Scanning Tunneling Microscopy as a versatile probe to investigate low-dimensional systems at the atomic scale

Optical, Electron, and Scanning Probe Microscopy Online Workshop November 6th, 2024

Outline

- Tunneling process and working principles of Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS)

- Example 1: atomistic mechanisms of surface diffusion investigated by imaging nanometric sized islands

- Example 2: study of the early stages of oxidation of a metallic surface

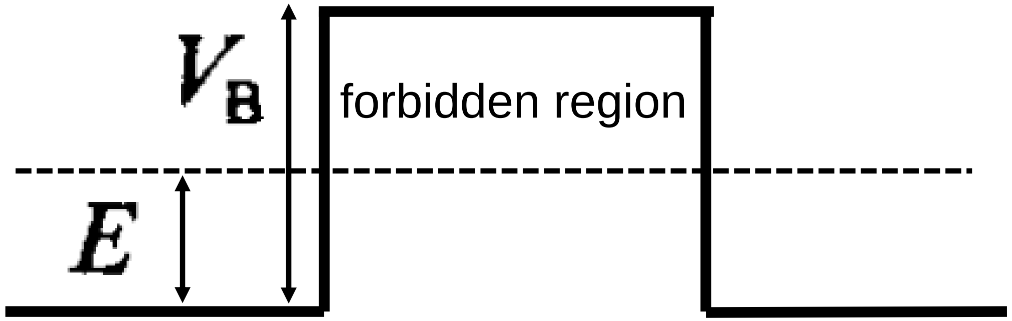
- Example 3: nucleation and electronic properties of organic films

Tunneling between two metallic electrodes

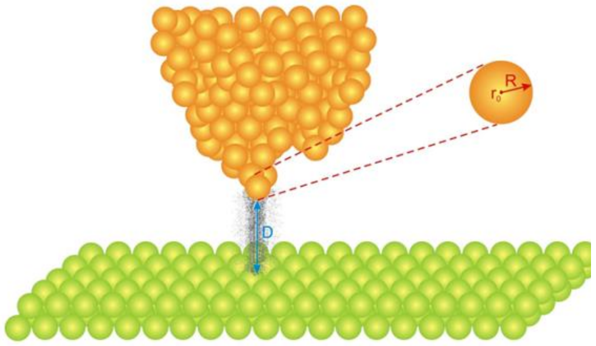
Energy

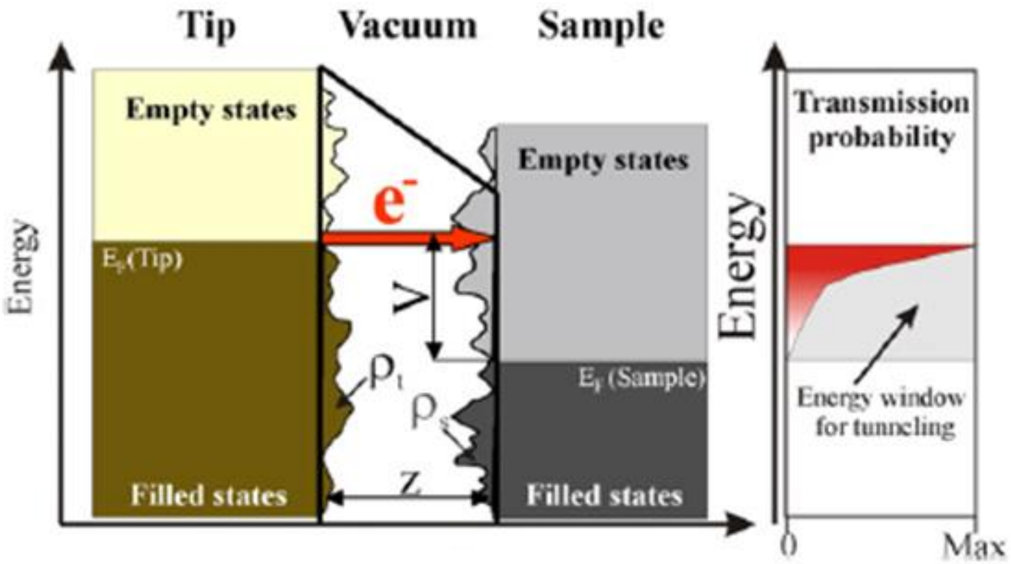
$$\psi = e^{\pm \kappa z}$$ In the forbidden region

$$\kappa^2 = 2m(V_B - E)/\hbar^2.$$



Tunneling microscopy





$$I \propto \int_{E_F}^{E_F+eV} dE\, \rho_s(r_{tip}, E)\rho_t(E-eV)T(z,E,V)$$

Sample density of electronic states ρ_s

Tip density of electronic states ρ_t

Tunneling transmission probability T

$$T(z,E,V) = \exp\left[-\frac{2z}{\hbar}\sqrt{2m(\phi - E + 1/2eV)}\right]$$

What about sample density of states (DOS)?

Starting from tunneling current:

$$I(S,V) \cong B\frac{2\pi e}{\hbar}\left(\frac{\hbar^2}{2m}\right)^2 \int_{-\infty}^{\infty} T(S,V,E)[f(E-eV)-f(E)]\rho_s(E)\rho_t(E-eV)dE$$

Tip-sample separation

Boltzmann factor

can we deconvolute the sample DOS ρ_s?

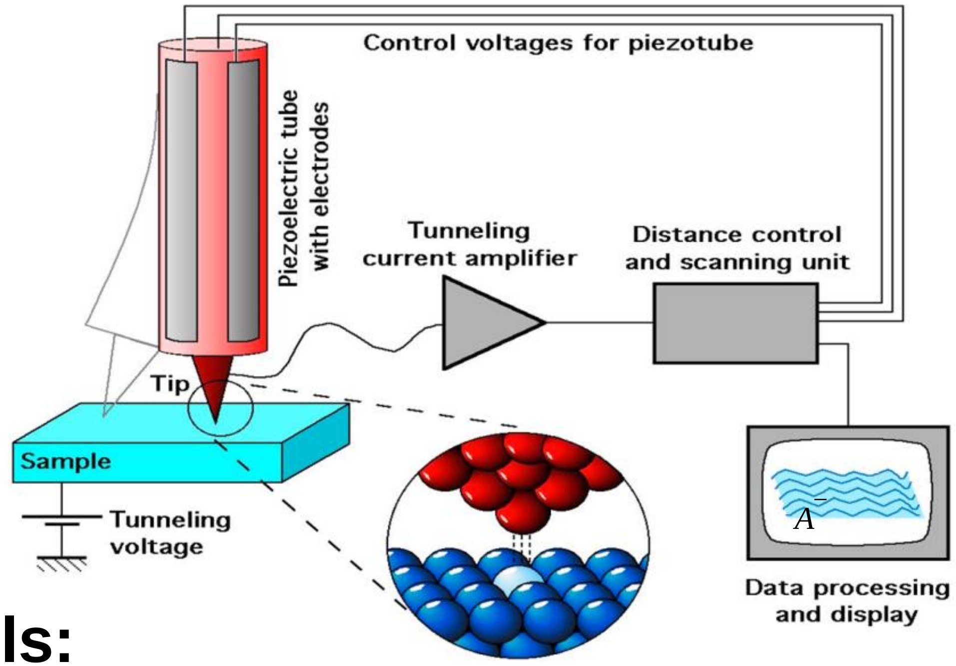
⇓

$$\frac{dI(S,V)}{dV} \cong A\left[eT(S,V,E)\rho_s(E)\rho_t(E-eV)\right]_{E=eV}$$

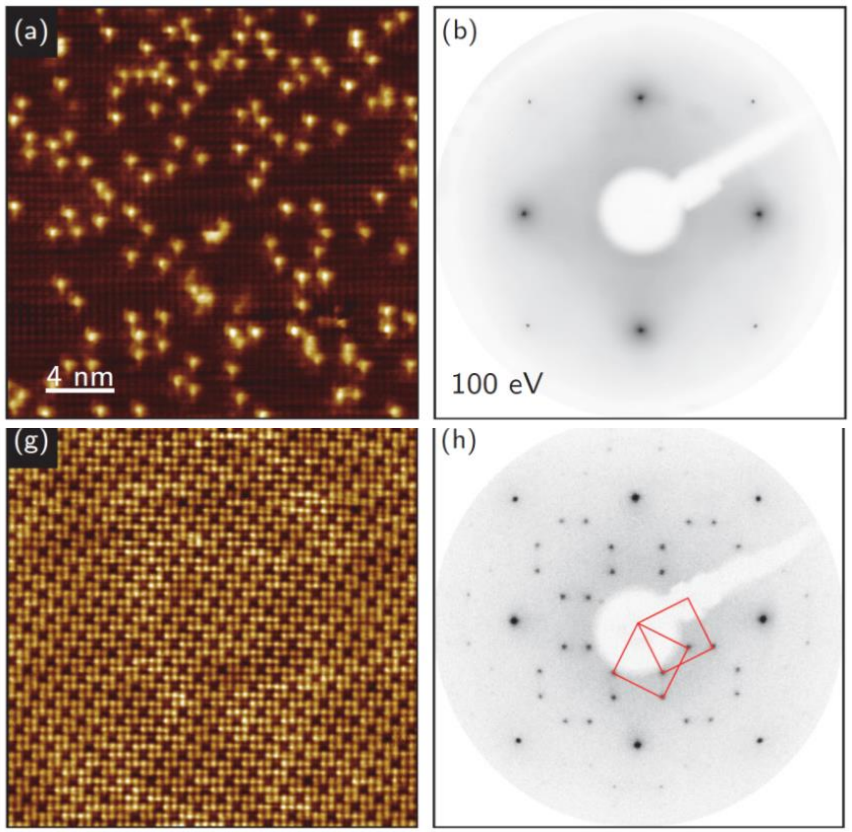
assuming constant tip DOS ➡ $$+\int_0^{eV} T(S,V,E)\rho_s(E)\frac{d\rho_t(E-eV)}{dV}dE$$

assuming constant *T(S,V,E)* ➡ $$+\int_0^{eV} \frac{dT(S,V,E)}{dV}\rho_s(E)\rho_t(E-eV)dE$$

Scanning tunneling microscopy



Direct space (STM) Reciprocal space (LEED)



Technical details:

Distance tip-sample: roughly 5-10 Å (10^{-10} m). Compare with the atomic radius of hydrogen (0.53 Å). We know the tip displacement during the scan, not the absolute value.

Number of pixel for one image: 500x500= 250.000 (but we have 4 images: forward, backward, up and down, total 1.000.000 pixel)

Speed of scan: 500 μs /pixel…. (i don't really want to calculate the time, but i think it is easy)

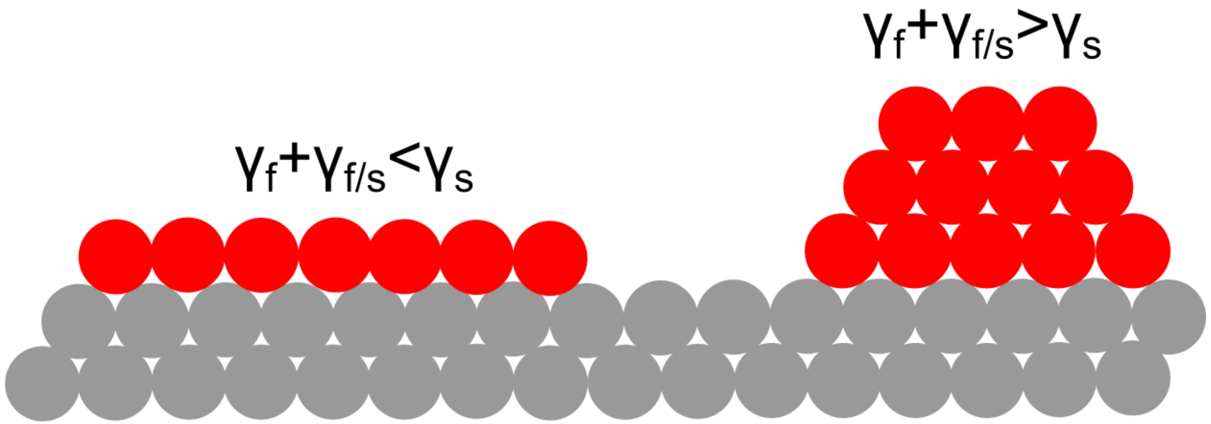
Voltage and current tip/sample: 0.001-5 V 1pA-50 nA (we need a good amplifier with low noise and very close to the tip /sample junction)

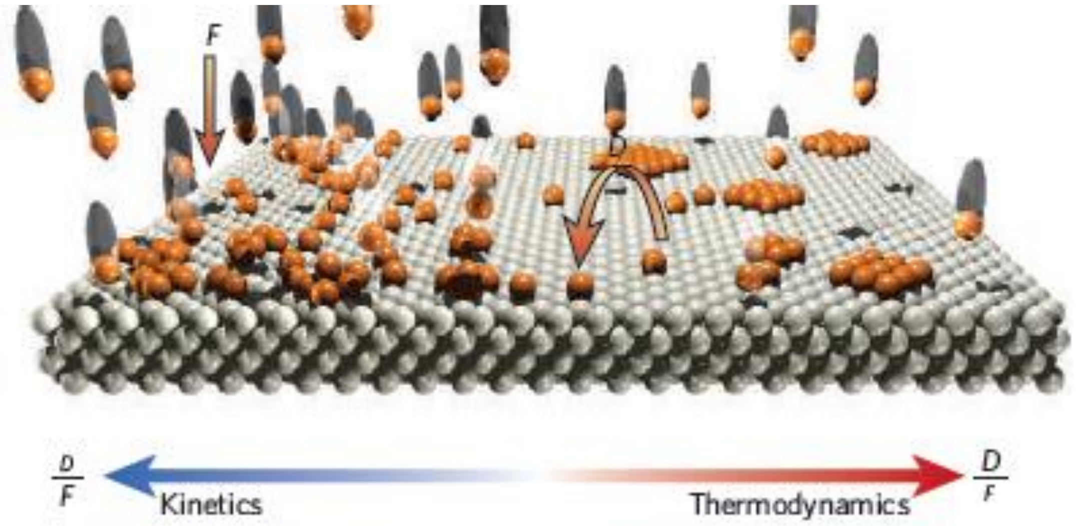
Vertical sensitivity : limited by external mechanical noise (in principle 0.01 Å, in the real world: tram 10 Å, cleaning lady 20 Å)

Lateral resolution: strongly depends on the tip shape and on the surface shape (let's say 2 Å, atomic resolution)

Example 1: Atomic diffusion on thin films growth

Thermodynamic





Johannes V. Barth, Giovanni Costantini & Klaus Kern NATURE Vol 437|29

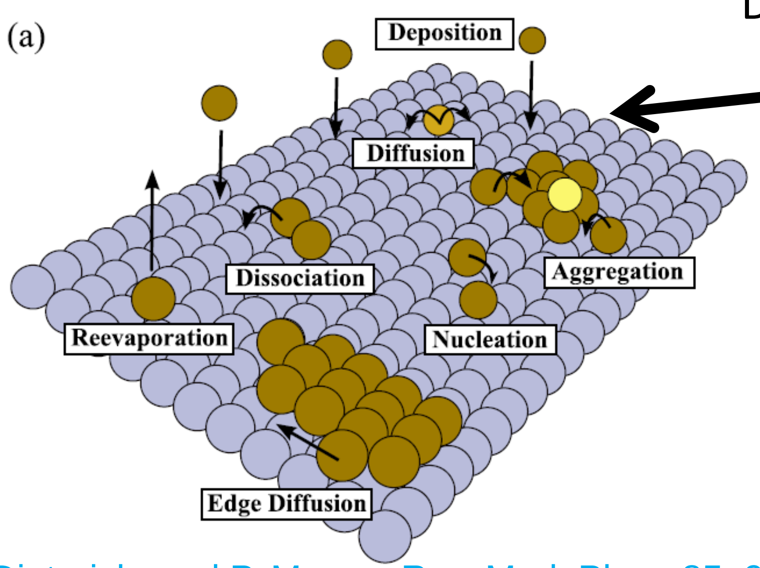
$$D = D_0 e^{-\frac{E}{k_B T}} \quad [m^2/s]$$

F flux

$D \gg F$ Thermodynamic regime

$D \ll F$ Kinetic regime

Islands density and atomic diffusion

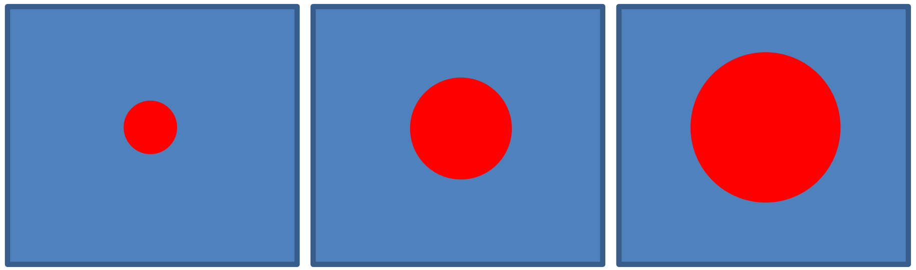


Deposition flux

Φ

M. Einax, W. Dieterich, and P. Maass, Rev. Mod. Phys. 85, 921 (2013)

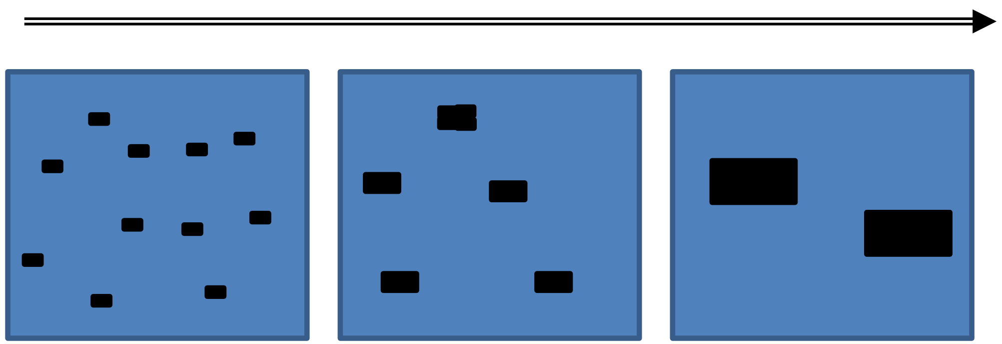
Random walk



Top view of the surface

● Area spanned by the adatom

Increasing *D*



Saturation island density is a measure of the adatom mobility

Islands density [nm^{-2}]

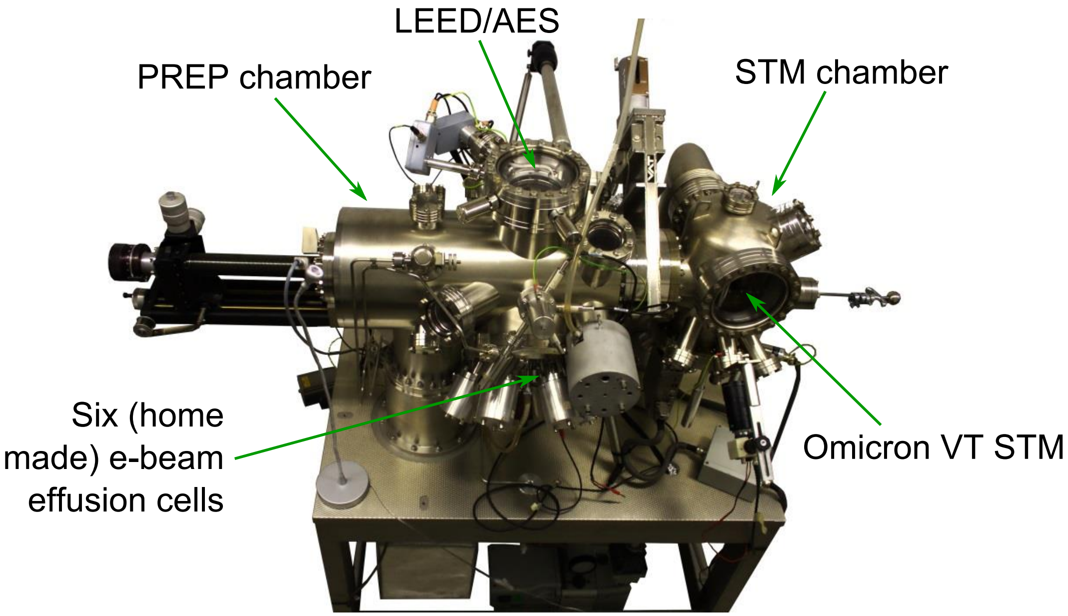
$$n_s = \eta \left(\frac{\Phi}{D} \right)^{i/(i+2)}$$

Diffusion coefficient

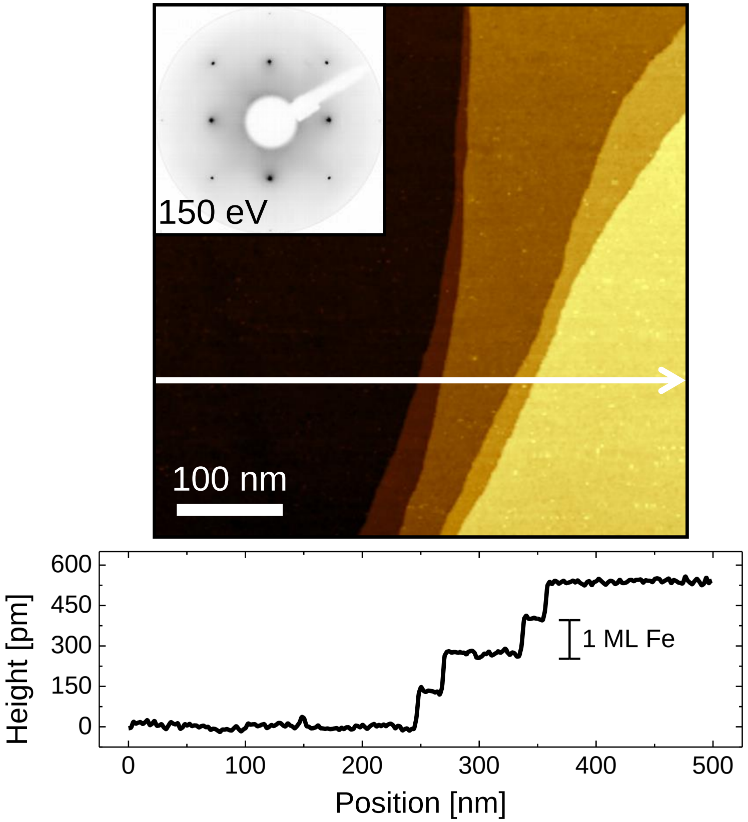
Typical values

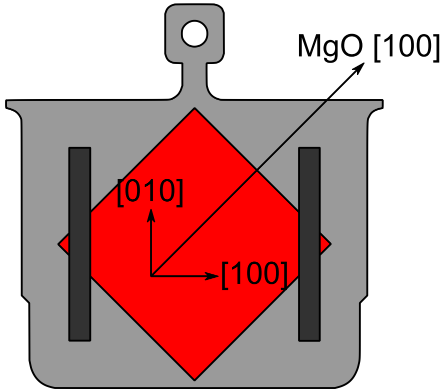
$D_0 = 7.2 \times 10^{-4}\ cm^2 s^{-1}$ E=0.05 eV

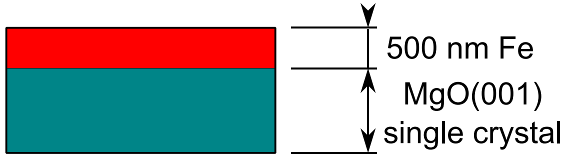
Experimental setup and substrate



Base pressure < 6 × 10^{-11} mbar in both chambers

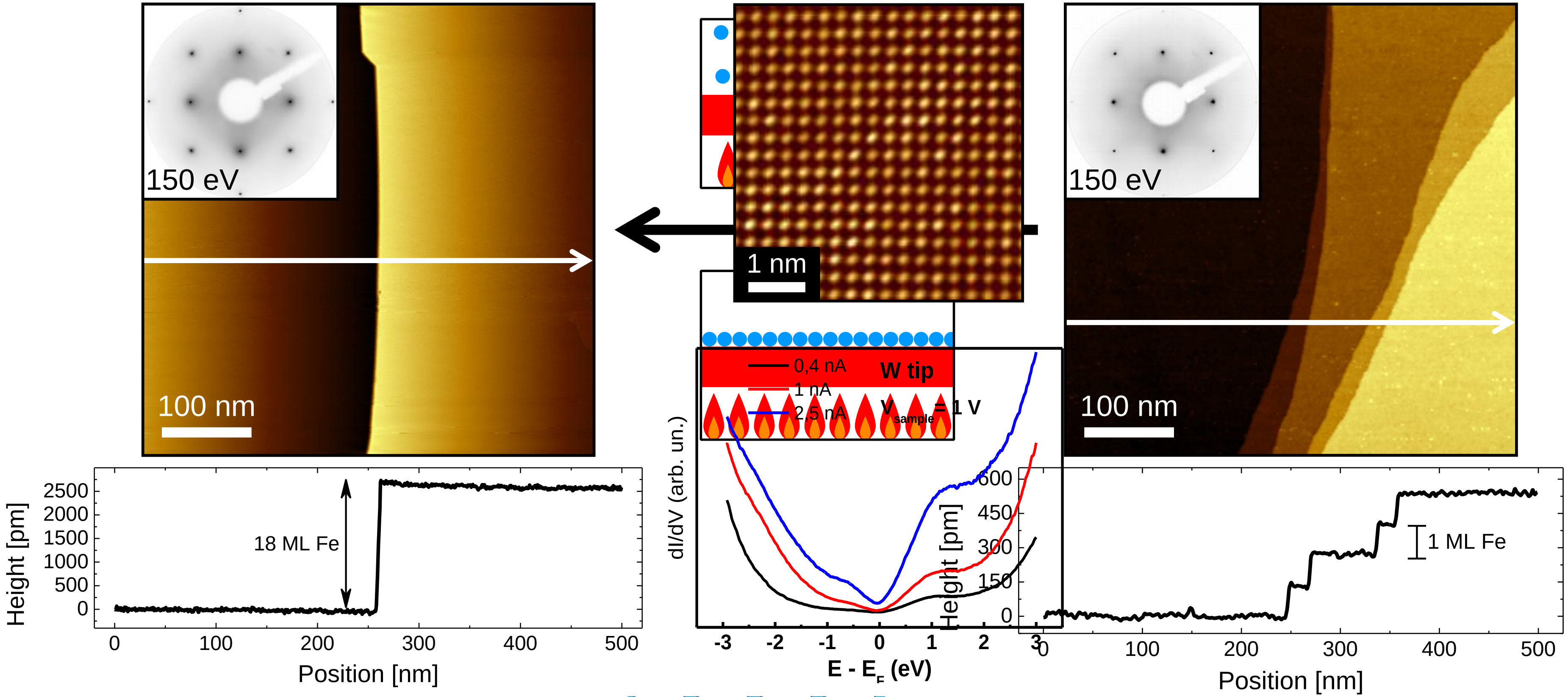




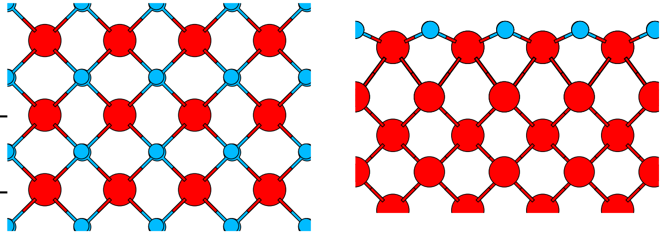


The well-defined Fe oxide: Fe(001)-*p*(1×1)O

Dose 30 L O_2 at 450°C, 2×10^{-7} mbar + Anneal at 700°C for 10 min



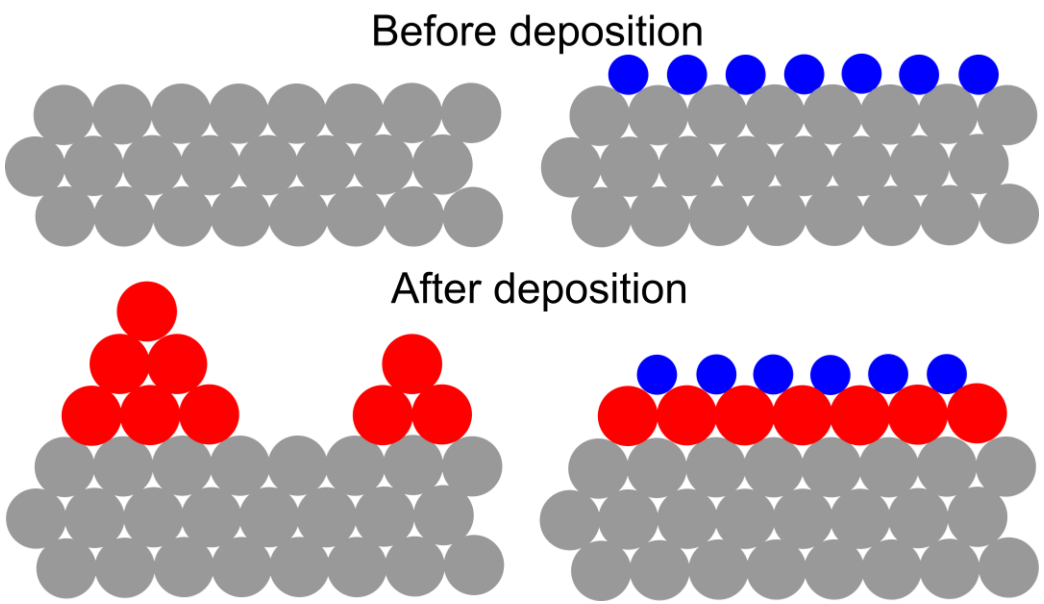
$$a_{Fe} = 287 \text{ pm}$$
$$[a_{Fe\text{-}O}/\sqrt{2} = 305 \text{ pm}]$$



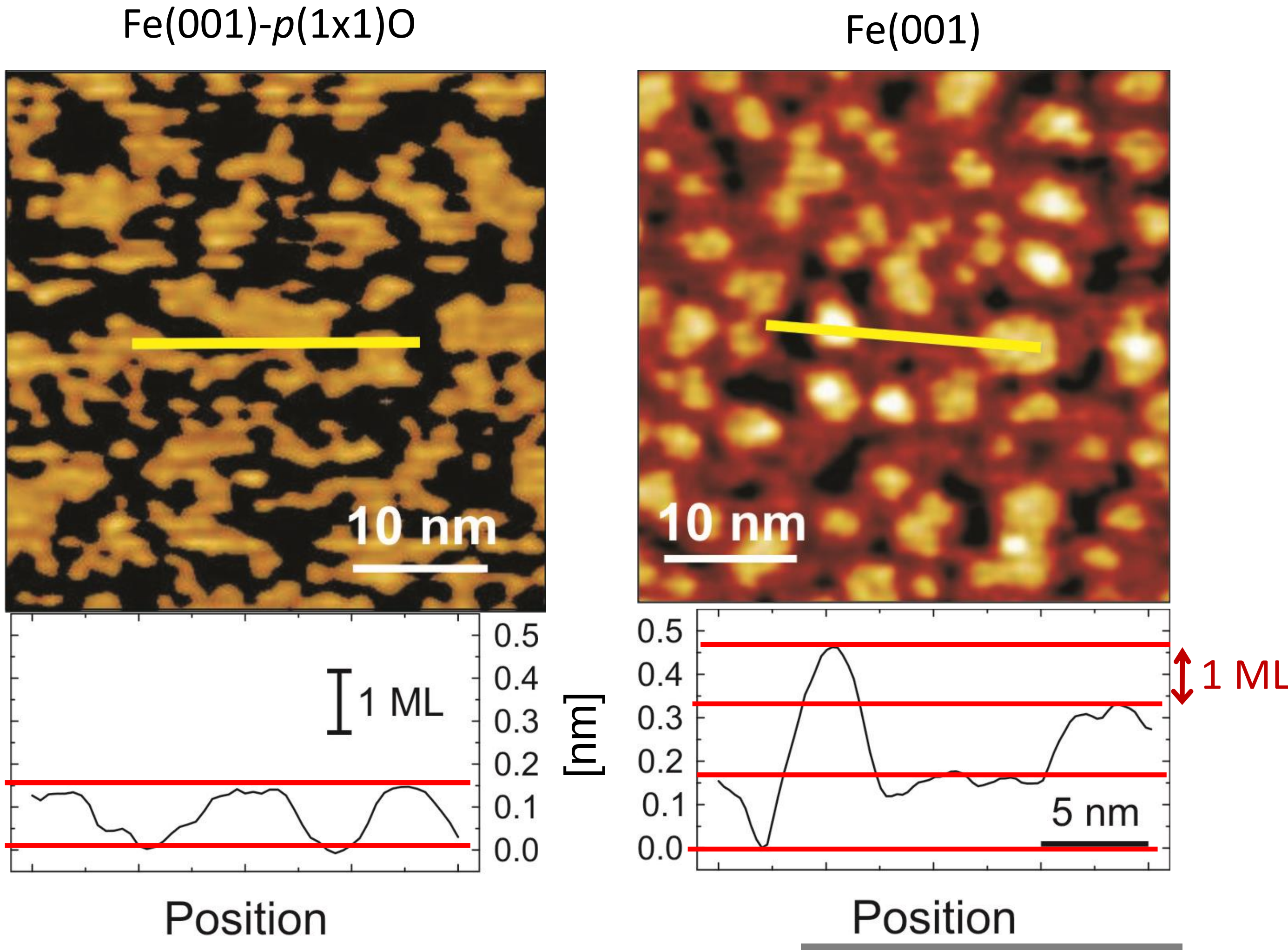
[3] Donati *et al.*, Phys. Rev. B **79,** 195430 (2009); Picone *et al.*, *ibid.* **81**, 115450 (2010)

Surfactant action

Without surfactant With surfactant



Deposition (Molecular Beam Epitaxy) of 3.5 monolayers of iron on…

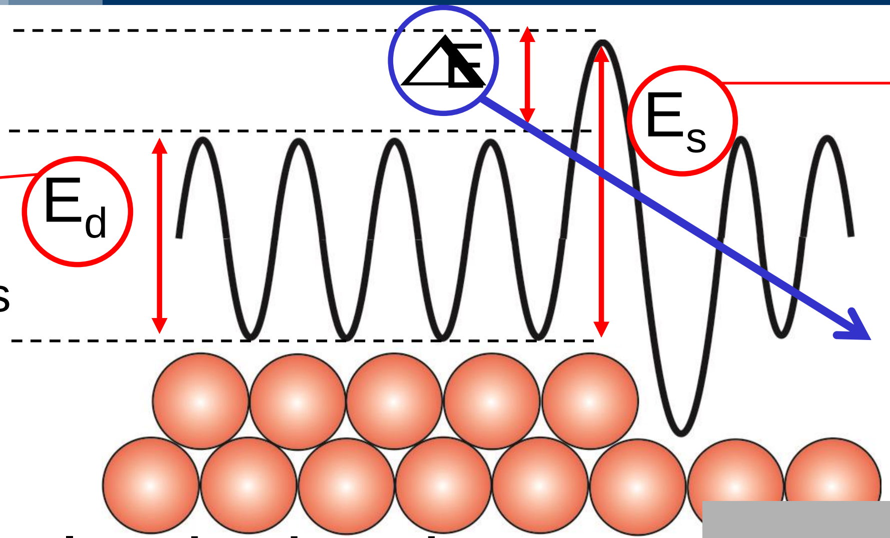


Surfactant can alter:

- Surface free energies balance (thermodynamis)
- Diffusion rate (kinetics)

Interlayer and intralayer mass transport

Diffusion barrier for the intra-layer mass transport



Diffusion barrier for the inter-layer mass transport

Interlayer mass transport / Intralayer mass transport

Fe(001)

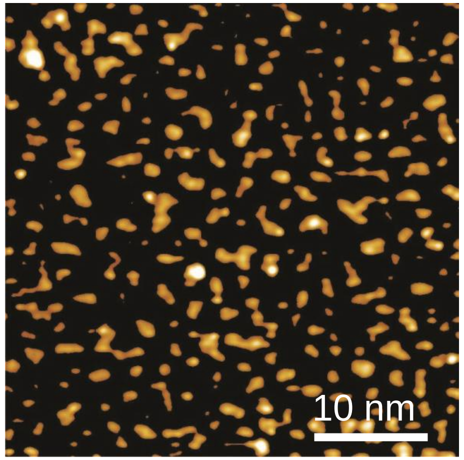
ΔE =45 meV

Bartelt et al., Phys. Rev. Lett.. 75, 4250 (1995)

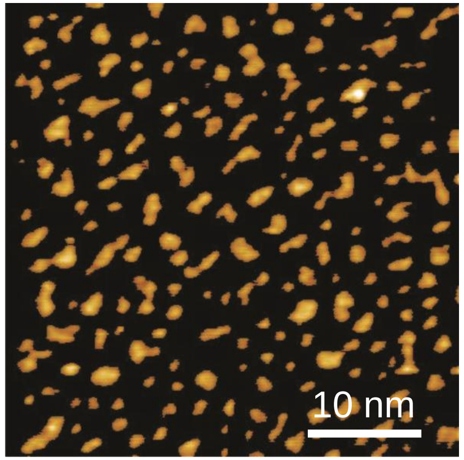
Islands density → $n_s \propto \exp[E_d/K_BT]$

Iron deposition at room temperature (rate=1 monolayer/min)

Fe(001)



Fe(001)-*p*(1x1)O



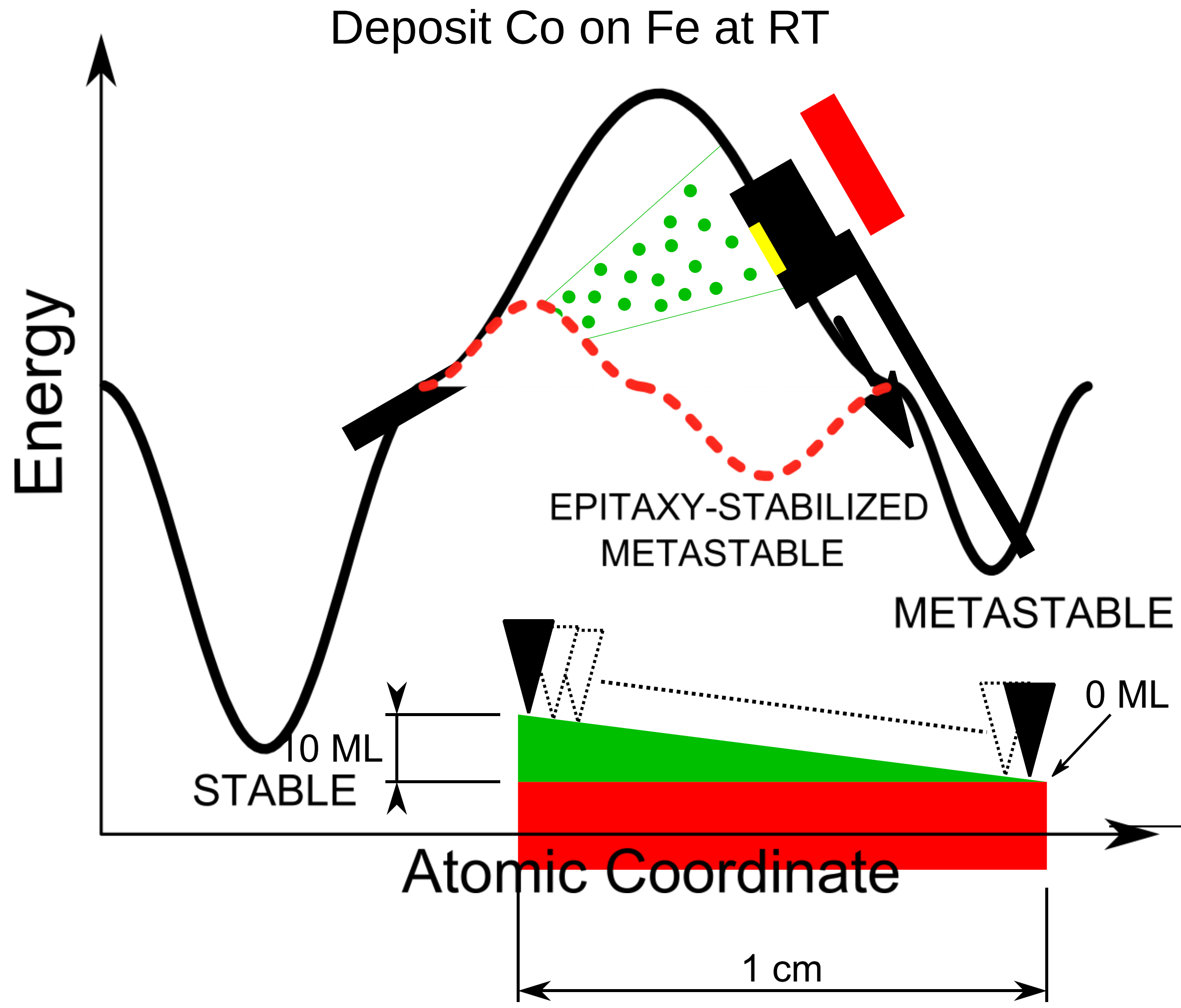
(010)

(100)

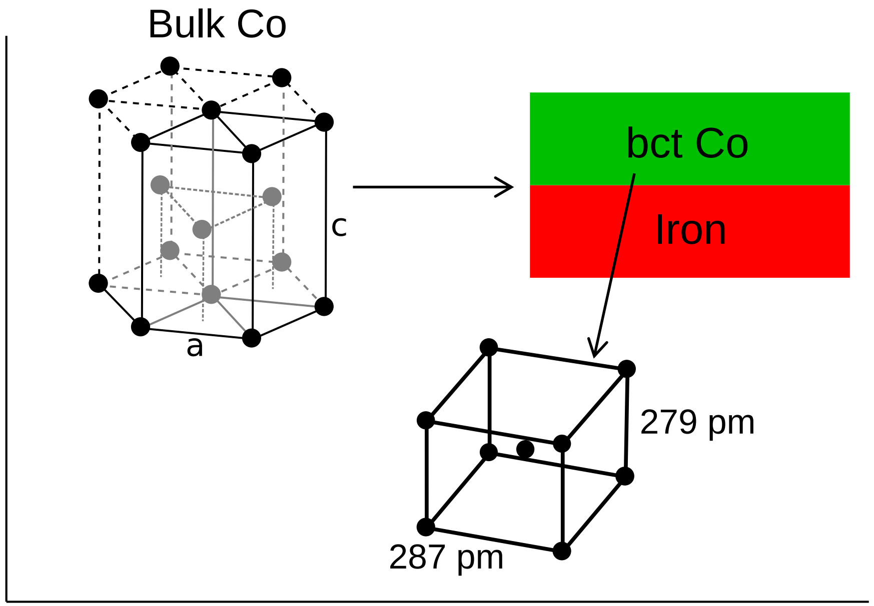
Oxygen reduces inter-layer mass transport barrier

Oxygen does not change intralayer diffusion

Co on Fe(001): intro and experimental



A. Picone et al. Phys. Rev. Lett., **113,**046102 (2014)



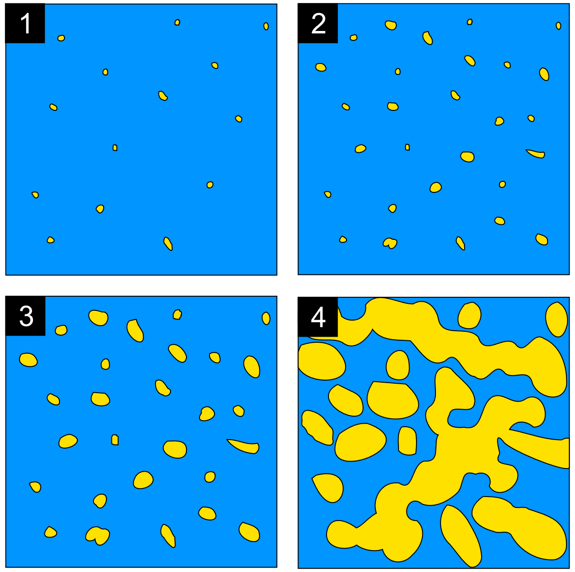
Pros:

- Constant and uniform flux;
- Exact measurement of the coverage by STM.

Cons: ~5 days to measure (can get contaminated)

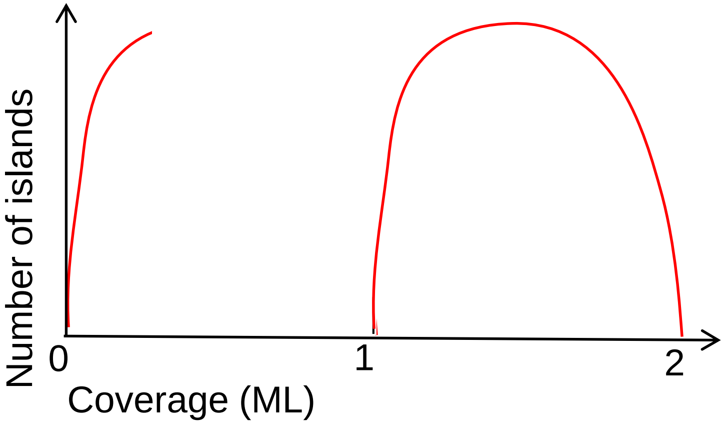
[12] Kim *et al.*, Phys. Rev. B **54**, 2184 (1996)

Evaluating diffusion with STM



nucleation / growth / coalescence

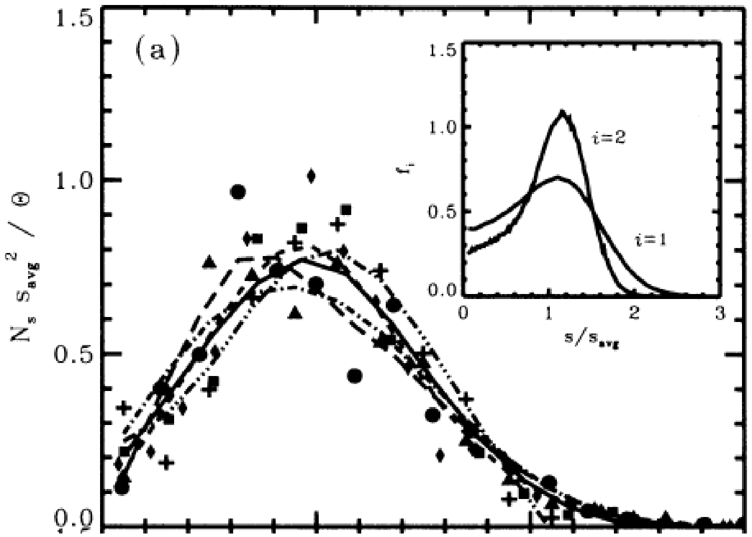
saturation



Critical nucleus (i): $i+1$ atoms form a stable island (do not collapse)

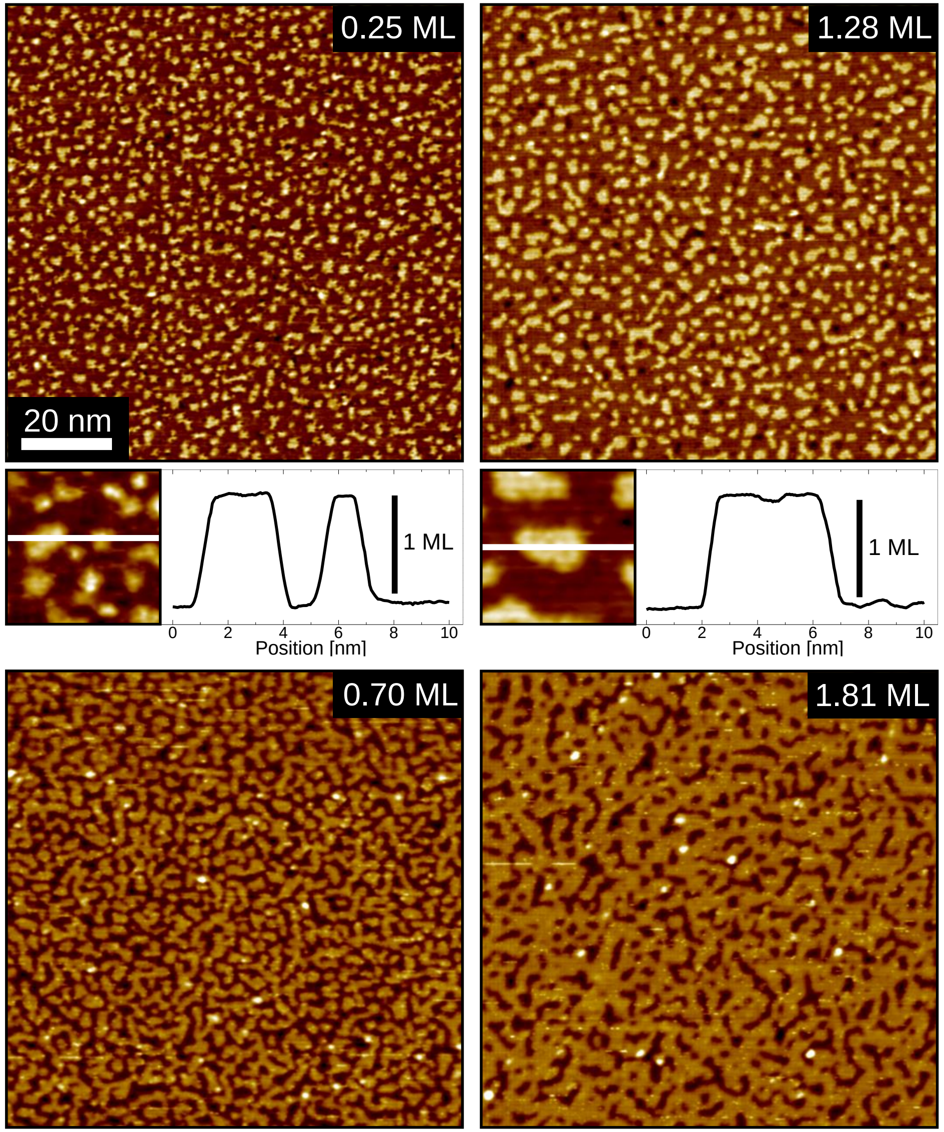
Scaled island size distribution (pre-coalescence) depends on i

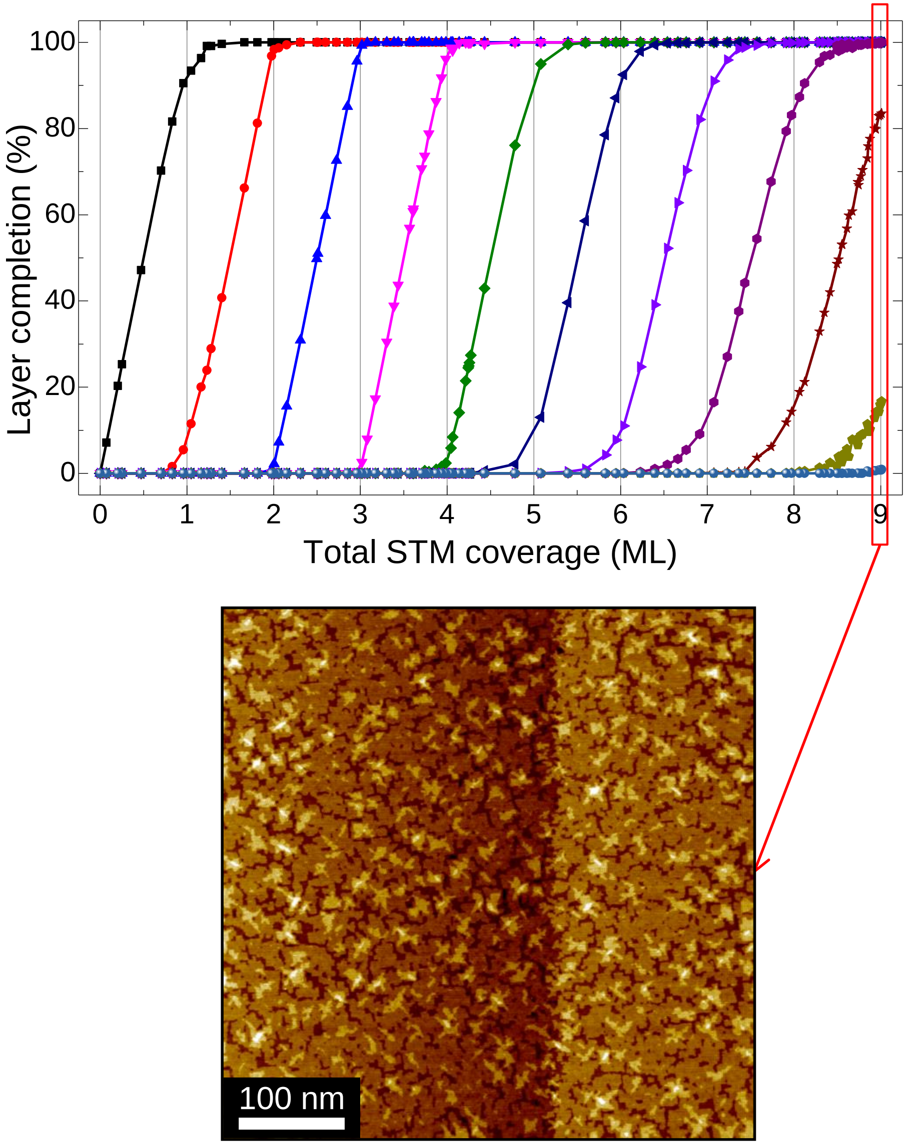
$$n_s = \eta \left(\frac{\Phi}{D}\right)^{i/_{i+2}} e^{E_i/(i+2)k_B T} \qquad D = D_0 e^{-E_D/k_B T}$$



[11] Stroscio *et al.*, Phys. Rev. Lett. **70**, 3165 (1993)

Co on Fe(001): enhanced atom mobility

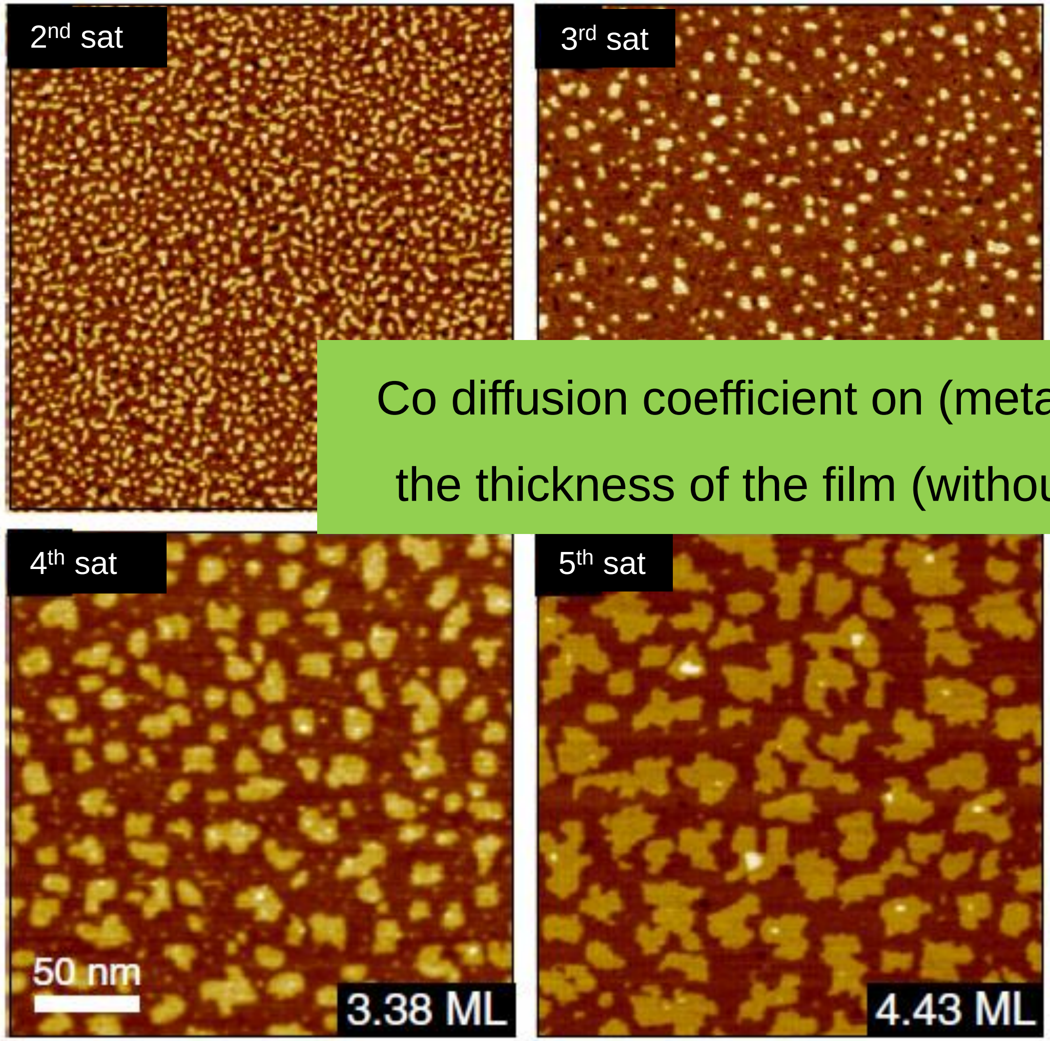


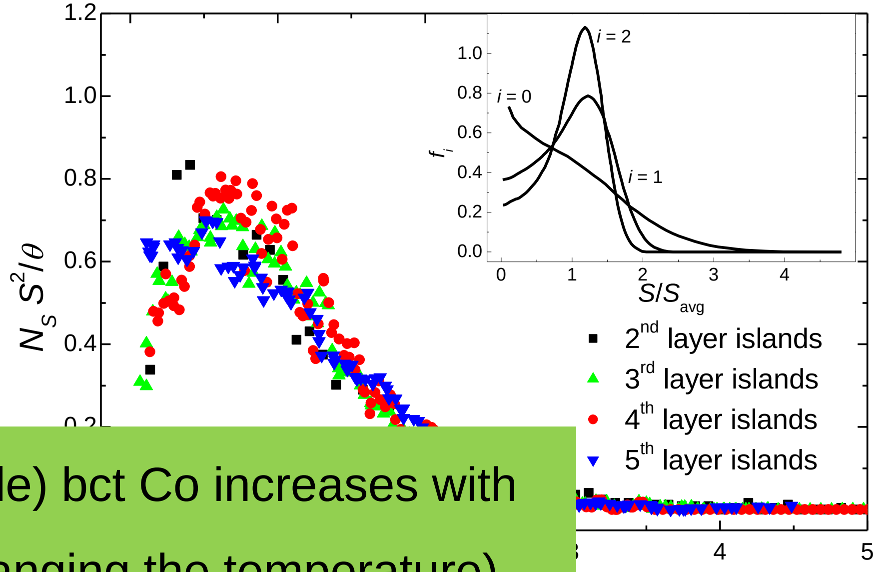


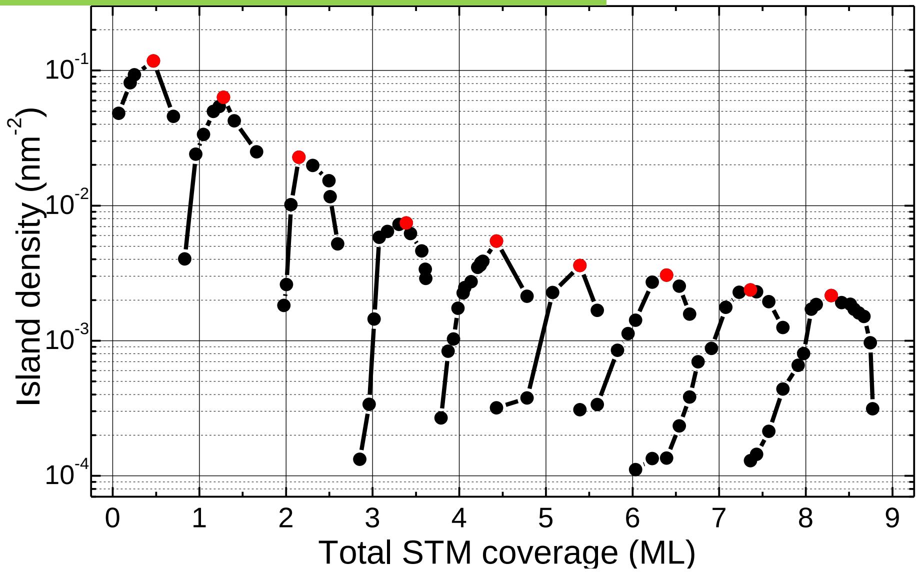
A. Picone et al. Phys. Rev. Lett., **113**,046102 (2014)

Co on Fe(001): enhanced atom mobility

At saturation of island density:





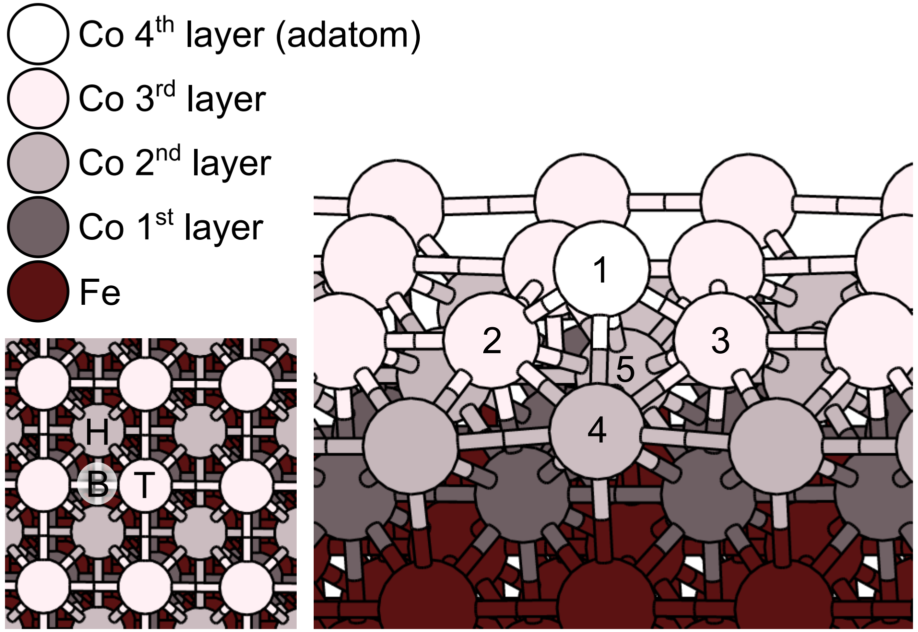


Co diffusion coefficient on (metastable) bct Co increases with the thickness of the film (without changing the temperature)

A. Picone et al. Phys. Rev. Lett., **113,**046102 (2014)

Co on Fe(001): enhanced atom mobility

DFT GGA-PBE → formation energies for adatoms in H, B, (T) positions



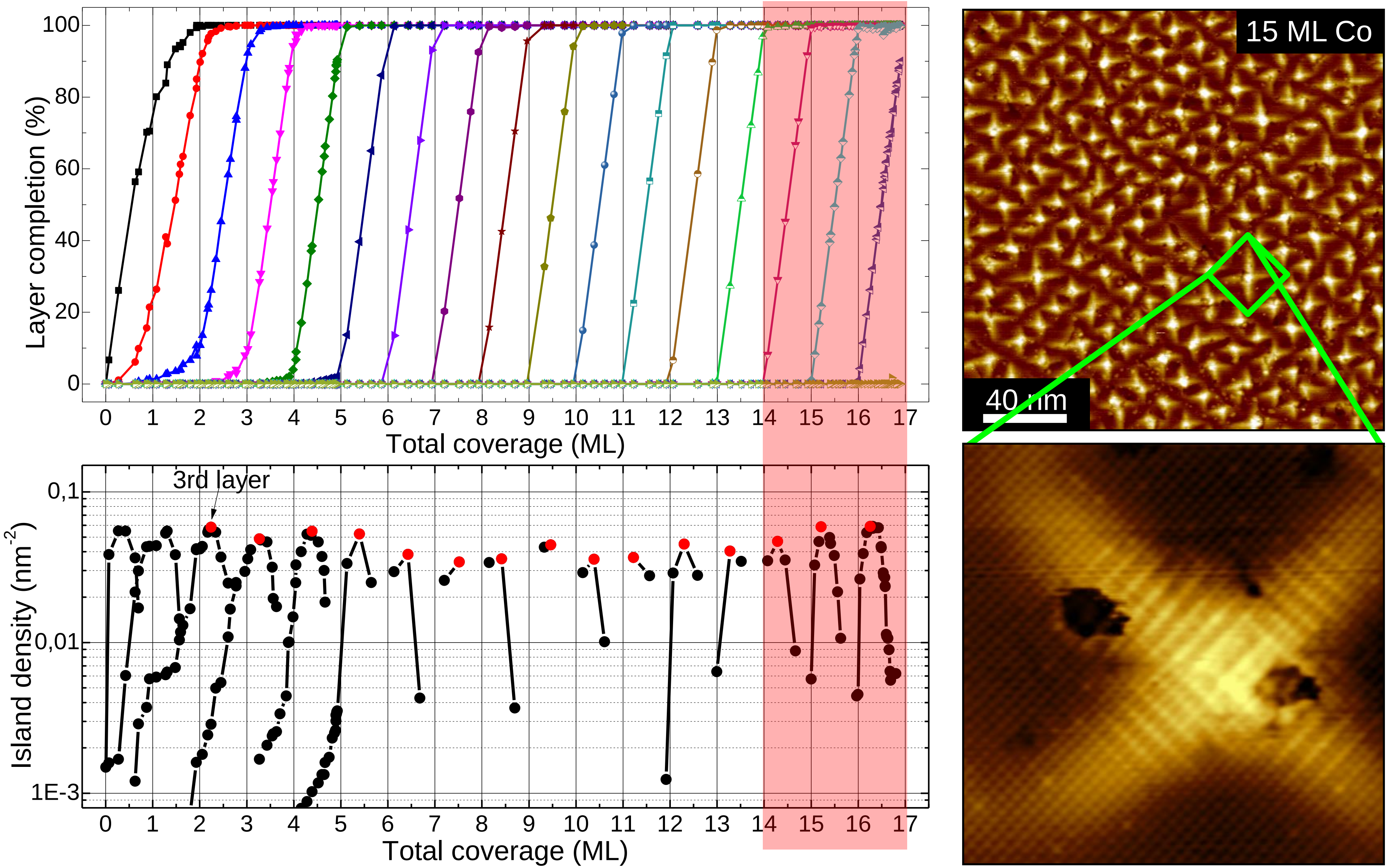
Mechanical softening of the film approaching the instability limit. Common of other metastable structures?

Coverage	F_H	F_B	E_b	E_b^{fix}
0 ML	0.15	1.36	1.21	1.37
1 ML	0.59	1.47	0.88	1.12
2 ML	0.48	1.33	0.85	0.97
3 ML	0.60	1.15	0.55	0.97
4 ML	0.52	0.64	0.12	0.98
5 ML	0.43	0.43	0.00	0.97

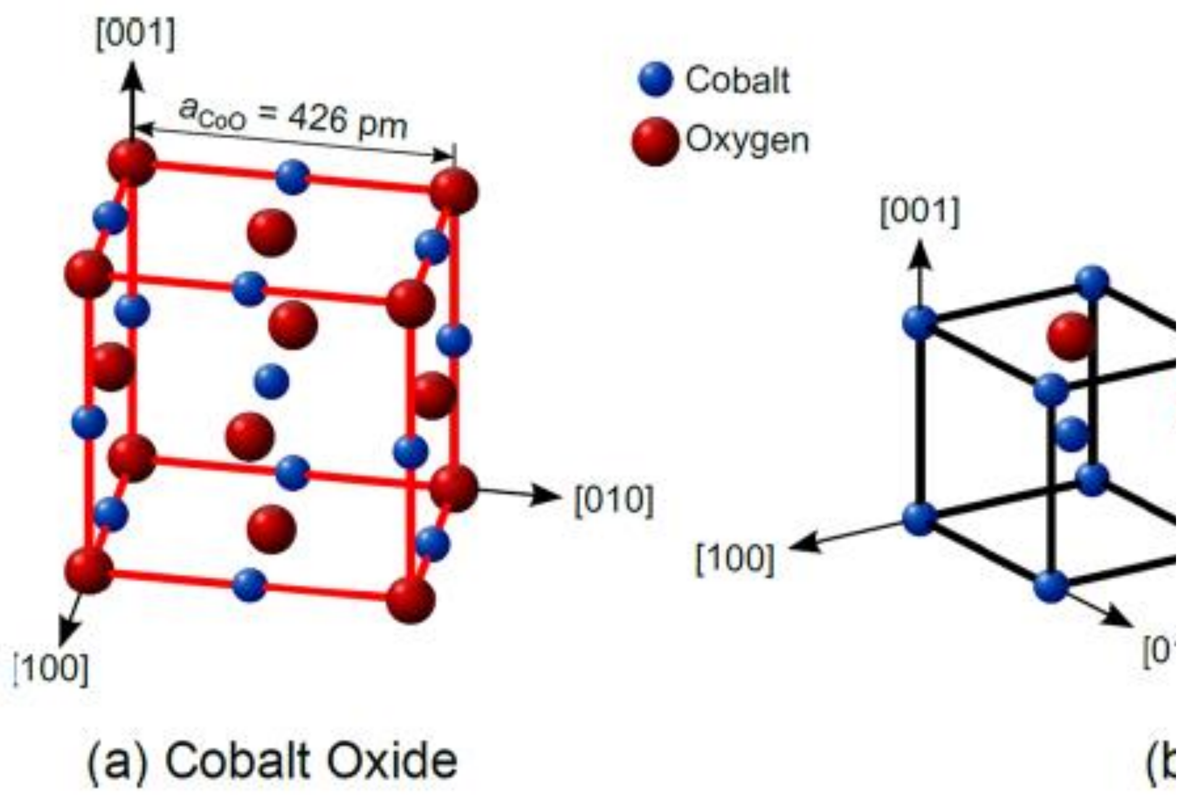
Energy barrier for atomic diffusion (eV)

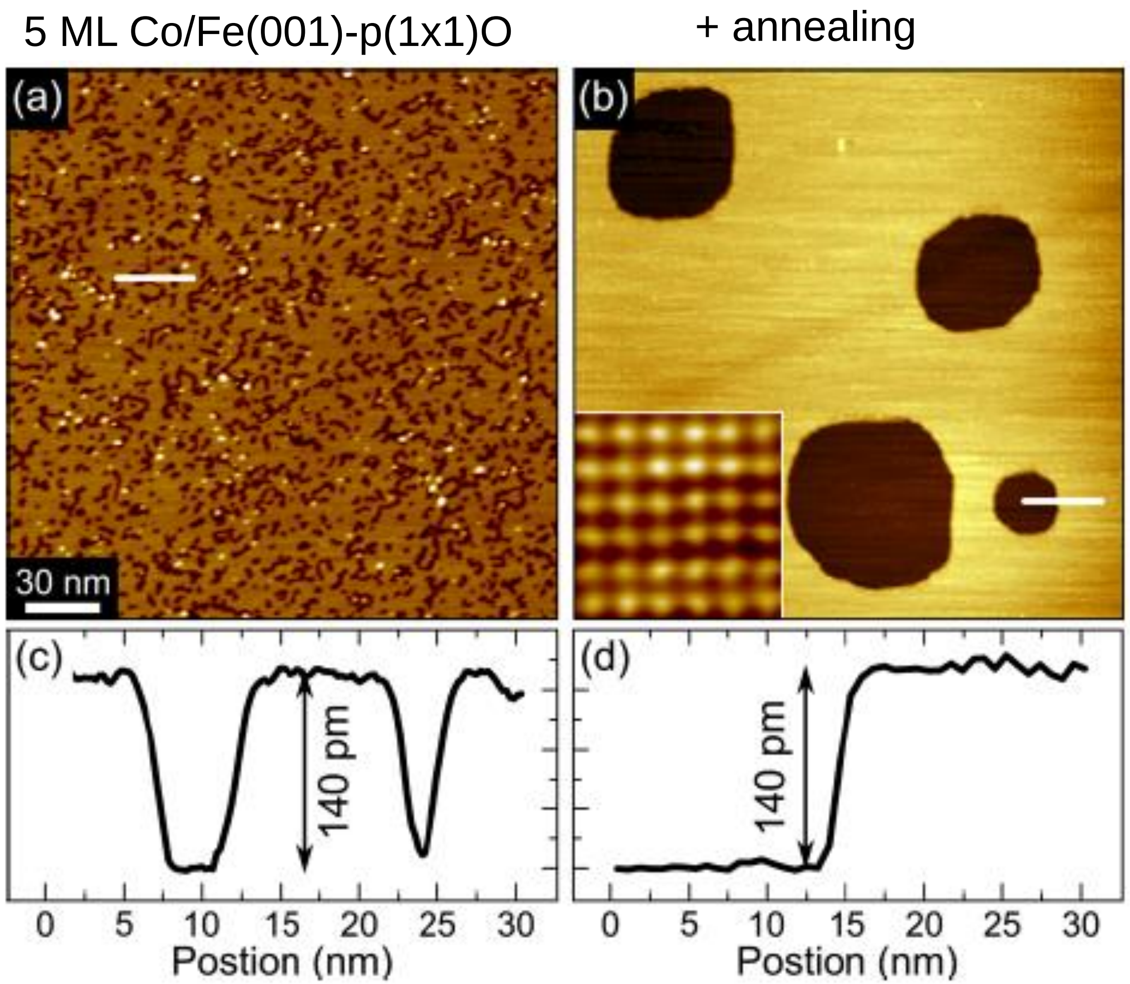
A. Picone et al. Phys. Rev. Lett., **113,**046102 (2014)

Co on $p(1\times1)$O: oxygen effect on thick films



Example 2: atomic scale investigation of the oxidation of cobalt films





A. Picone *et al.*, J. Phys. Chem C **120,** 5233 (2014)

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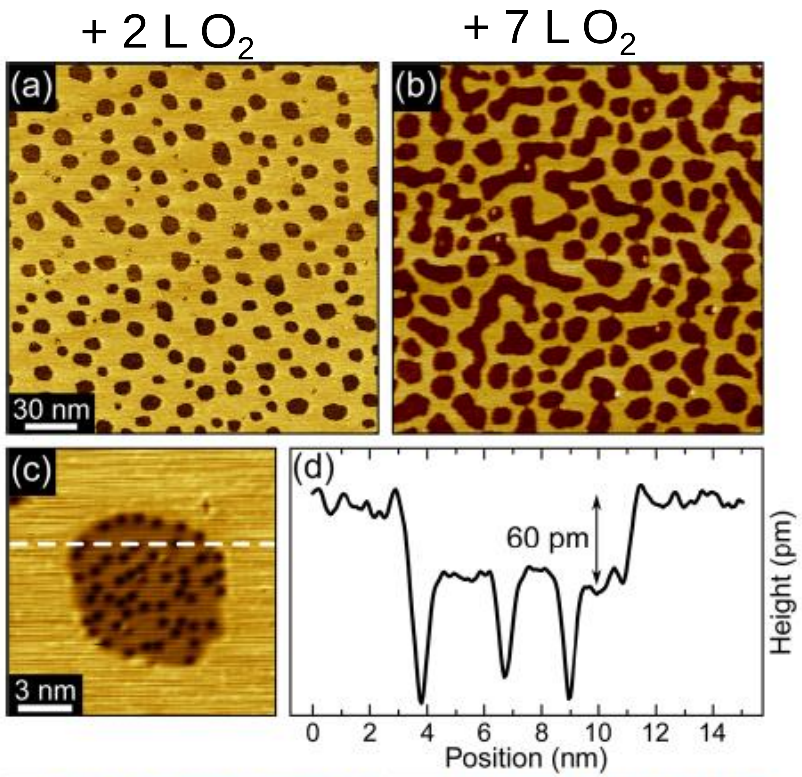

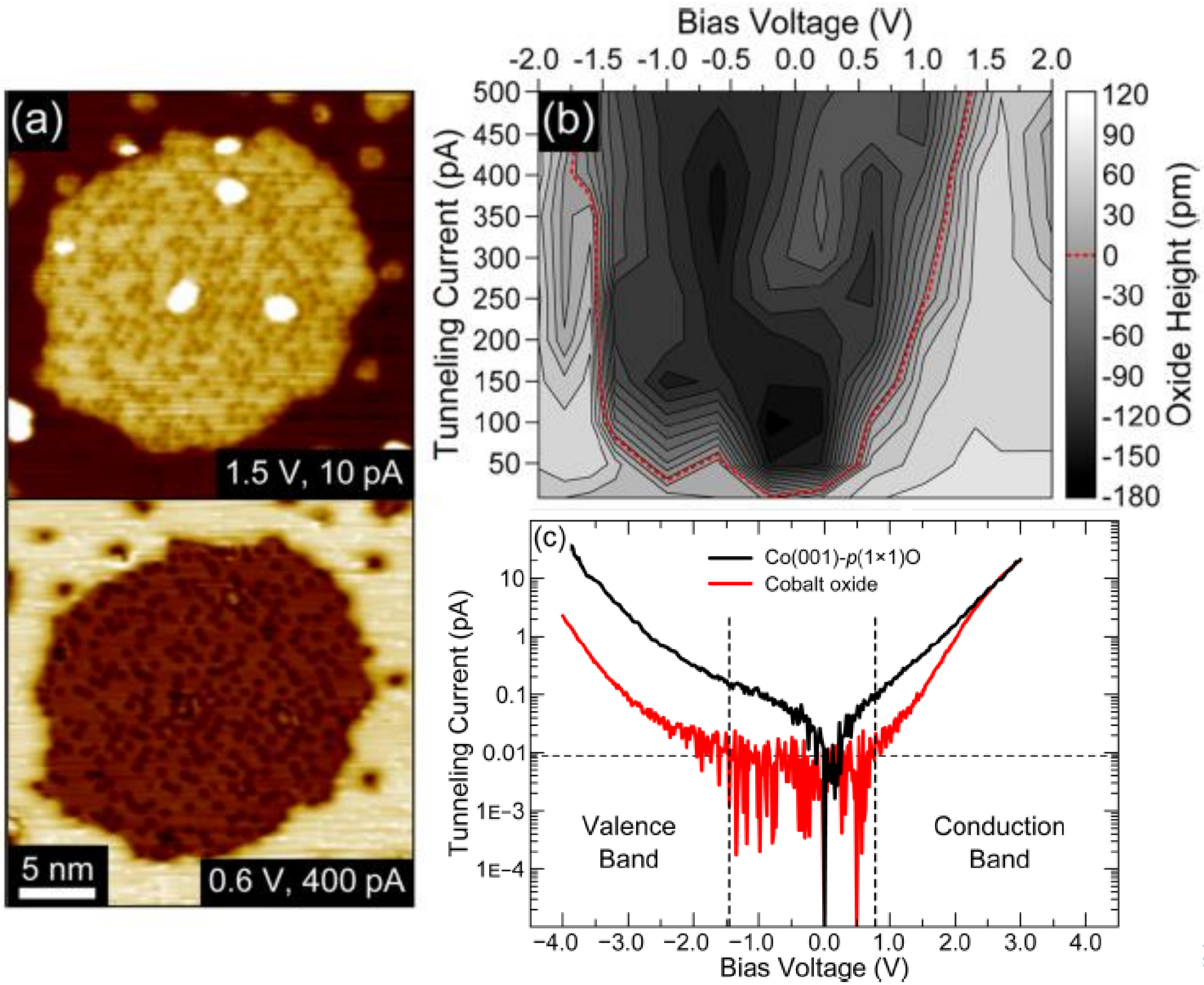

233 (2014)

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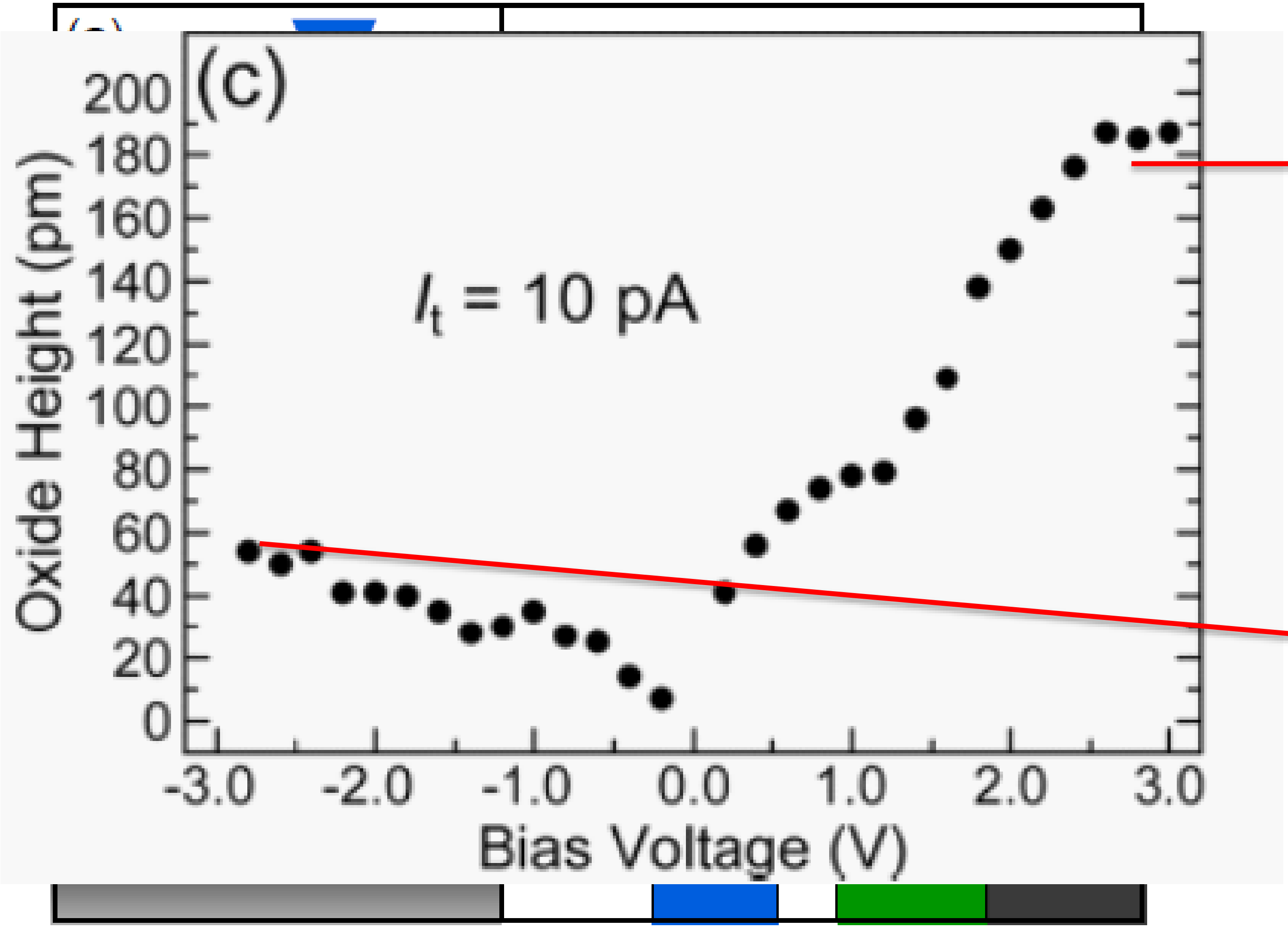
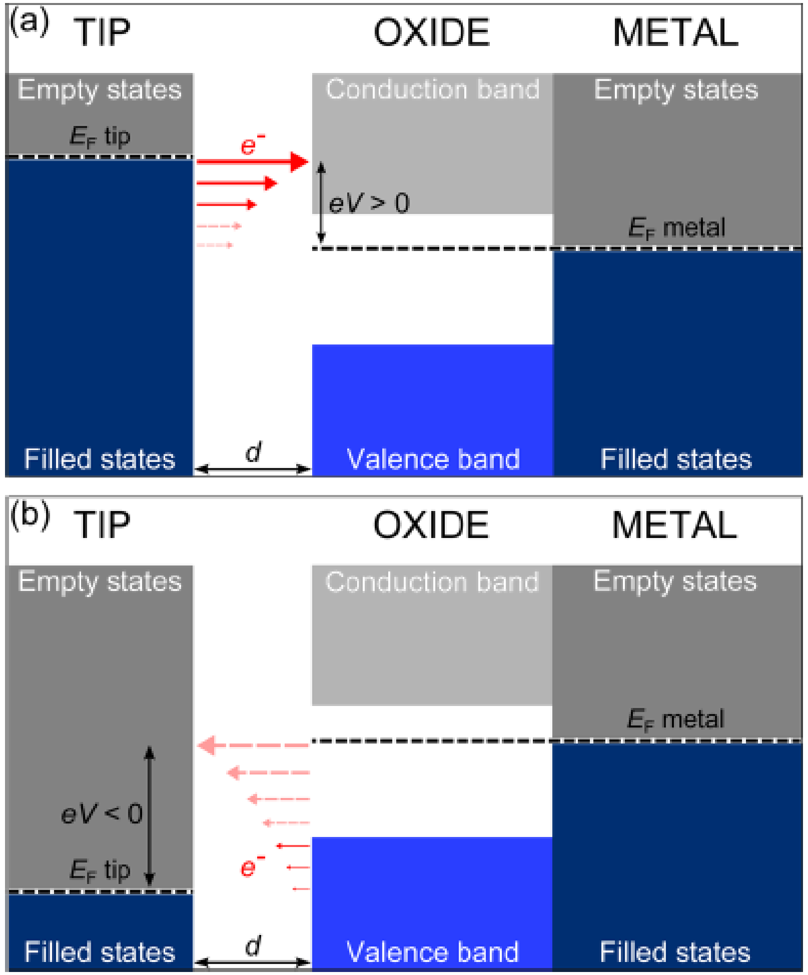
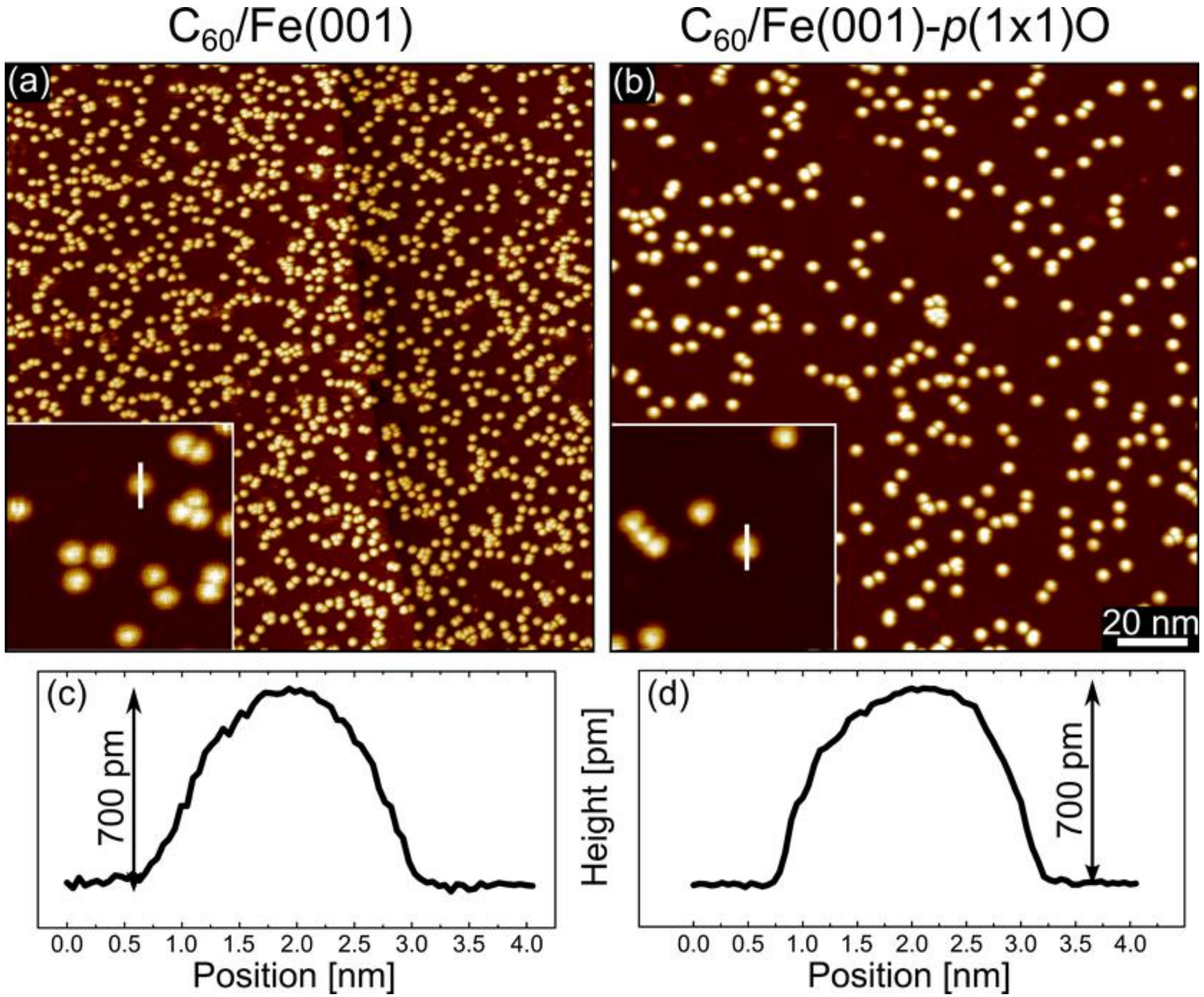


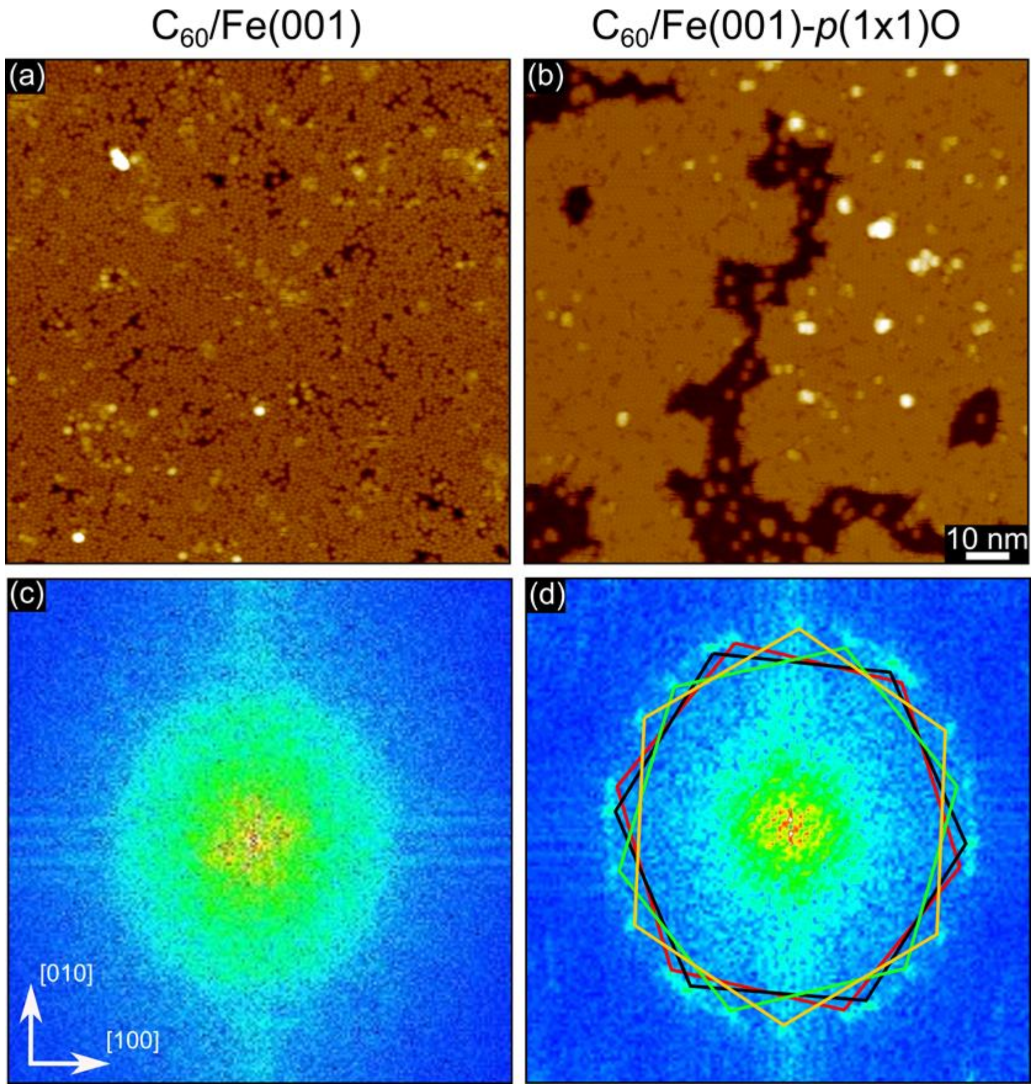


A. Picone *et al.*, J. Phys. Chem C **120,** 5233 (2014)

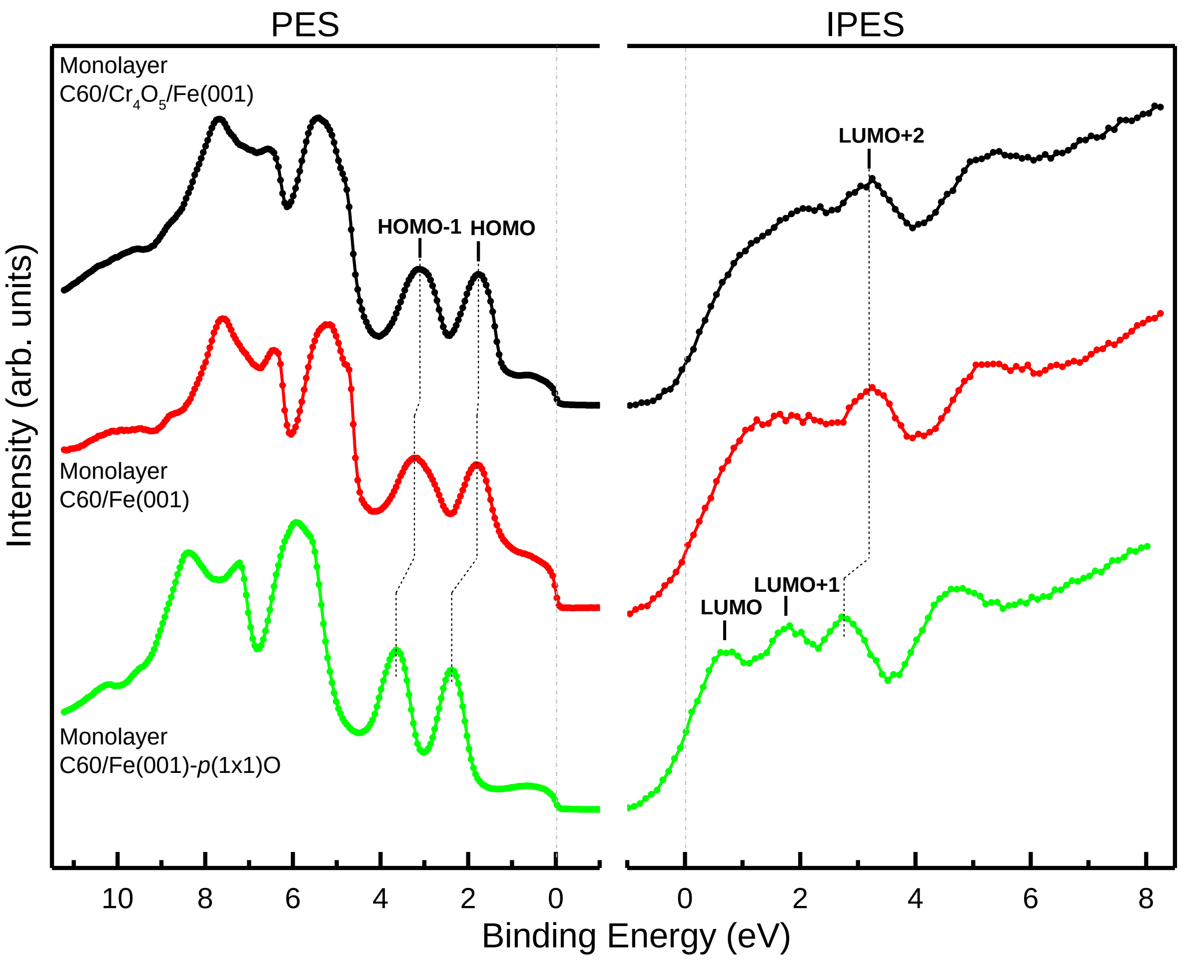
Organic Films

Early stages
t < 0.1 ML



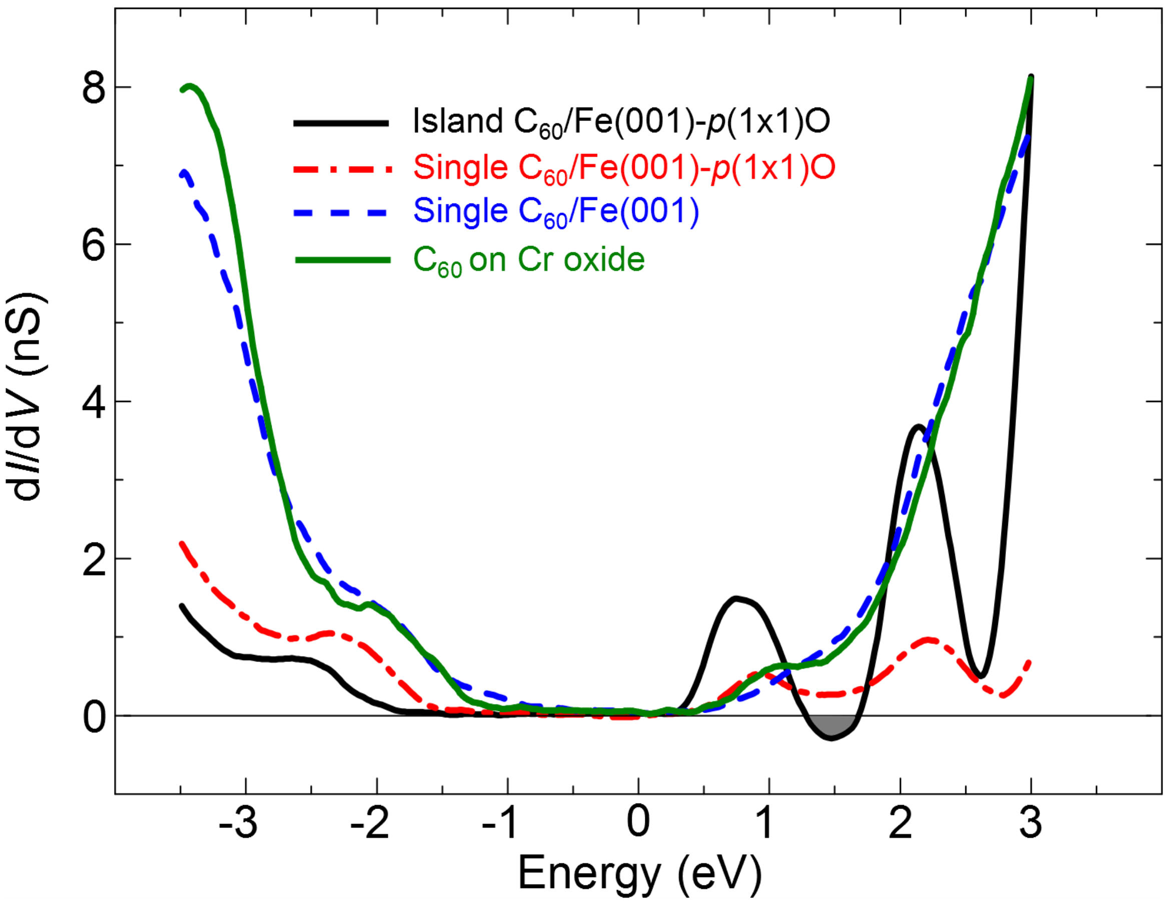


Charge transfer and hybridization



A. Brambilla et al., Nano Lett. **17**, 7440 (2017)

A. Picone et al., ACS Appl. Mater. Interfaces **8**, 26418 (2016)



Conclusions

- Scanning tunneling microscopy and spectroscopy is a powerful tool for the investigation of topographic and electronic properties at the atomic scale

- **Case of study 1:** post growth islands density analysis can be used to get informations on atomic diffuison

- **Case of study 2:** the evolution of the electronic properties during metal oxidation can be investigated

- **Case of study 3:** the nucleation and small organic molecules can be investigated along with their electronic properties

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