography



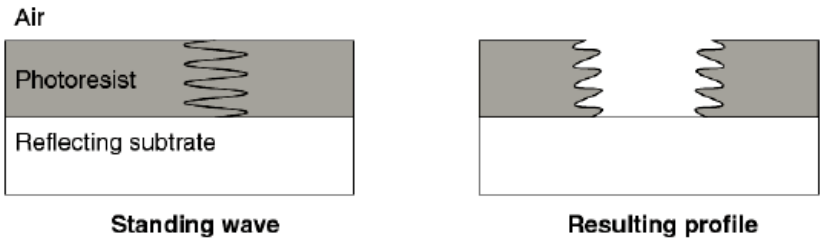
K. Kern courtesy

Photolithography limits

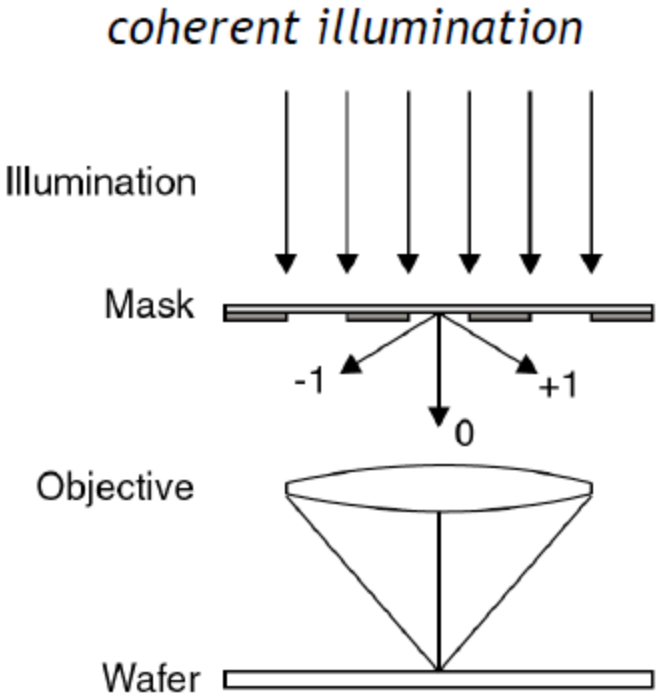
Interference



reflection from film/air and film/substrate interface can produce variation of light intensity due to a standing wave:



Diffraction limit



1st order diffraction: $\sin\Theta = \frac{\lambda}{d} = NA$

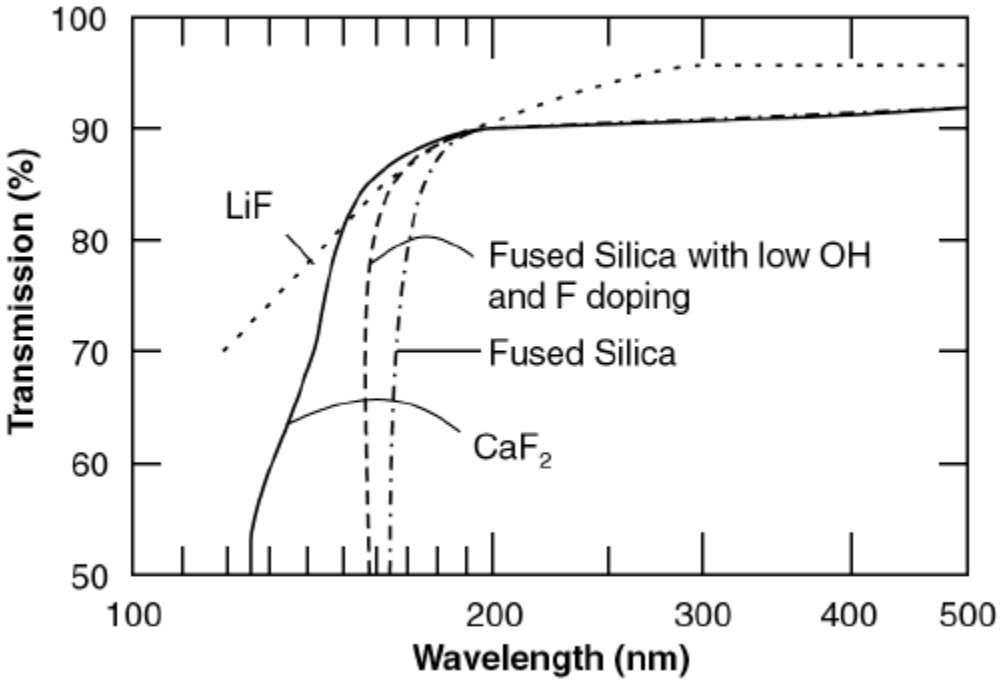
minimum resolvable line width: $W = 0.5d = \boxed{0.5}\frac{\lambda}{NA}$

NA = numerical aperture ~1.5 in modern optics

K. Kern courtesy

Photolithography limit: ultraviolet light

issue: optical transparency of available lens materials



below 200 nm, only special low-doped fused silica and CaF_2 are suitable

Limit ~100 nm

K. Kern courtesy

e-beam lithography

Electrons in place of photons

$\lambda = h / (2 m e V)^{1/2}$ → No diffraction limit, but …

e energy = 200 eV -> λ ~ 0.09 nm

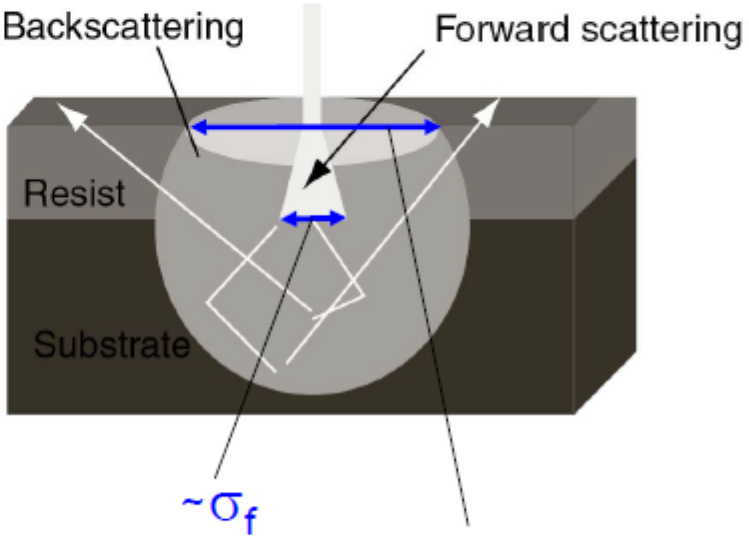
two-Gaussian model (Monte Carlo simulation):

characteristic diameter for forward-traveling electrons

$$\sigma_f\,[\mu m] = \left(\frac{9.6\, z\,[\mu m]}{V\,[keV]} \right)$$

z … thickness of resist film
V … energy of incident e-beam

for V = 20 keV and z = 500 nm
→ σ_f = 80 nm



…for backward-traveling electrons

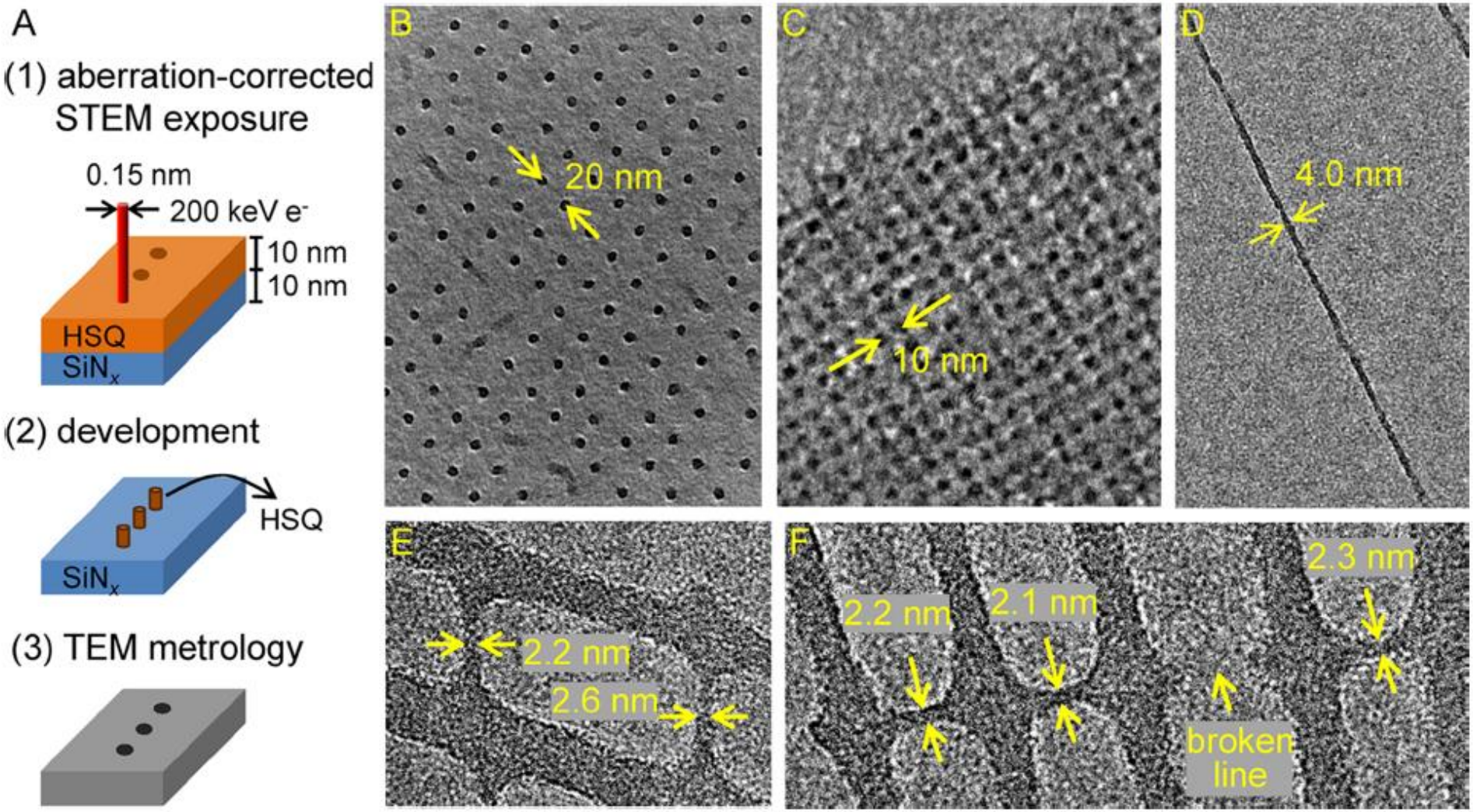
$\sigma_b = \text{several}\,\mu m$

→ limits resolution

A.N. Broers; IEEE Electron. Dev. 28 (1981), 1268.

e-beam lithography: resolution limit

2 nm isolated feature size and 5 nm half-pitch

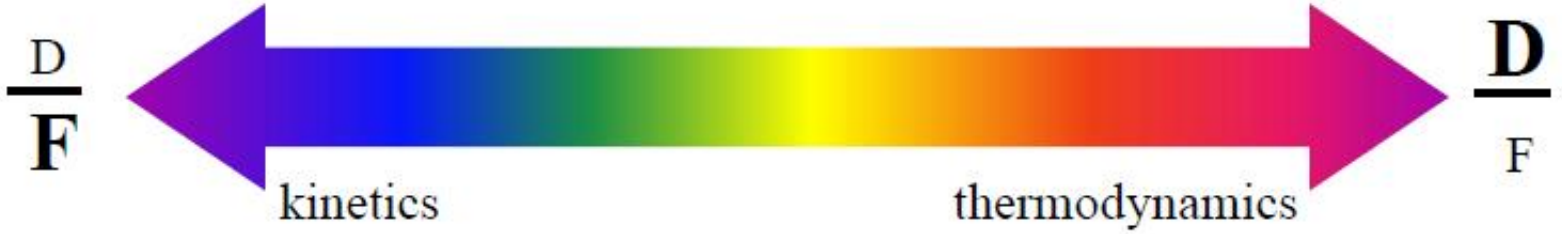


STEM = Scanning Transmission Electron Microscope -> serial process

-> long process for nm patterns repeated on in^2 surfaces

V.R. Manfrinato, Nano Lett. **13**, 1555 (2013)

Self-organized growth at surface



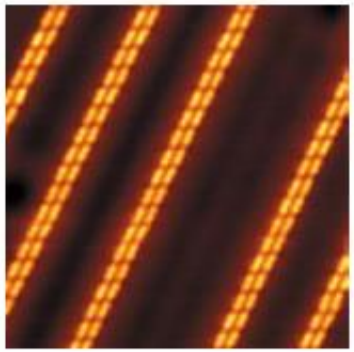
Deposition Rate F ⟺ **Diffusion D**

Arrhenius Law (Temp. T)

$D \sim n_0 \exp(E_{barr}/k_B T)$

metal epitaxy

semiconductor MBE



molecular self-assembly

K. Kern courtesy

Growth as a non equilibrium phenomenon: kinetics

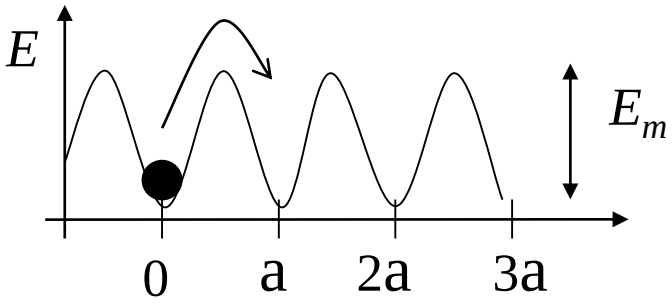
Epitaxial thin film growth is a non-equilibrium kinetic phenomena.

In thermodynamic equilibrium all atomic processes proceed in opposite directions at equal rates, i.e. there is hence no net growth and average macroscopic quantities such as surface coverage or roughness stay constant.

a 2D laboratory: single crystal surfaces

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

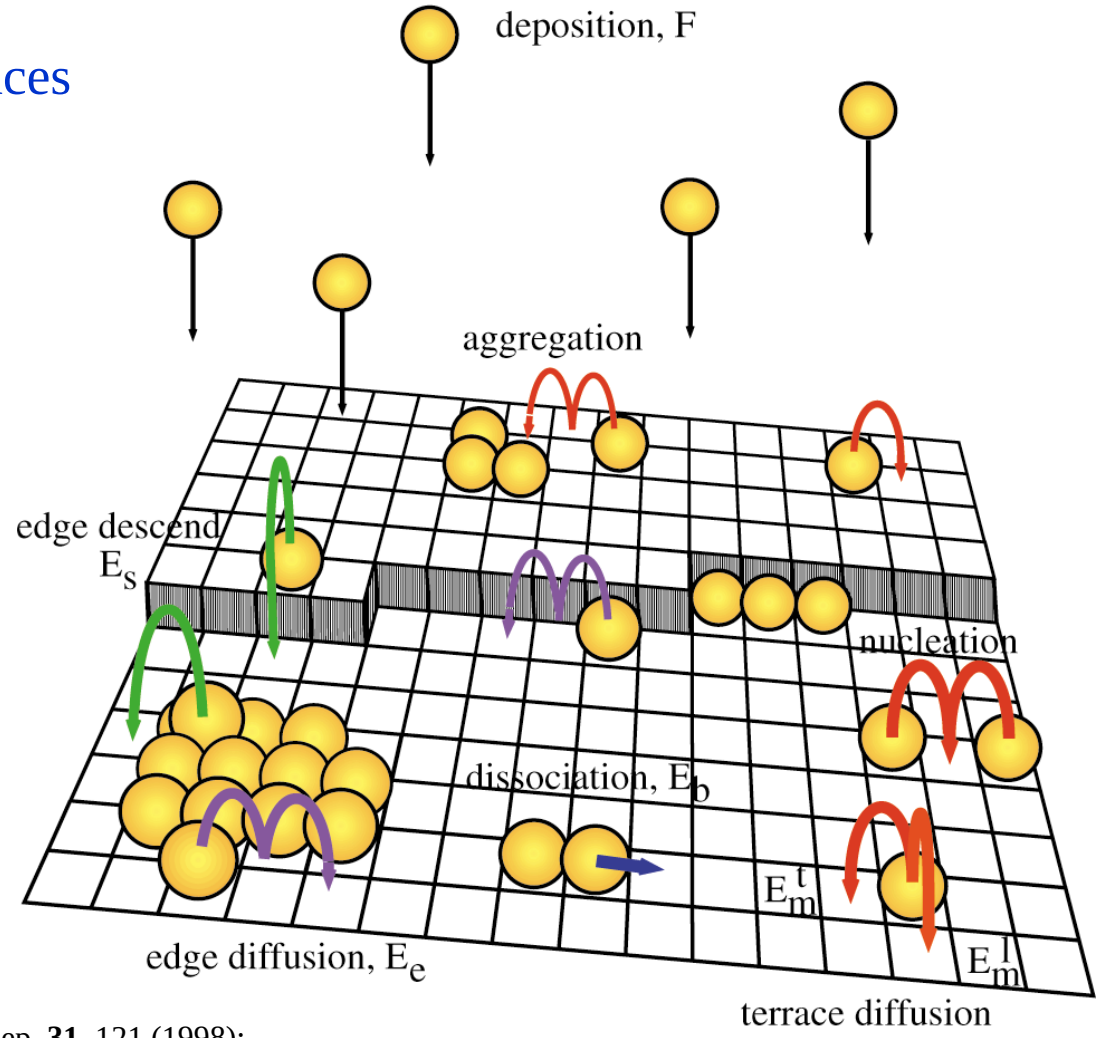
$$\nu = \nu_0 \exp(-E_i / kT)$$



diffusion processes:

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

a –> lattice constant, t –> time



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

Growth as a non equilibrium phenomenon

Aim: controlling

- mean size

(size distribution)

- density
- shape
- composition

Control parameters:

- substrate temperature T
- deposition flux F
- surface coverage Θ
- substrate/overlayer material

(strain, mixing, etc.)

- substrate symmetry or

patterning

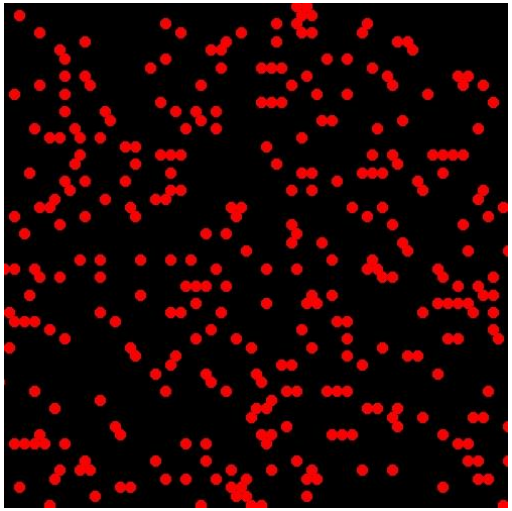
Statistical growth: $T \rightarrow 0$ K

- thermally-activated diffusion is frozen

$$\nu = \nu_0 \exp(-E_i / kT) \rightarrow 0$$

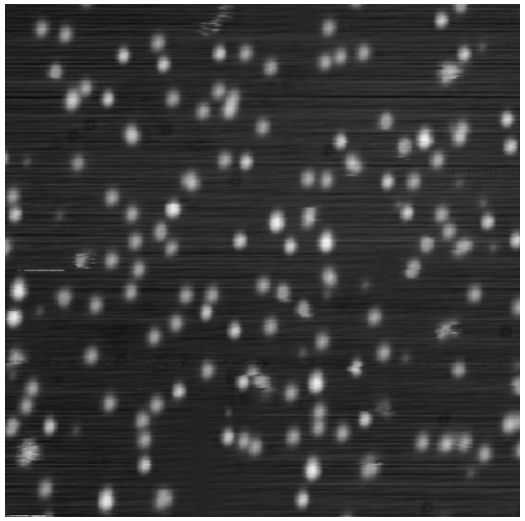
- coverage determines mean island size *n*
- large size distribution

Kinetic Monte Carlo simulation



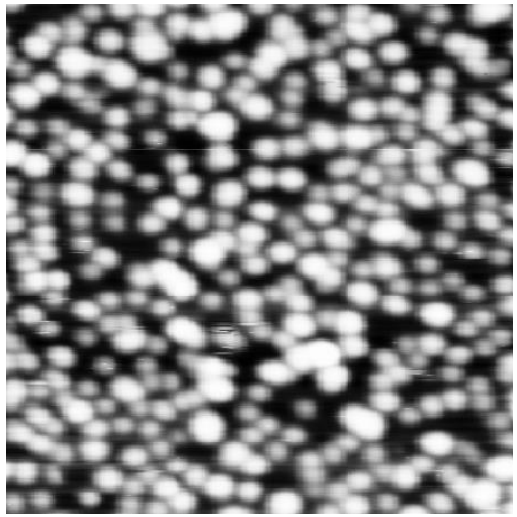
Co/Pt(111)

0.03 ML, T = 50 K: n = 1.2

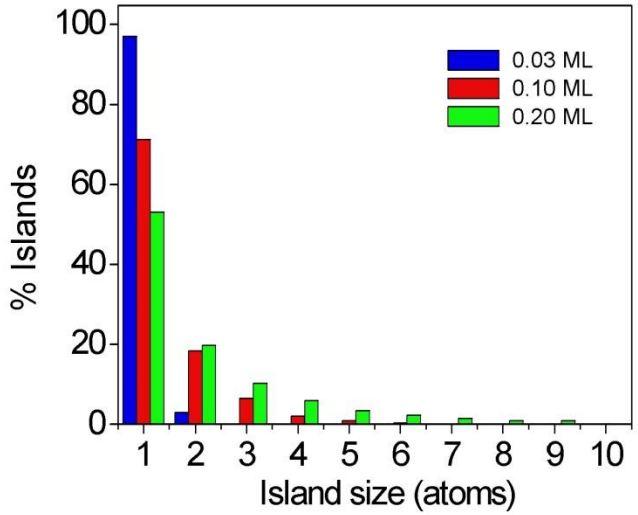


50 Å

0.10 ML, T = 50 K: n = 2.9

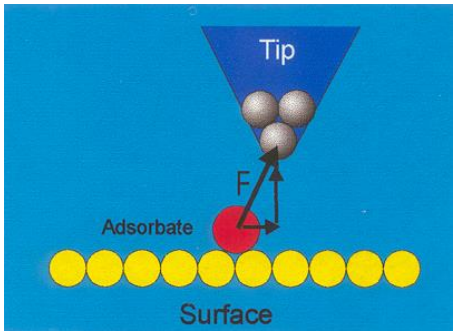


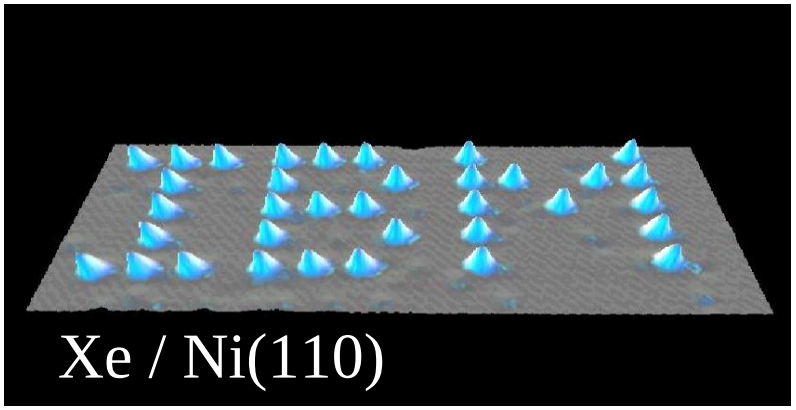
50 Å



n = mean island size = coverage/island density

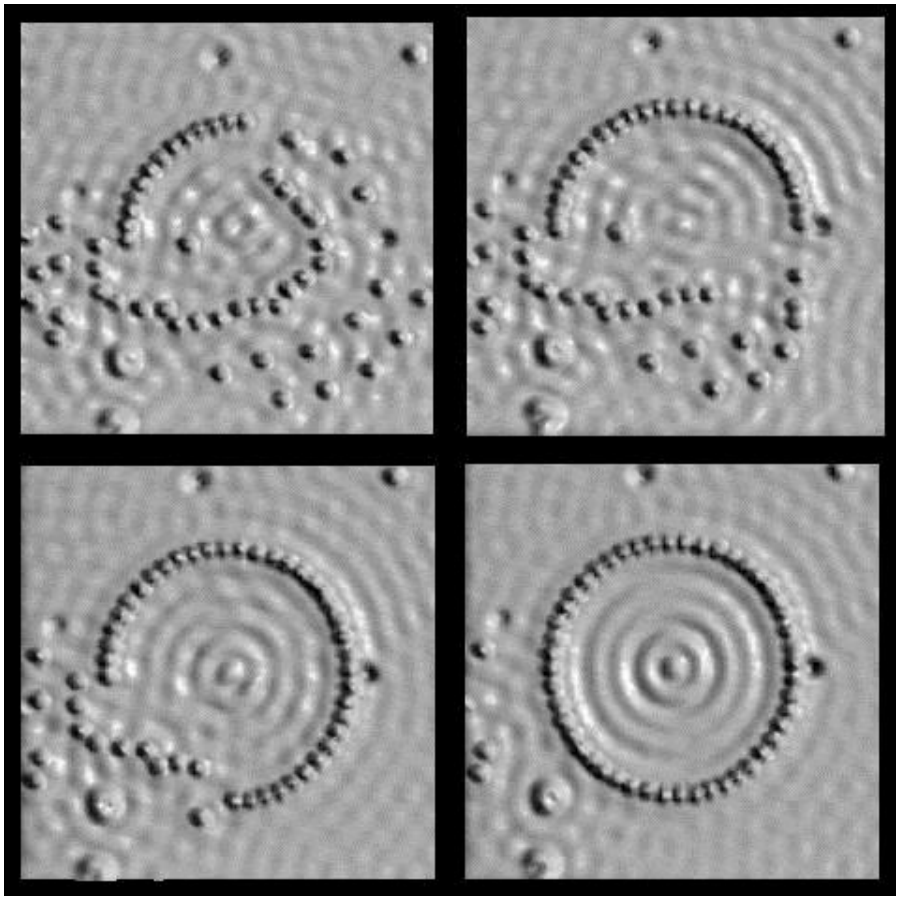
STM manipulation





D. Eigler & E. Schweizer,
Nature **344**, 524 (1990)

Quantum corral



Fe on Cu(111)

Atomic Superlattice in a Two-Dimensional Electron Sea

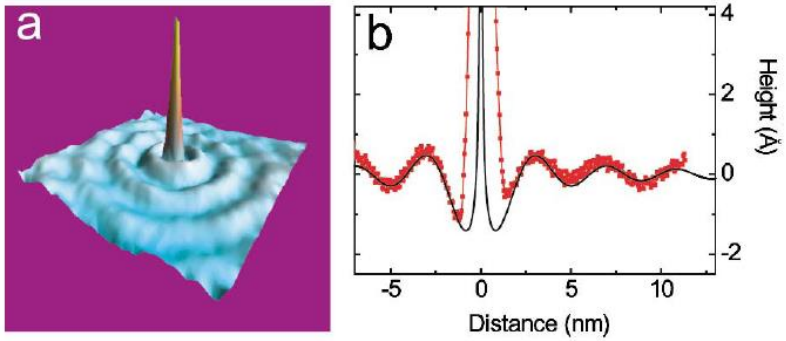
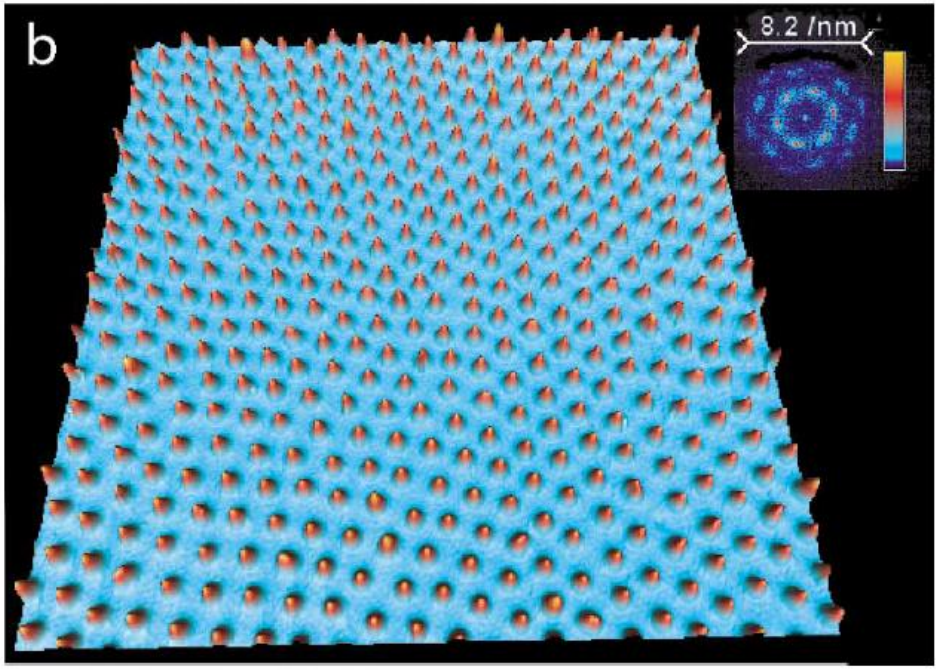


FIG. 3 (color online). (a) The 21 × 21 nm^2 3D STM image of a standing-wave pattern around an isolated Ce adatom on Ag(111) at 3.9 K ($U_s = -3$ mV, $I_s = 19$ pA). (b) Dotted line: topographic profile as a function of distance from a single Ce adatom. Solid line: fit using Eq. (1).

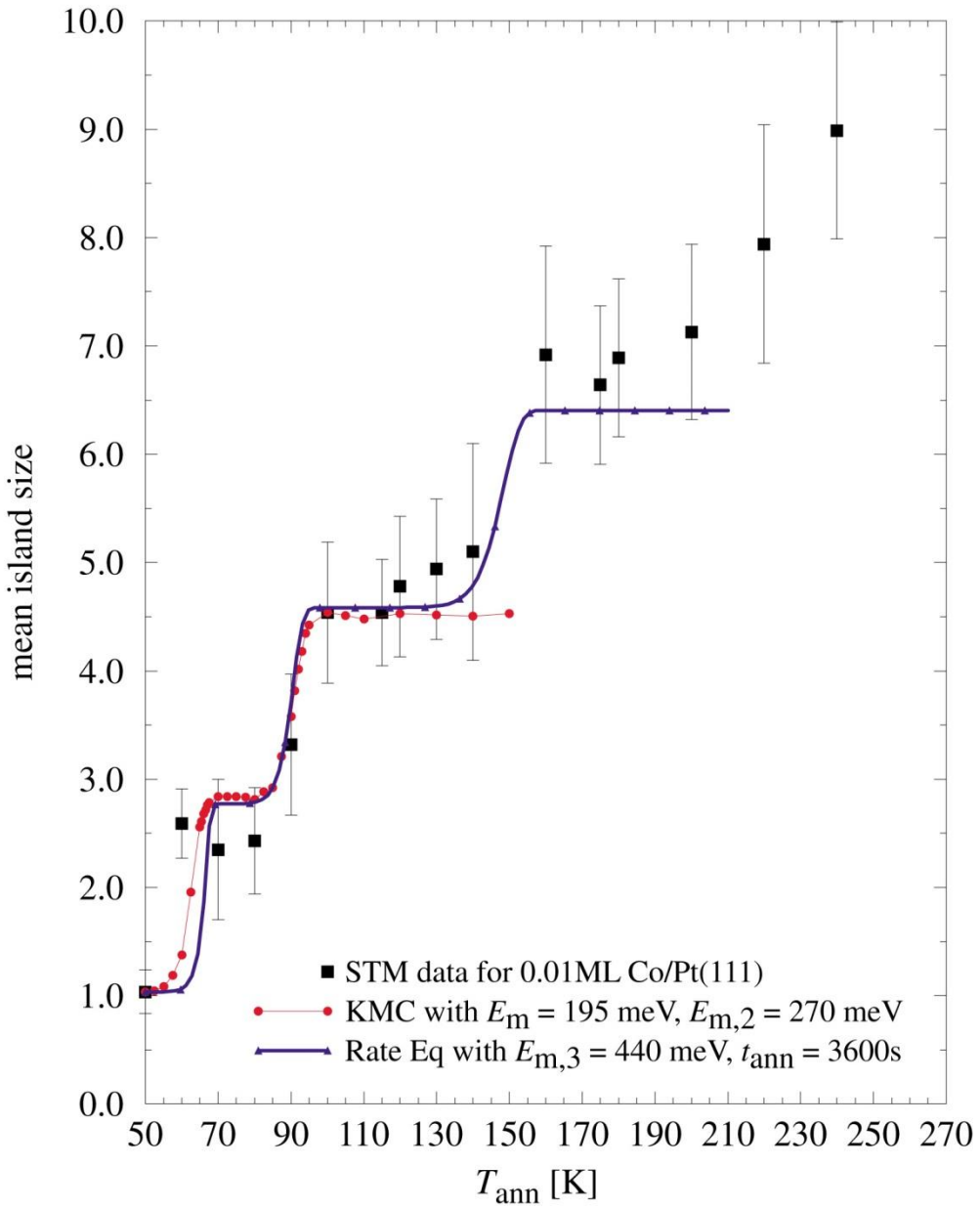
At the Fermi energy (E_F) the local density of states (LDOS) oscillates around the impurity with a wavelength of $\lambda_F = 2\pi/k_F$, where λ_F is the Fermi wavelength and k_F the Fermi wave vector. This variation of the LDOS at E_F due to standing-wave formation modifies the adsorption energy of the adsorbates.

Ce superlattice on Ag(111) at 4.8 K



F. Silly *et al.*, Phys. Rev. Lett. **92**, 016101 (2004)

Cluster diffusion: Co/Pt(111)

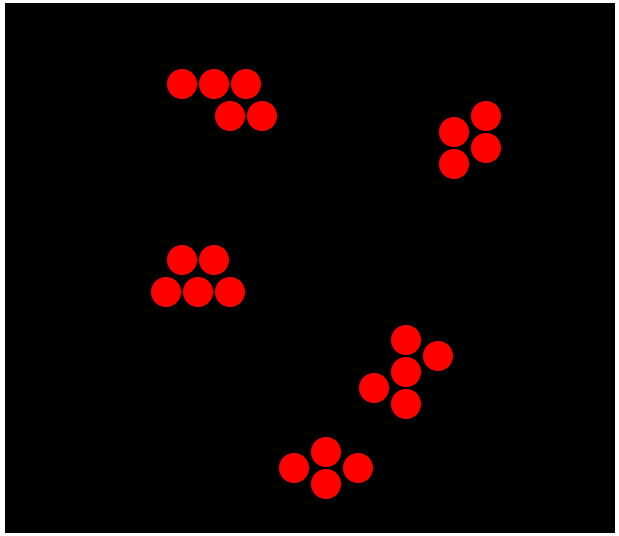


Sequential activation of cluster diffusion results in size selection

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: i = 1

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

Adatom density

Growth flux

Dimer creation

Adatom-island attachment

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

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

$$D = D_0 \exp(-E_m / kT)$$

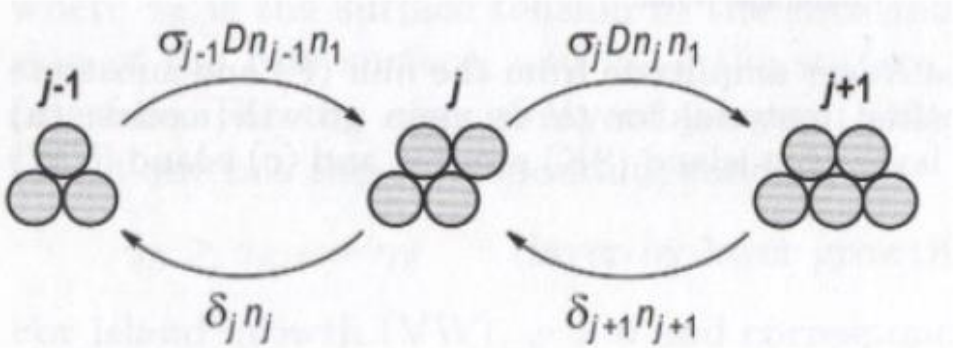
Direct impinging on an island

Direct impinging on an adatom

Rate equations give the formation rate for adatom and stable islands

Rate equations: i > 1

- Capture and decay processes → cluster size



- Rate equations:

adatom density

subcritical clusters

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{ads}} + \left(2\delta_2 n_2 + \sum_{j=3}^{i} \delta_j n_j - 2\sigma_1 Dn_1^2 - n_1 \sum_{j=2}^{i} \sigma_j Dn_j \right) - n_1 \sigma_x Dn_x$$

stable clusters

deposition rate

$$\frac{dn_j}{dt} = n_1 \sigma_{j-1} Dn_{j-1} - \delta_j n_j + \delta_{j+1} n_{j+1} - n_1 \sigma_j Dn_j$$ → metastable clusters

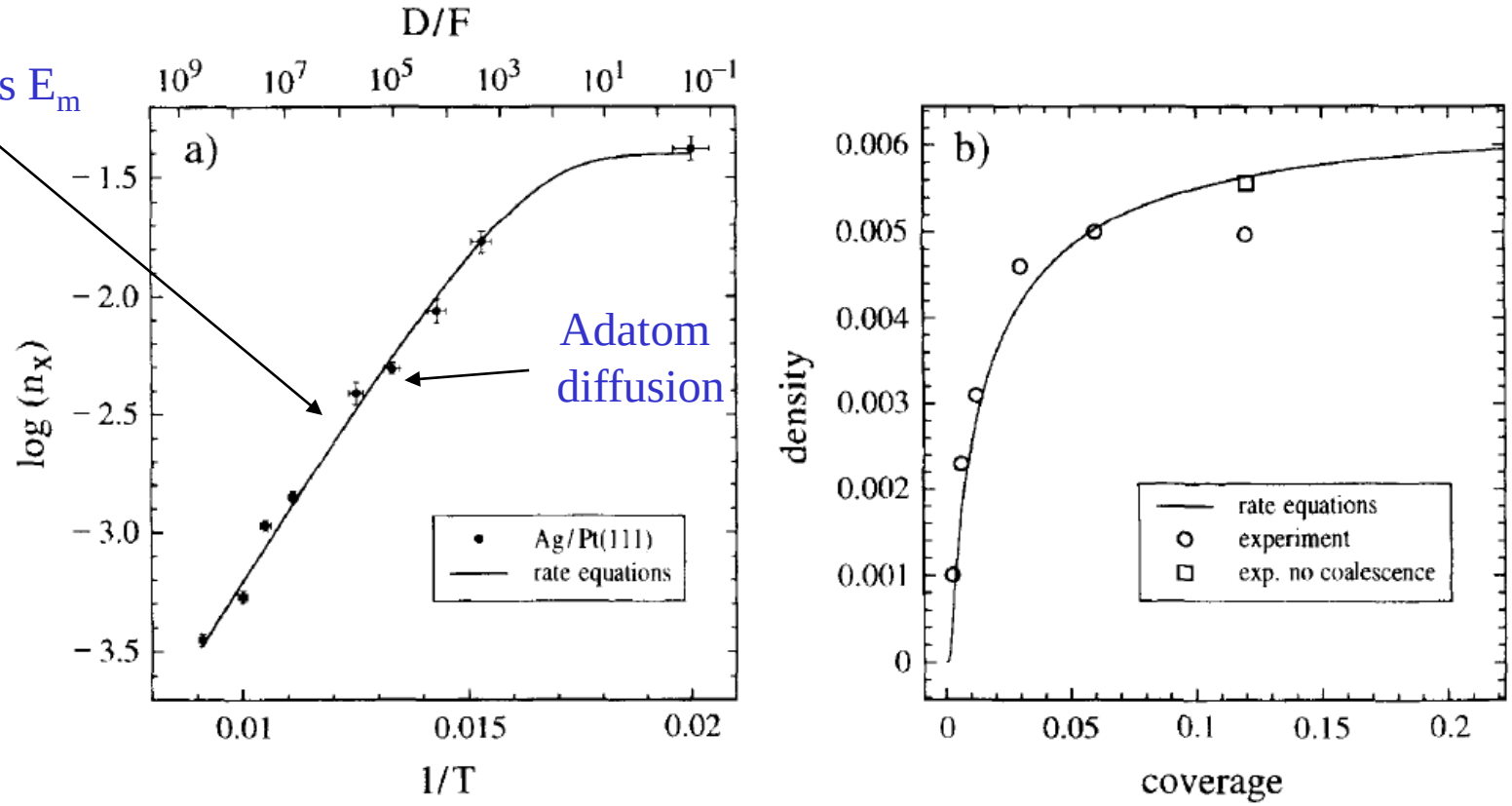
$$\frac{dn_x}{dt} = n_1 \sigma_i Dn_i$$ → stable clusters

Island density

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

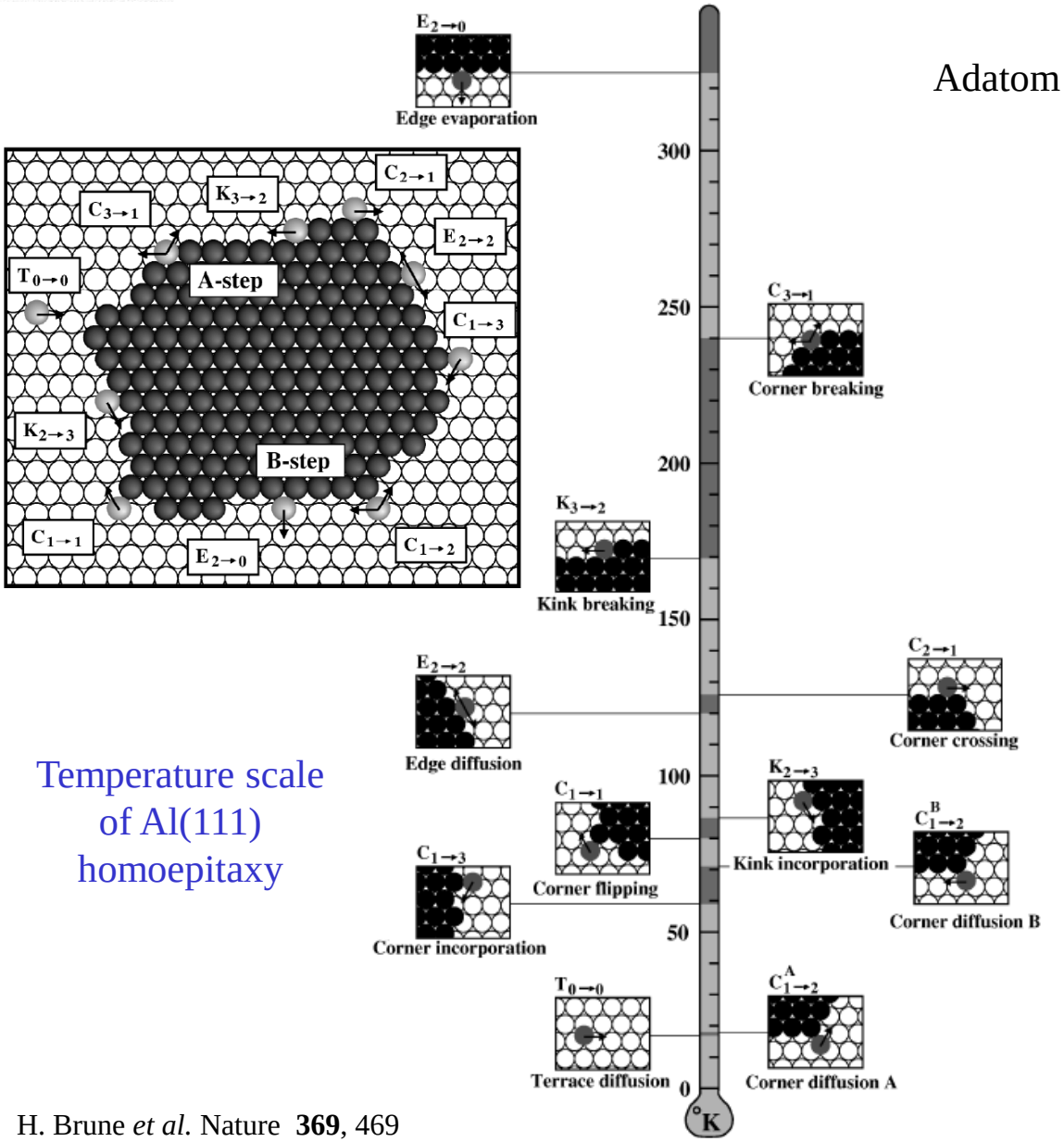
$$i = 1 \rightarrow E_i = 0 \rightarrow n_x = \eta(\theta, i)\left(\frac{D}{F}\right)^{-1/3} = n_x = \eta(\theta, i)\left(\frac{D_0}{F}\right)^{-1/3} \exp\left(\frac{E_m}{3kT}\right)$$

The slope gives E_m



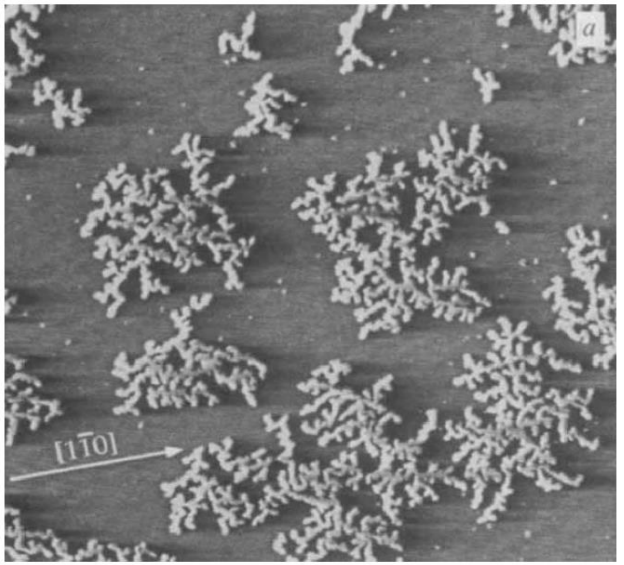
Comparison of experimental island densities for Ag/Pt(111) with self-consistent calculations from mean-field nucleation theory. (a) Arrhenius plot of saturation island densities ((cov. = 0.12 ML) for the regime where dimers are stable nuclei. (b) Island density vs. coverage at 75 K).

Island shape

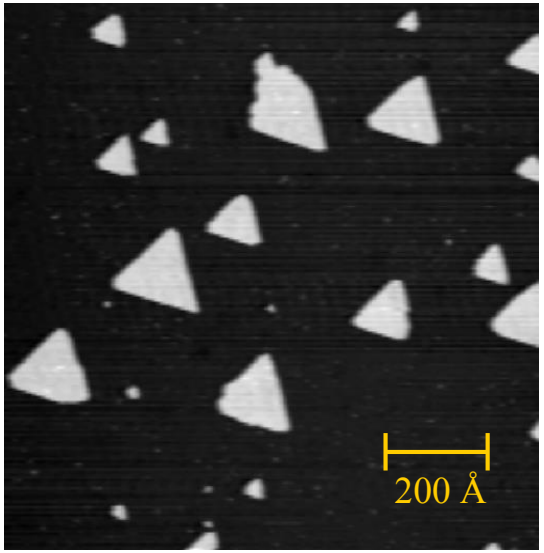


Temperature scale of Al(111) homoepitaxy

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



20 nm

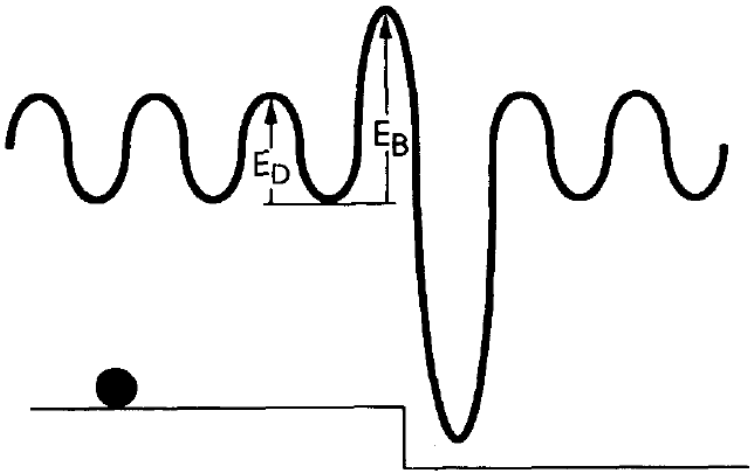


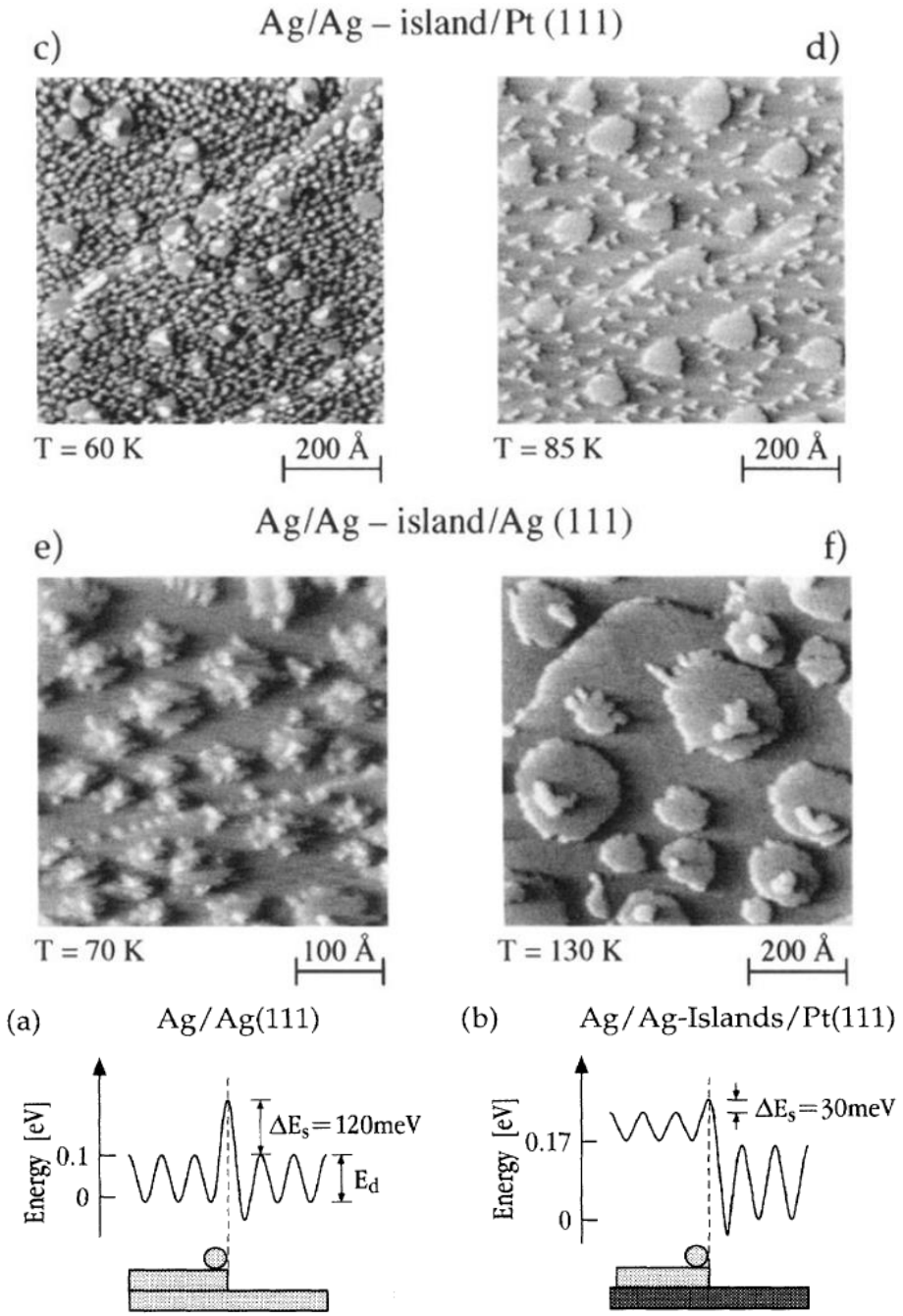
Co/Pt(111) T=270K:
Adatom edge diffusion is activated

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)

Inter-layer mass transport: Schwoebel barrier

Schematic of the energy landscape seen by an adatom approaching a step edge





K. Bromann *et al.* Phys. Rev. Lett. **75**, 677 (1995);
K. Kyuno *et al.* Surf. Sci. **383**, L766 (1997)

Reentrant layer-by-layer growth

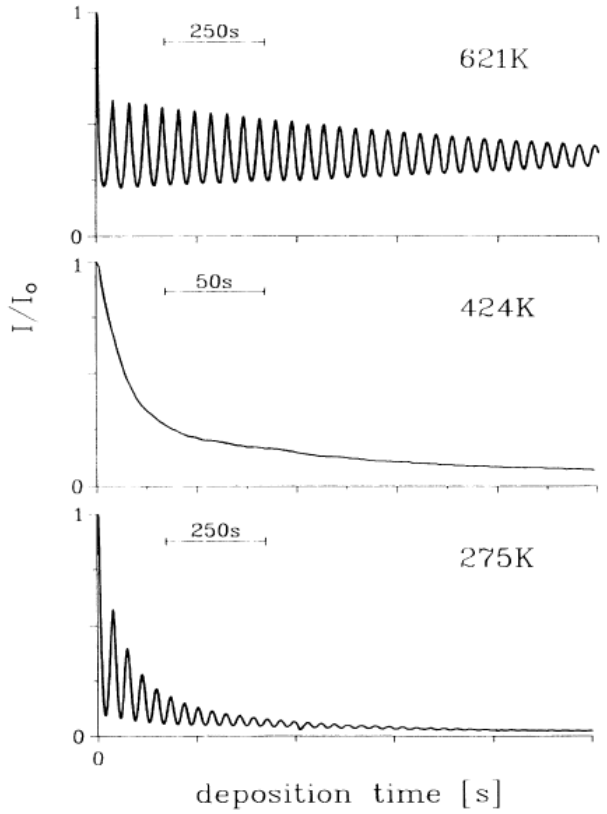


FIG. 1. The normalized He specular peak height vs Pt on Pt(111) deposition time measured at three different surface temperatures. All other parameters including the deposition rate (confined between 1/40.6 and 1/36 ML/s) are identical. The oscillatory behavior at high and low temperature is evidence for layer-by-layer growth (denoted in the text by $2D_h$ and $2D_l$ growth, respectively); the monotonic decrease in the intermediate region indicates 3D growth.

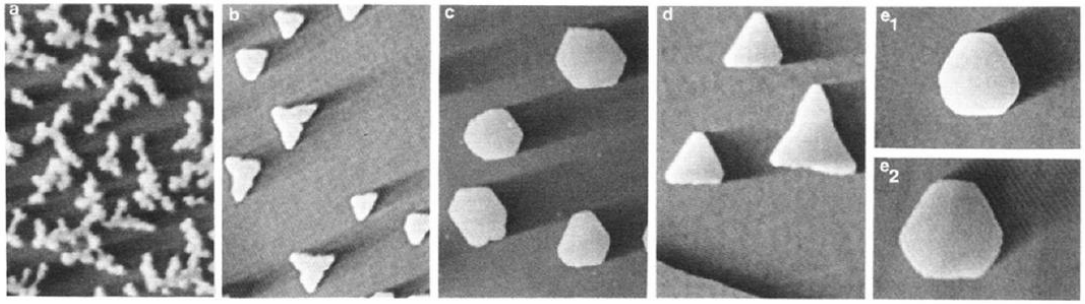
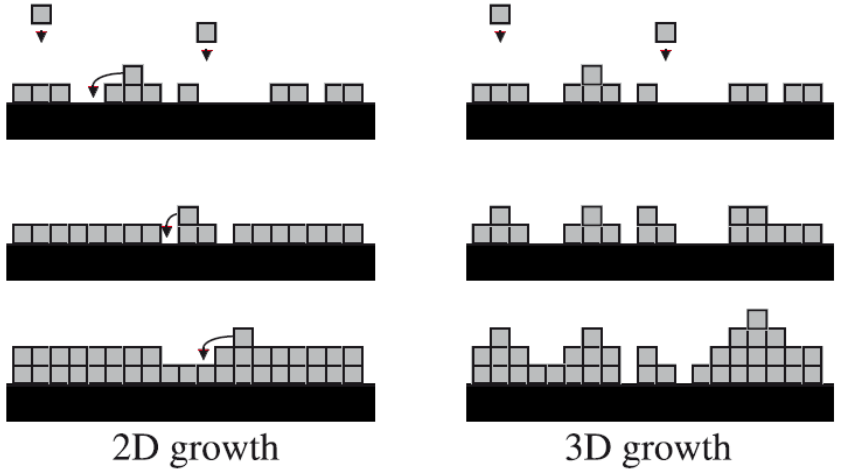


FIG. 1. Island shapes on Pt(111) resulting at various surface temperatures T_s after deposition of an amount Θ with a typical rate of 1×10^{-2} ML/s on images with a size S. (a) $T_s=200$ K, $\Theta=0.2$ ML, $S=280$ Å$\times400$ Å; (b) $T_s=400$ K, $\Theta=0.08$ ML, $S=1300$ Å$\times1900$ Å; (c) $T_s=455$ K, $\Theta=0.14$ ML, $S=770$ Å$\times1100$ Å; (d) $T_s=640$ K, $\Theta=0.15$ ML, $S=2300$ Å$\times3300$ Å; (e_1) $T_s=710$ K, $\Theta=0.08$ ML, $S=1540$ Å$\times1100$ Å; (e_2) after deposition at $T_s=425$ K ($\Theta=0.08$ ML) the sample was *additionally annealed* to 710 K for 1 min and then imaged ($S=630$ Å$\times900$ Å).



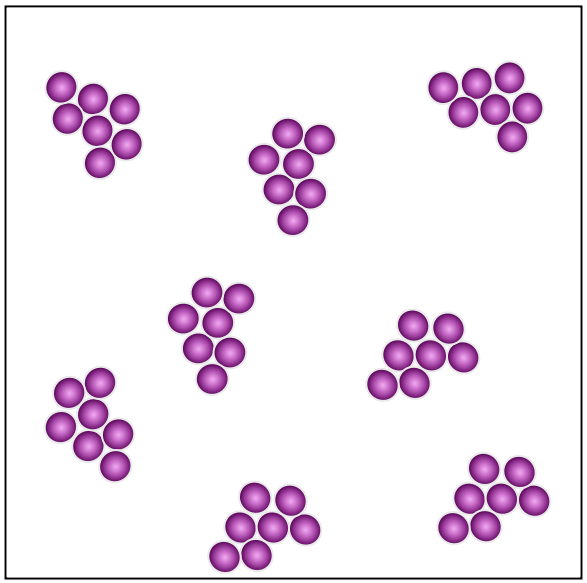
Inter-layer diffusion depends on the island size and shape

R. Kunkel *et al.* Phys. Rev. Lett. **65**, 733 (1990); T. Michely *et al.* Phys. Rev. Lett. **70**, 3943 (1993); M. Schmid *et al.* Appl. Phys.A **72**, 405 (2001)

Epitaxial growth of two-dimensional alloys

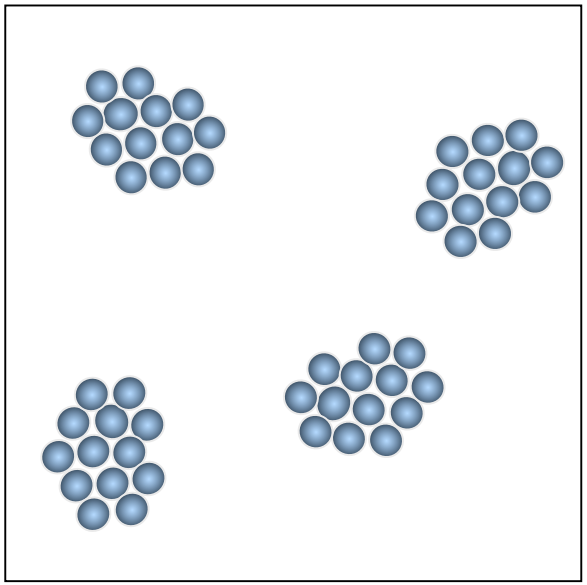
Fe

$$\nu = \nu_0 \exp(-E_i / kT)$$



Co

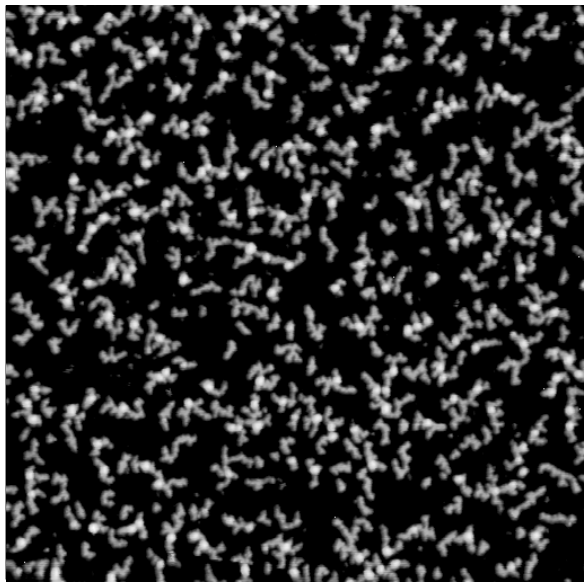
$$\nu = \nu_0 \exp(-E_i / kT)$$



Epitaxial growth of two-dimensional alloys

Fe

$\nu = \nu_0 \exp(-E_i / kT)$



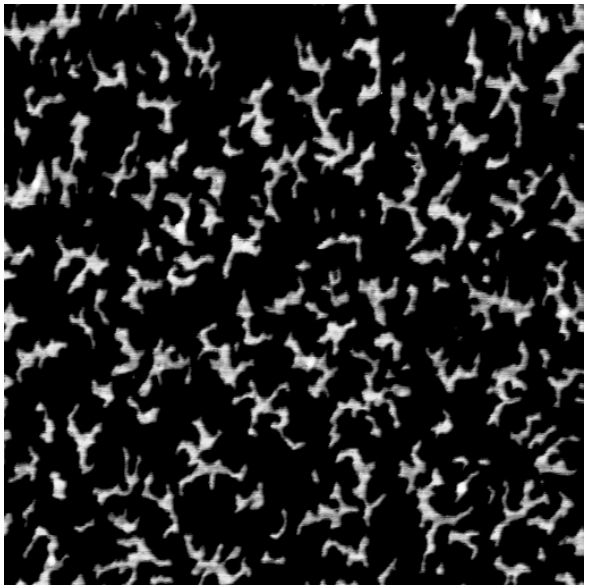
Island size = 90 atoms/isl

$T_{dep} = 140$ K

$\Theta = 0.25$ ML

Co

$\nu = \nu_0 \exp(-E_i / kT)$



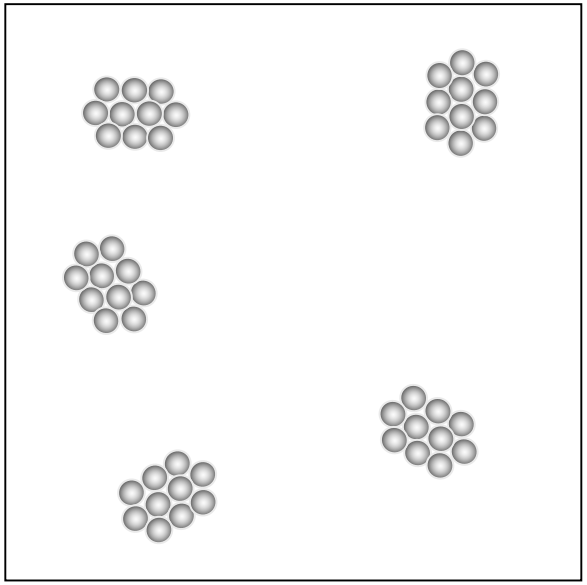
Island size = 390 atoms/isl

Alloy (Fe_xCo_{1-x}) growth by co-deposition:
the island size (density) depends on the relative percentage of the two elements!!!!

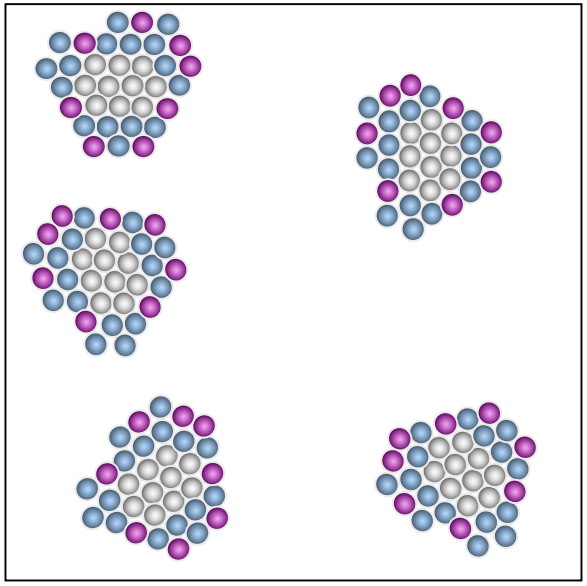
Nanostructured surface

Epitaxial growth of two-dimensional alloys

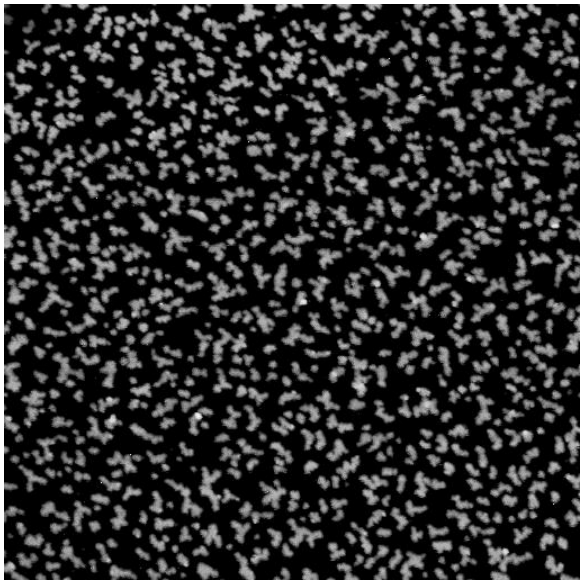
Pre-defined nucleation sites to define the island density



Growth of the alloyed nanostructures on the template substrate



Epitaxial growth of two-dimensional alloys



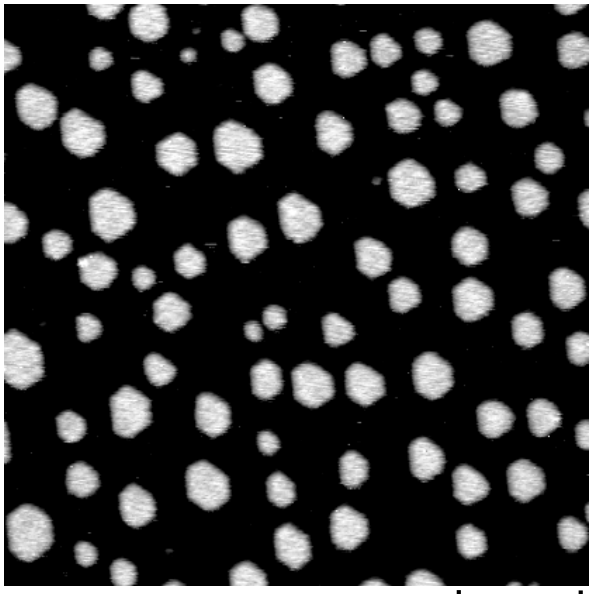
10 nm

Pt

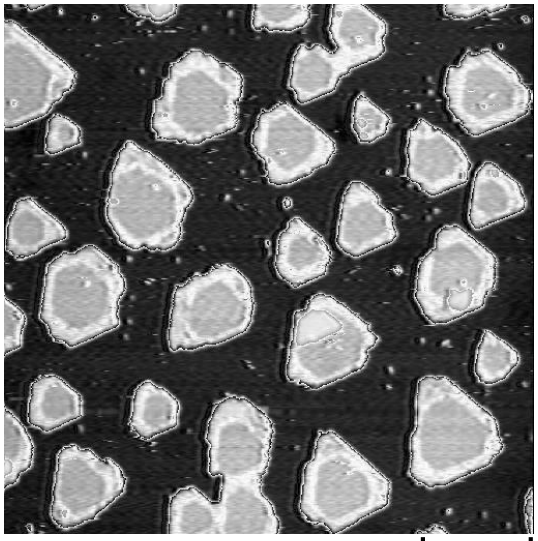
T_{dep} = 200K

Θ = 0.2 ML

Annealing to 800 K



10 nm



30 nm

Co_xFe_{1-x} decoration

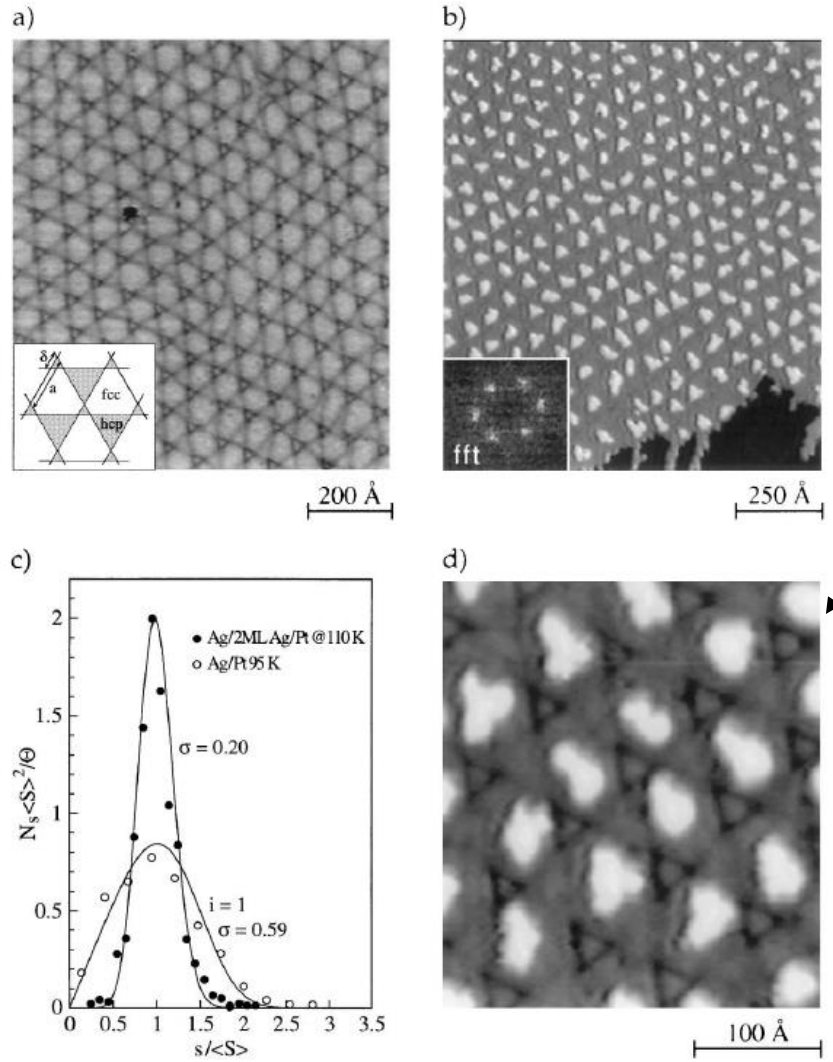
T_{dep} = 250K

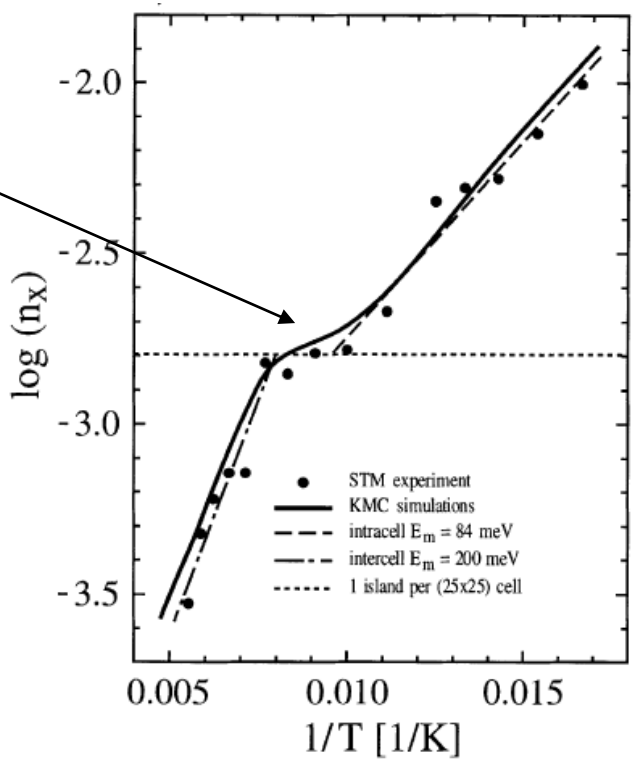
Θ = 0.2 ML

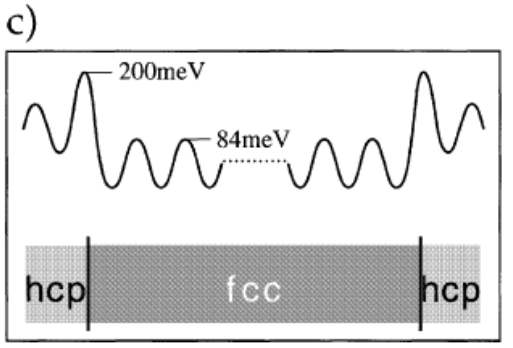
Self assembled nanostructure arrays: superlattices

Self-organized growth of nanostructure arrays on strain-relief patterns

Island confinement



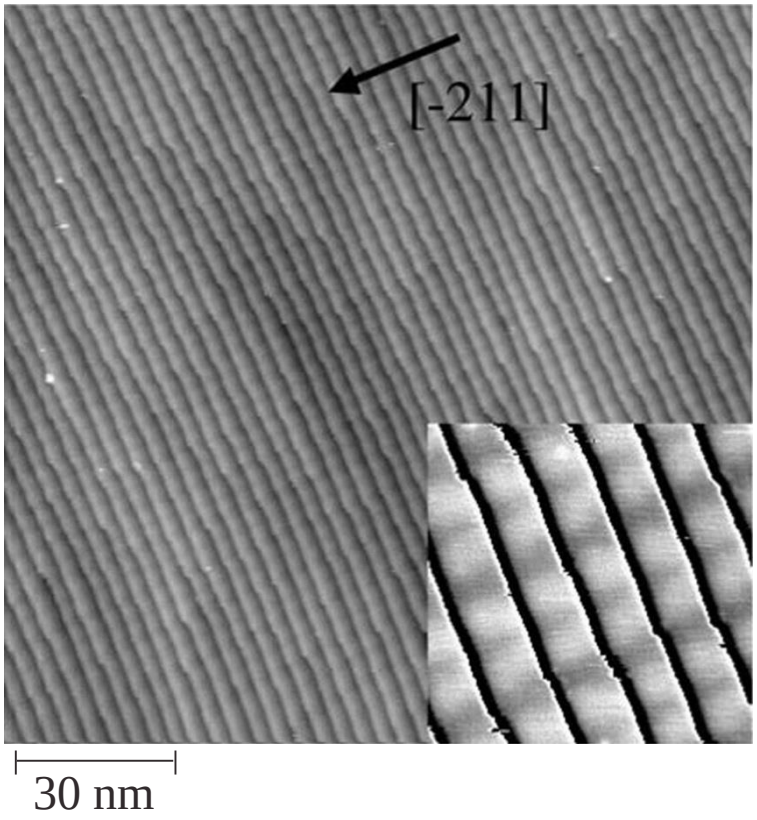




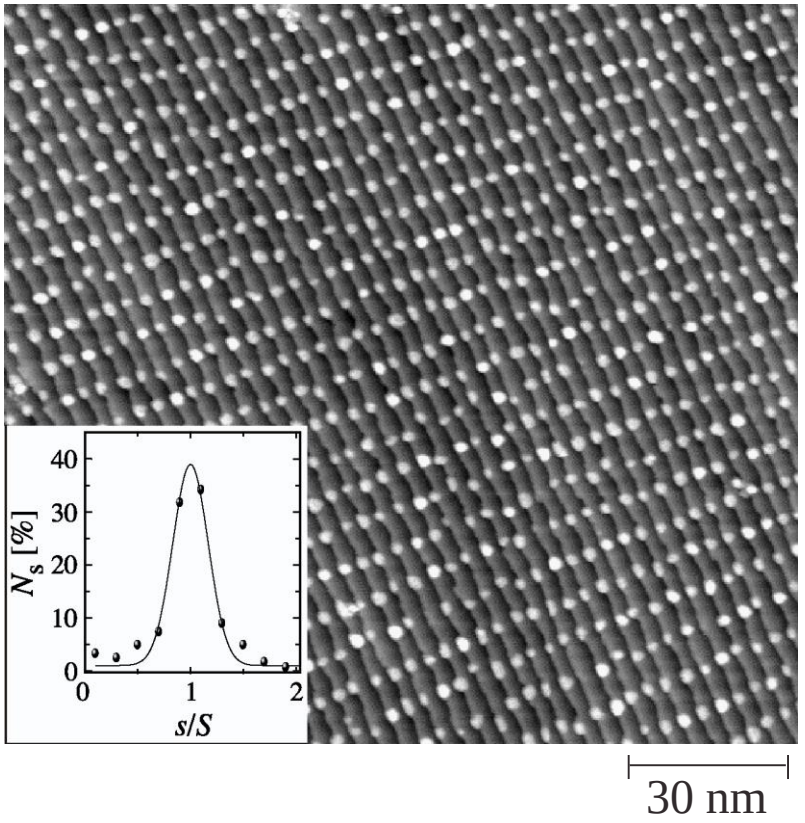
Nucleation of an island superlattice on a reconstruction network. (a) STM image of the domain wall network formed by the second Ag monolayer on Pt(111). (b) Ag nucleation on this network at T =110K (θ = 0.10 ML). (c) Almost monodispersed size distributions are associated with the periodic island spacing. (d) Detail showing that islands form exclusively on the fcc stacking areas

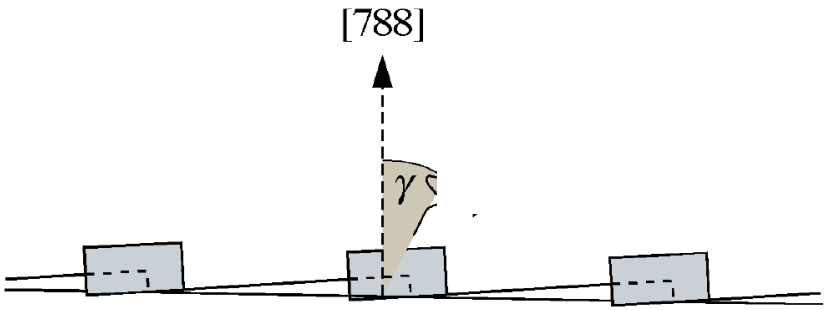
H. Brune *et al.* Nature **394**, 451 (1998); H. Brune Surf. Sci. Rep. **31**, 121 (1998);

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



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



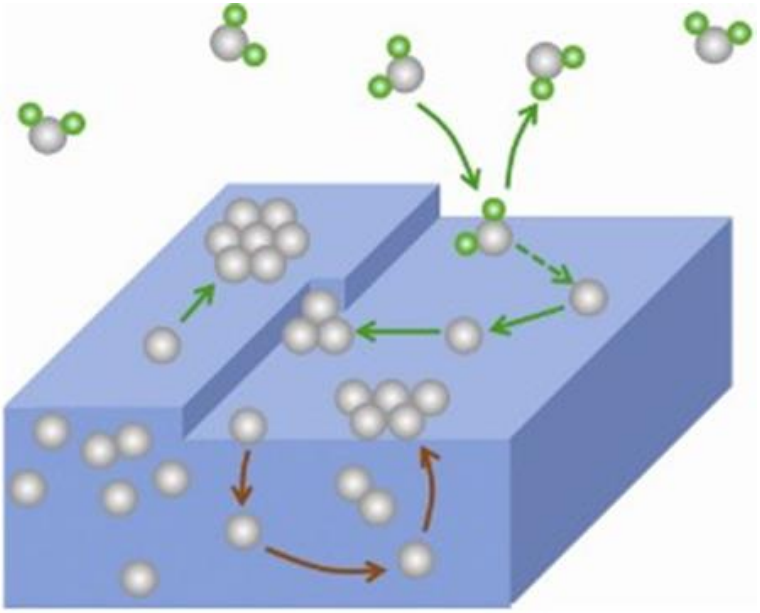


V. Repain *et al.* Europhys. Lett. **58**, 730 (2002); N. Weiss et al. Phys. Rev. Lett. **95**, 157204 (2005);

Self assembled nanostructure on graphene

Graphene growth

hydrocarbons flux



- Hydrogen
- Carbon

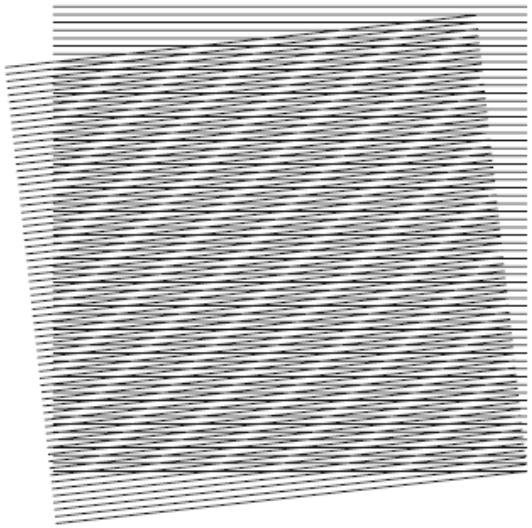
Hydrocarbons molecules brakes on the hot surface: H atoms leave the surface while C atoms organize in the honeycomb network of graphene

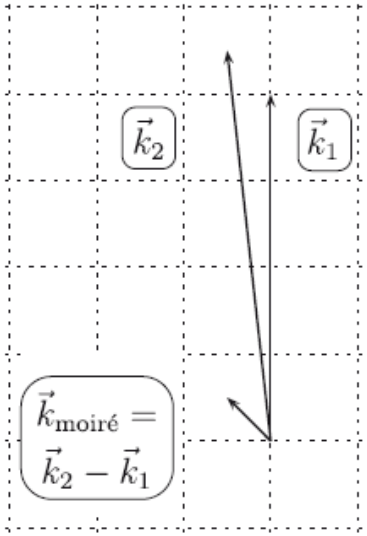
C atoms dissolved in the bulk segregate to the sample surface and form graphene

Self assembled nanostructure arrays

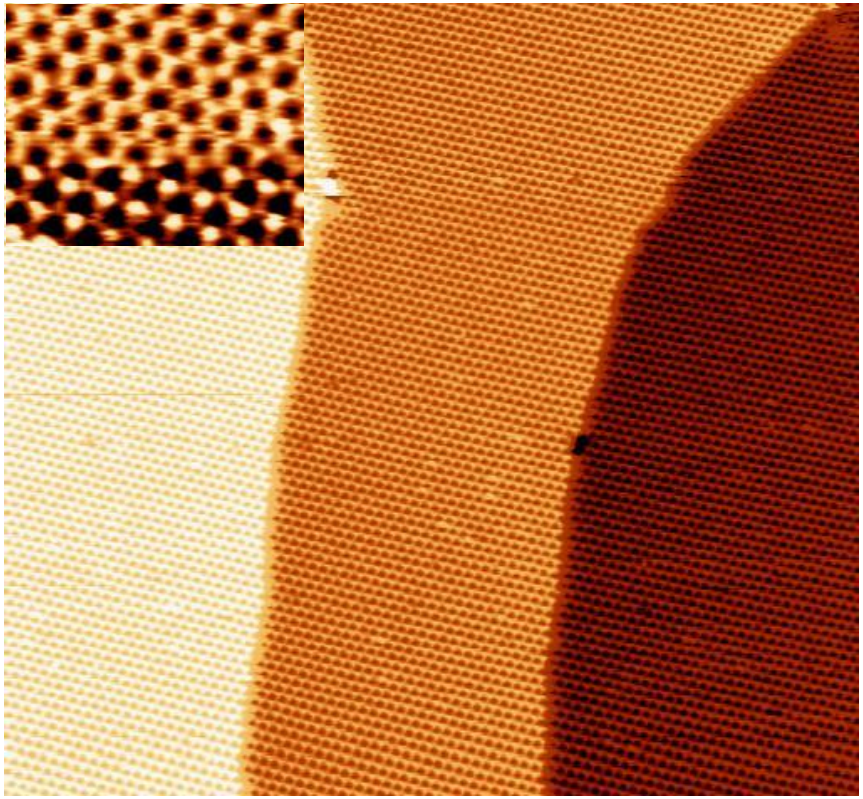
Self-organized growth of nanostructure arrays on moiré patterns: Graphene/Ir(111)

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

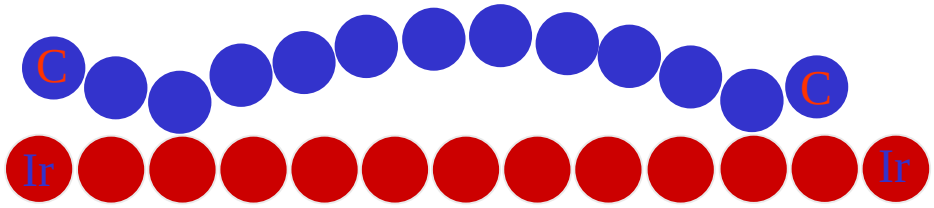




a_{Ir} = 0.27 nm
a_c = 0.245 nm



180 x 200 nm2



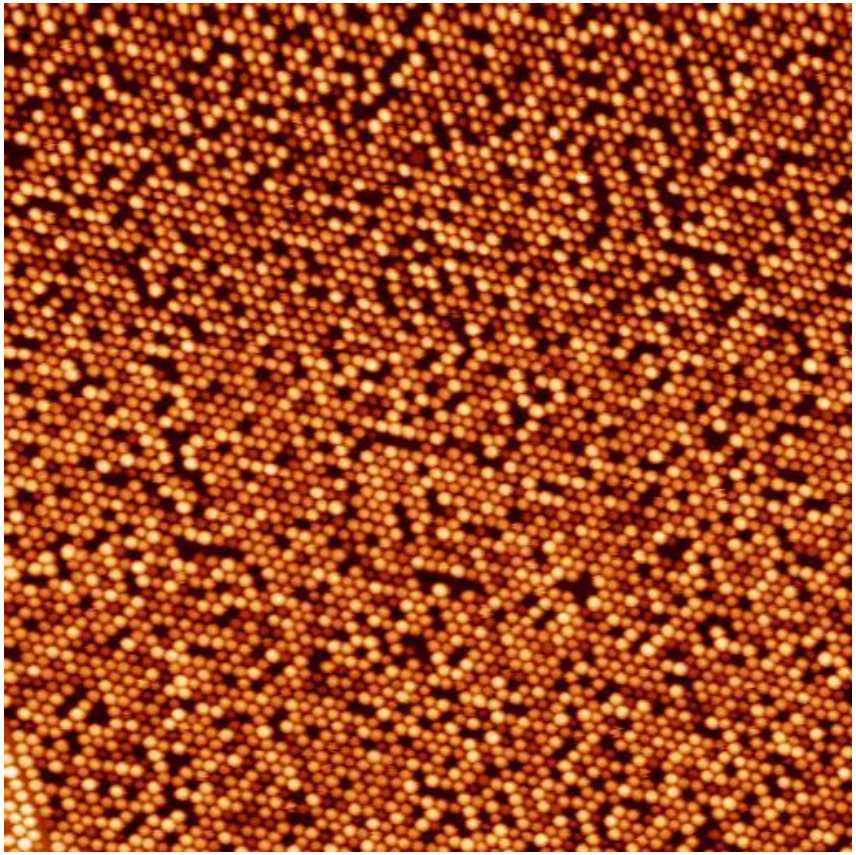
Supercell with (10x10) C atoms
on (9x9) Ir substrate atoms

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

Self assembled nanostructure arrays

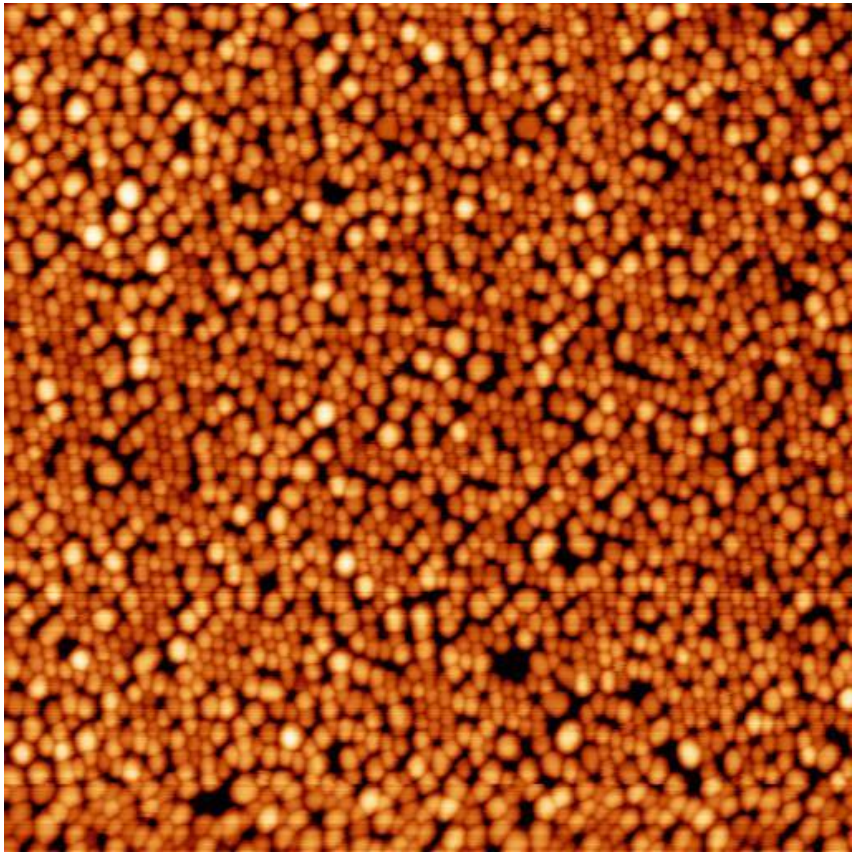
Self-organized growth of nanostructure arrays on moiré patterns: Graphene/Ir(111)

Graphene/Ir(111)+Ir
Ir deposition:
I=10.5 A, V=4.90 volts T=375 K



150 x 150 nm2

Graphene/Ir(111)+Ir+Co
Ir dep.:I=10.5 A, V=4.90 volts T=375 K
Co dep.:1 ML tdep=8 min T=300 K

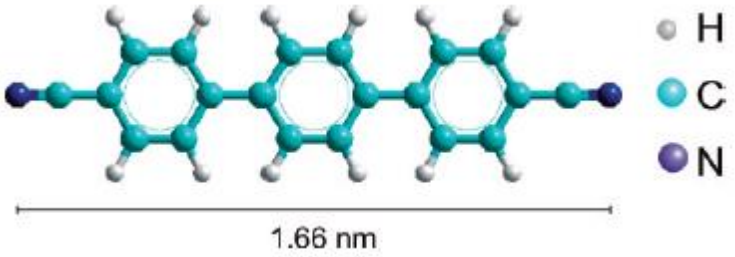


150 x 150 nm2

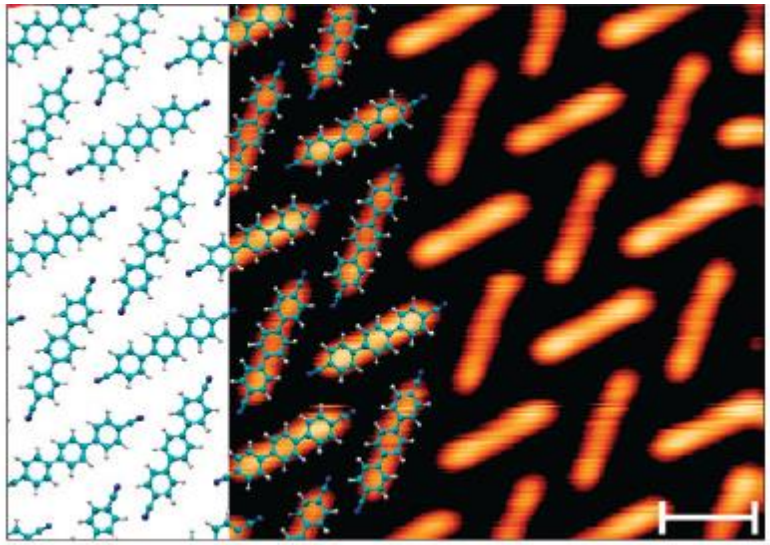
S. Rusponi not published; A. T. N'Diaye *et al.* Phys. Rev. Lett. **97**, 215501 (2006)

Molecolar network

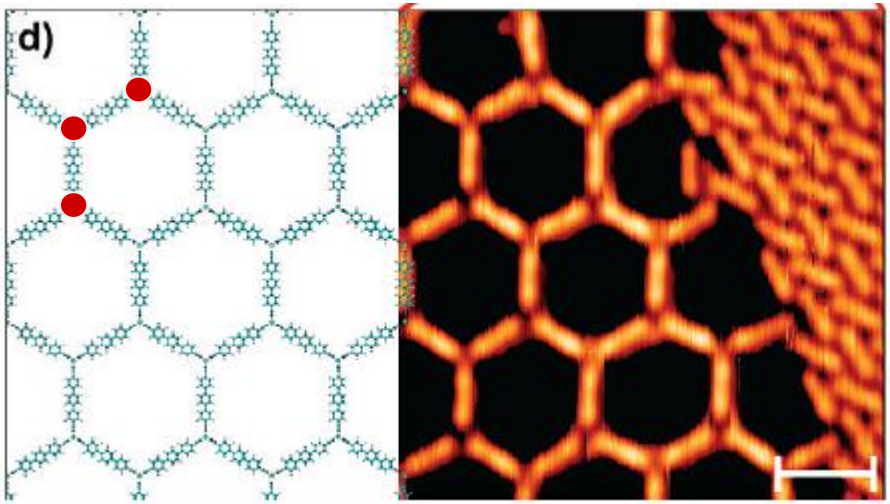
NC-Ph_3-CN



On Ag(111)



Cobalt

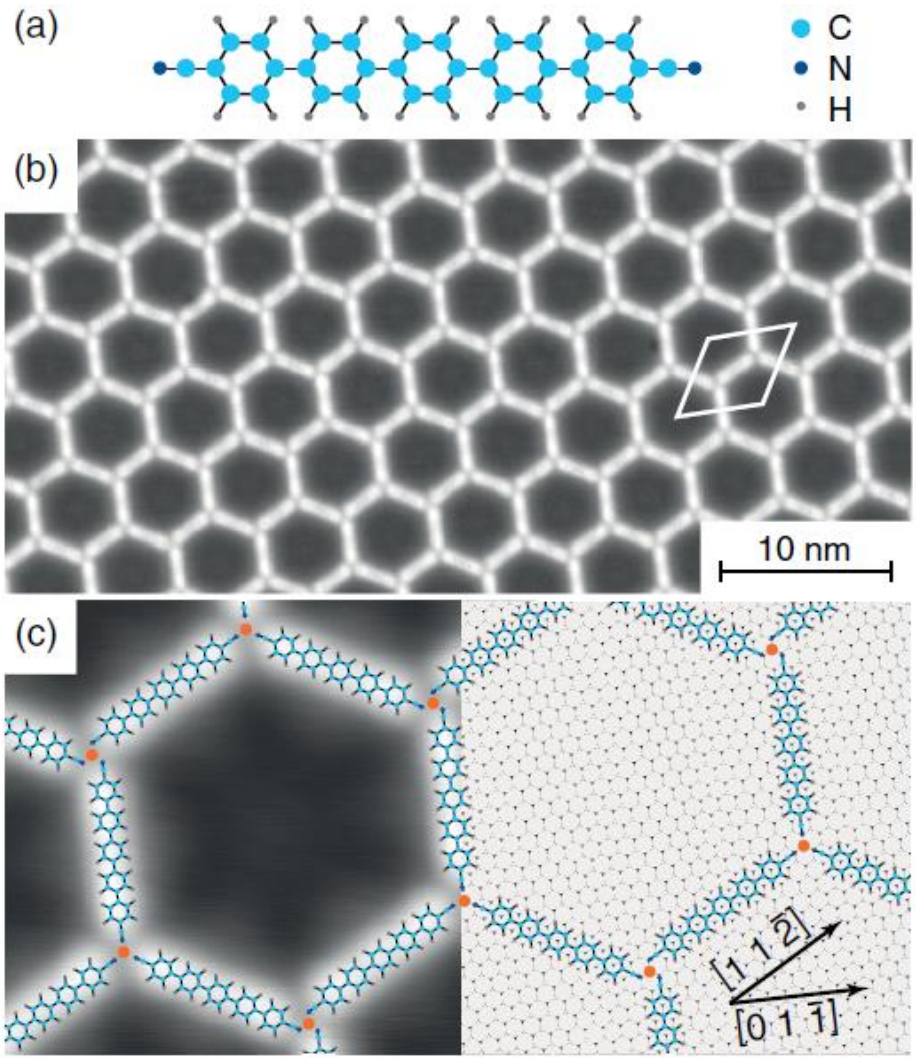


Co atoms added at room temperature coordinate the molecules in a 3-fold coordinated motif

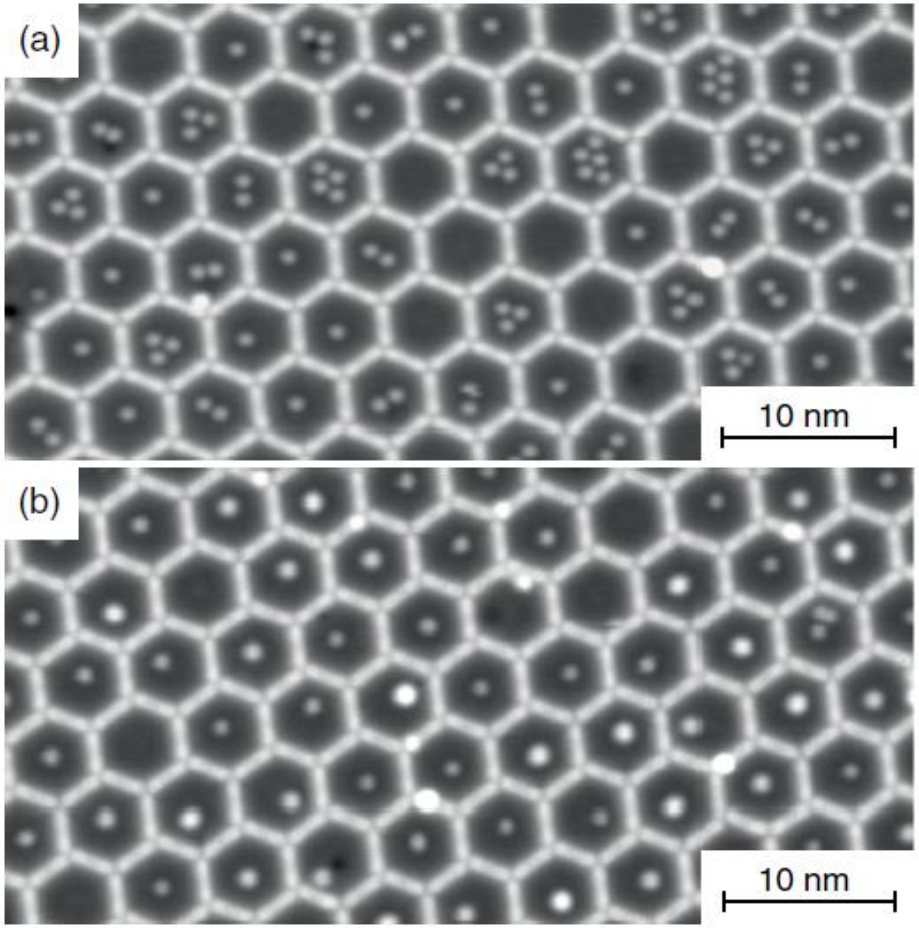
U. Schlickum *et al.* J. Phys. Chem. (2010)

Cluster Superlattice in a metal-organic quantum box network

Metal organic quantum box network



Metal organic quantum box network
a) after Fe deposition



Metal organic quantum box network
b) after Fe deposition and annealing to T_{ann} = 18K

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

Superlattices: blocking T *vs* density

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-Ph3-CN/Cu(111)	90 Tdot/in2	?
$Fe/Al_2O_3/Ni_3Al(111)$	92 T_{dot}/in^2	?
Co/Ir/graphene/Ir(111)	116 Tdot/in2	< 50 K