united nations educational, scientific and cultural organization
international atomic energy agency

the **abdus salam** international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 34

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

NANOSCALE SURFACE PHYSICS WITH LOCAL PROBES:
(i) Two-dimensional self-assembly of supermolecules and of atomic superlattices; (ii) Insulators at the limit
PART III

Wolf-Dieter SCHNEIDER
EPF de Lausanne, IPN
CH-1015 Lausanne, Switzerland

Insulators at the Ultrathin Limit:

MgO on Ag(001)
NaCl on Ag(001)

INSTITUT DE PHYSIQUE
DES NANOSTRUCTURES

Insulator at the Ultrathin Limit: MgO on Ag(001)

Experiment: ⟷ Theory:

Experiment		Theory	
S. Schintke	(Uni Basel)		
S. Messerli	(REAlmedia Lausanne)	M. Stengel	(IRRMA, Lausanne)
L. Libioulle		A. De Vita	(Trieste, London)
M. Pivetta		WDS	
F. Patthey			

Phys, Rev. Lett. **87**, 27681 (2001)

MOS-FET

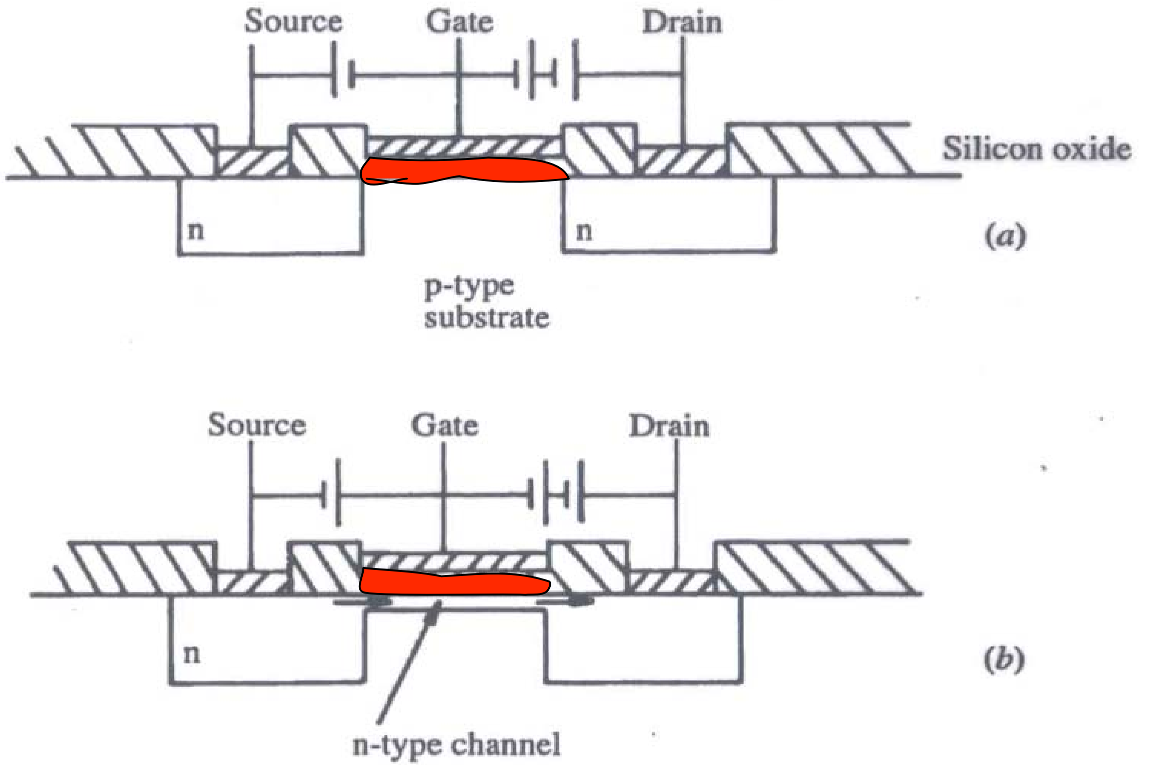
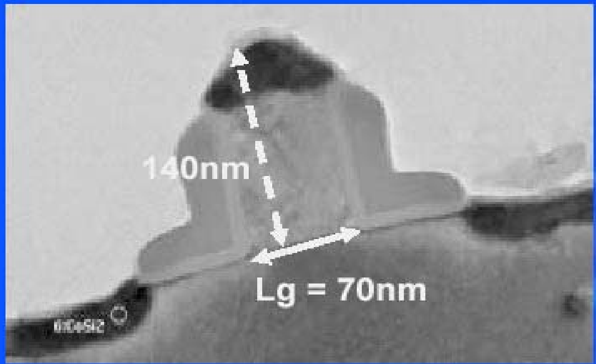


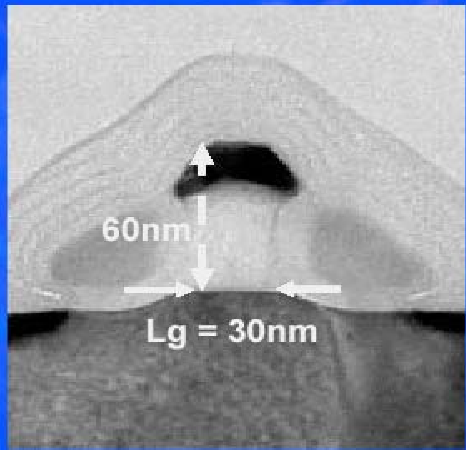
Fig. 7.15 Structure of metal oxide semiconductor field effect transistor (MOS-FET). (*a*) Gate forward biased with respect to its source. Drain forward biased with respect to gate. (*b*) Gate reverse biased with respect to its source.

B. K. Tanner, Introduction to the Physics of Electrons in Solids, Cambridge University Press, 1995

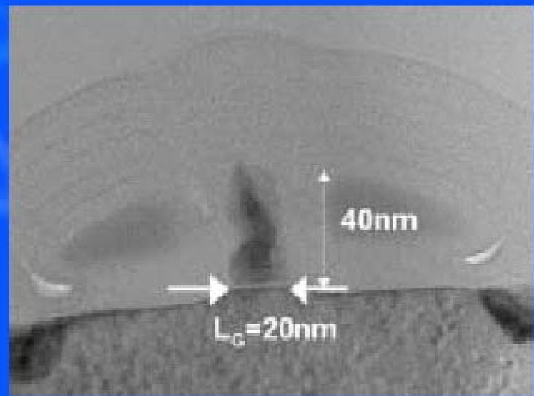
Transistor Scaling Continues



70 nm transistor (in production)

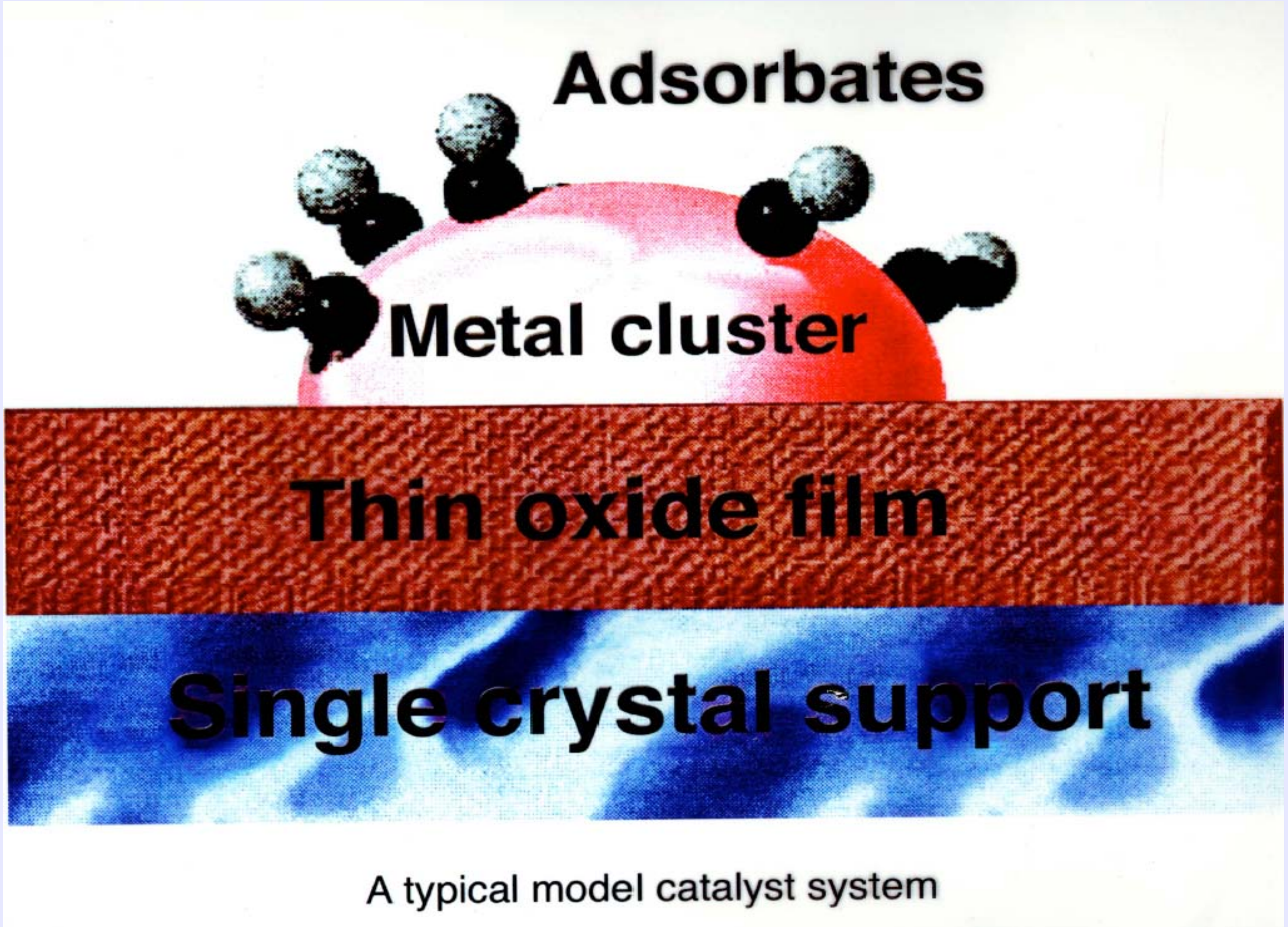


30 nm transistor (development phase, production 2005)



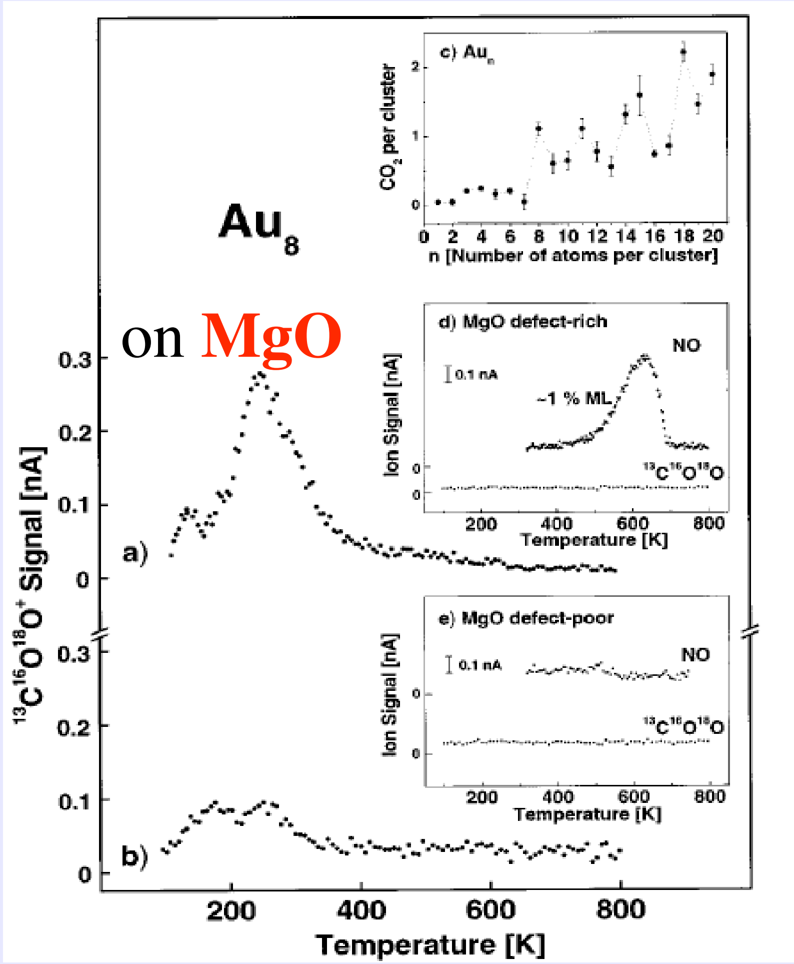
20nm transistor (research phase)

http://intel.com/labs/



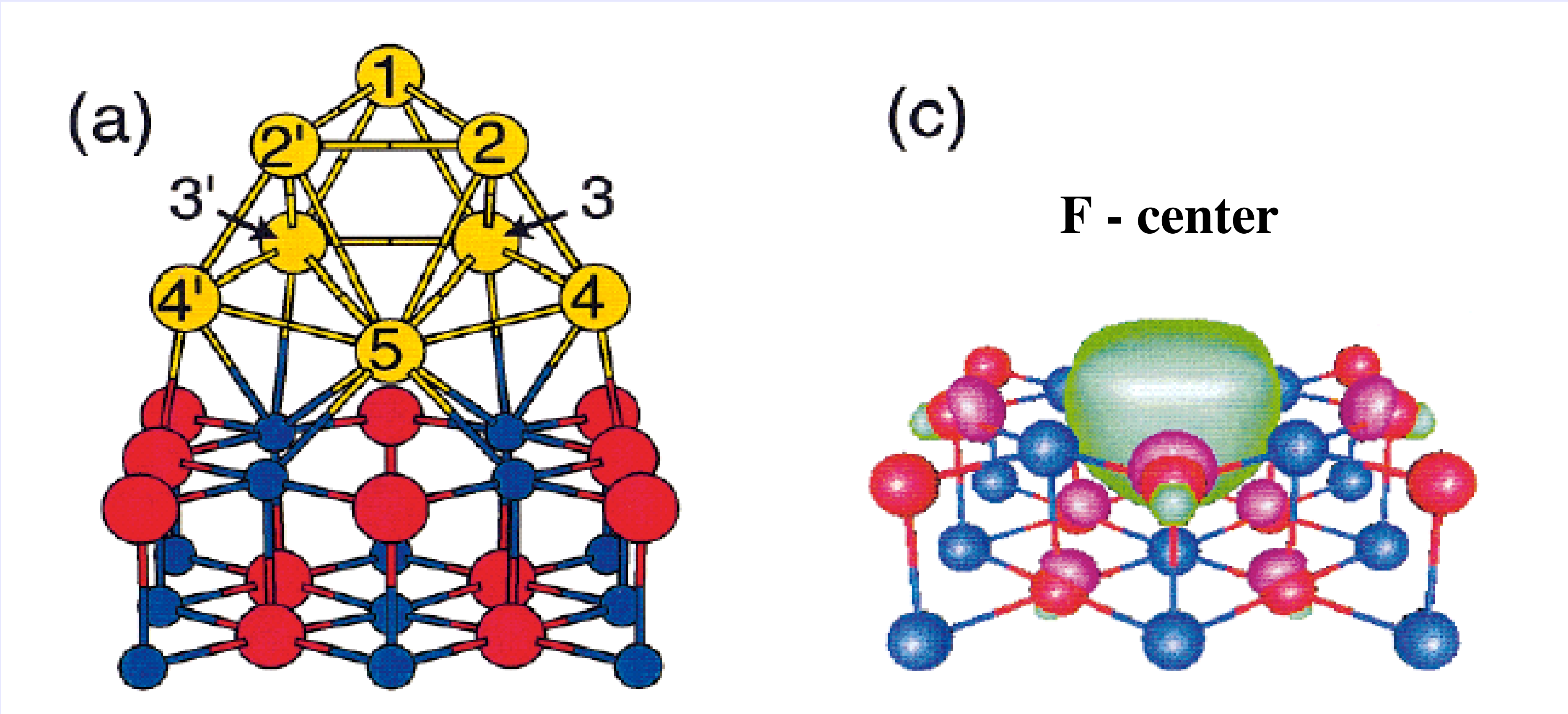
S. Andersson, PhD Thesis, Uppsala University (1998)

Supported nanoscale gold catalysts: Experiment

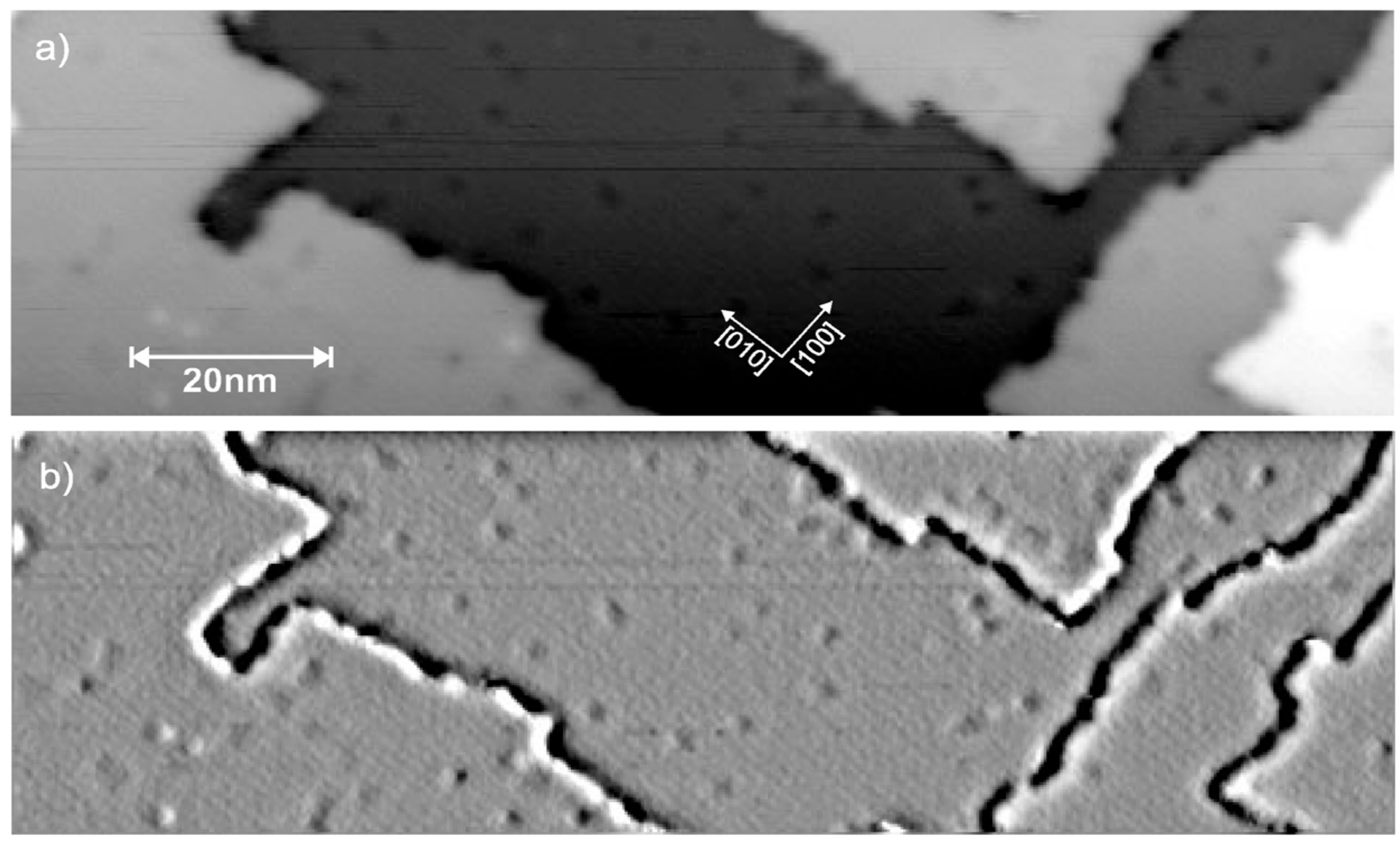


A. Sanchez, S. Abbet, U. Heiz, WDS, H. Häkkinen,
R. N. Barnett, U. Landman, J. Chem. Phys. A **103**, 9573 (1999)

A local view of supported nanoscale gold catalysts:
Theory (U. Landman et al.)



A. Sanchez, S. Abbet, U. Heiz, WDS, H. Häkkinen, R. N. Barnett, U. Landman, J. Chem. Phys. A **103**, 9573 (1999)



S. Schintke, PhD thesis, Lausanne (2001),

U. Heiz and WDS, J. Phys. D: Appl. Phys. 33 R85 (2000)

S. Schintke and WDS, J. Phys. Condens. Matter **16**, R49 (2004)

Motivation

Film thickness ⟷ Function

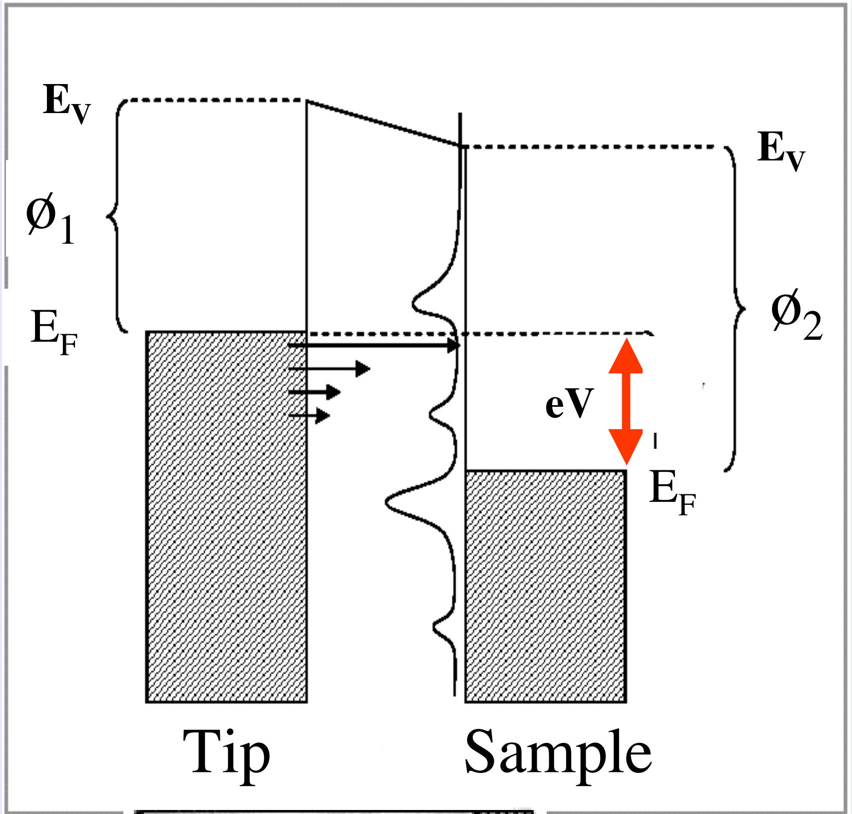
⇕

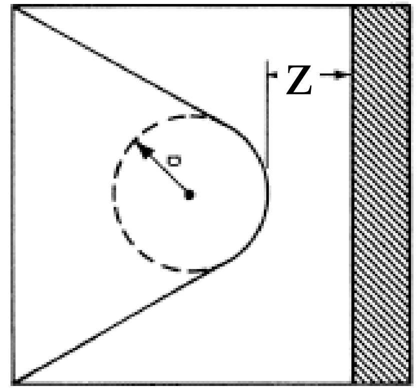
Insulator pushed to the limit

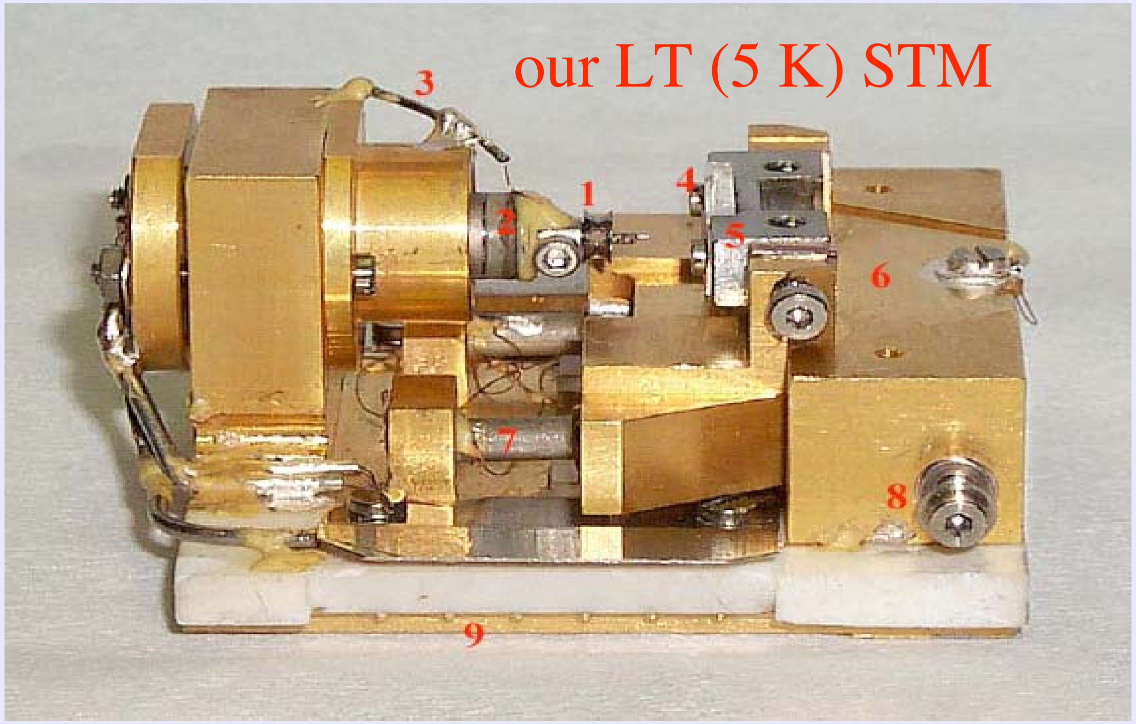
Model system:

Ultrathin films of MgO(100)/Ag(100)

Scanning probe methods: STM, STS







$$I(V) \propto \int_0^{eV} \rho_t(\pm eV \mp E)\, \rho_s(E)\, T(E, eV)\, dE$$

$$\frac{dI}{dV}(V) \propto e\, \rho_t(0)\, \rho_s(eV)\, T(eV, eV)$$

Tunneling spectroscopy

dI/dV ~ LDOS J. Tersoff & D. R. Hamann, PRB **31**, 805 (1985)

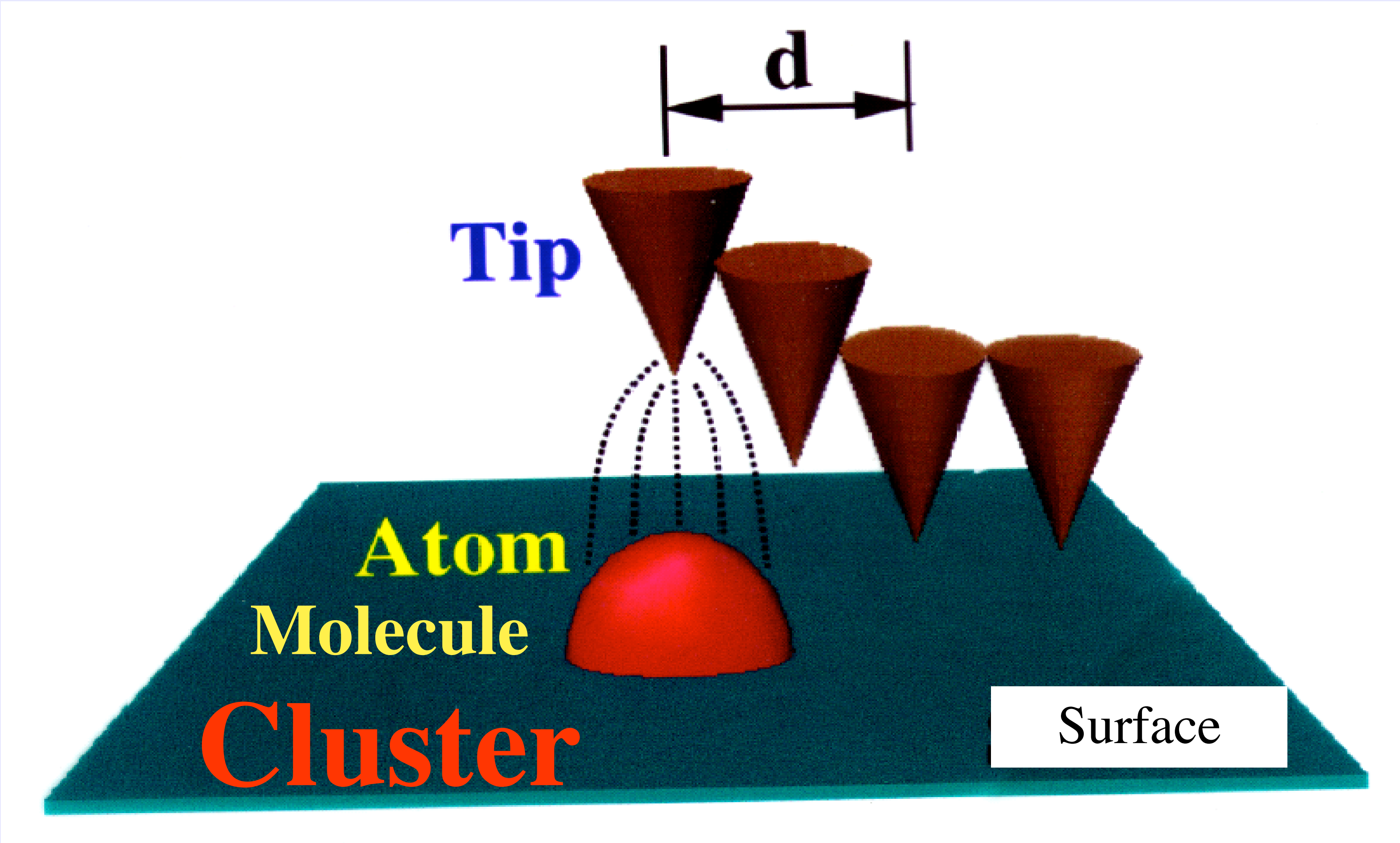
- tip position z (I, V), open feedback loop for V-sweep
  lock-in detection of dI/dV, modulation 270 Hz, 5 mV

- continuous z-variation during V-sweeps
  linear ramp $z = z_0 - dz/dV$ with $dz/dV = const$
  R. M. Feenstra & P. Mårtensson, PRL **61**, 447 (1988)

- constant current: G. Binnig et al., PRL **55**, 991 (1985)

- constant resistance: W. J. Kaiser & R. C. Jaclevic,
  Surf. Sci. **181**, 55 (1987)

A typical « local » experiment



After J. Li, PhD Thesis, University of Lausanne (1997)

Ultrathin dielectric films

Some recent STM/STS results….

MgO /Mo(001)

M. C. Gallagher et al., Surf. Sci. **339**, L909 (1995) (S. A. Joyce)

NaCl /Al(111)

W. Hebenstreit et al., Surf. Sci. **424**, L321(1999) (P. Varga)

NaCl /Cu(111)

J. Repp (PhD thesis, FU Berlin, 2002) (K.-H. Rieder)

CaF_2/Si(111)

A. Viernow et al., PRB **59**, 10 356 (1999) (F.-J. Himpsel)

Al_2O_3/Re(0001)

X. Lai et al. Chem. Phys. Lett. **330**, 226 (2000) (D.W. Goodman)

CoO/Ag(001), NiO/Ag(001)

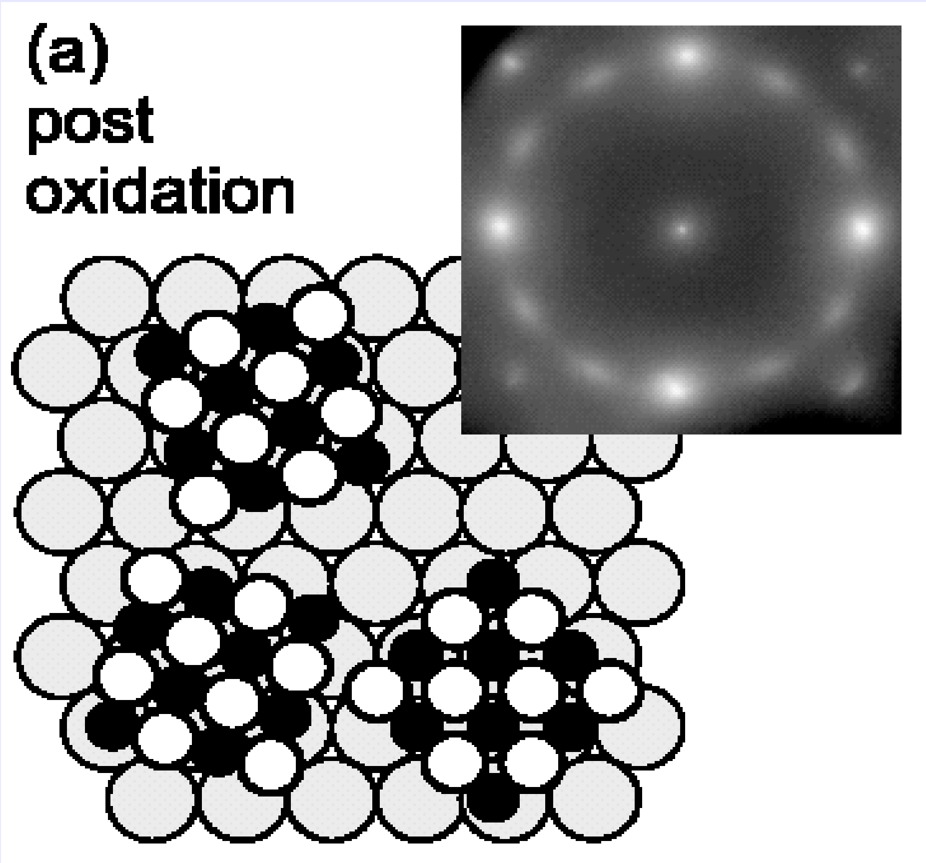
I. Sebastian et al., Faraday Discuss. **144**, 129 (1999) (H. Neddermeyer)

MgO(100)/Ag(100)

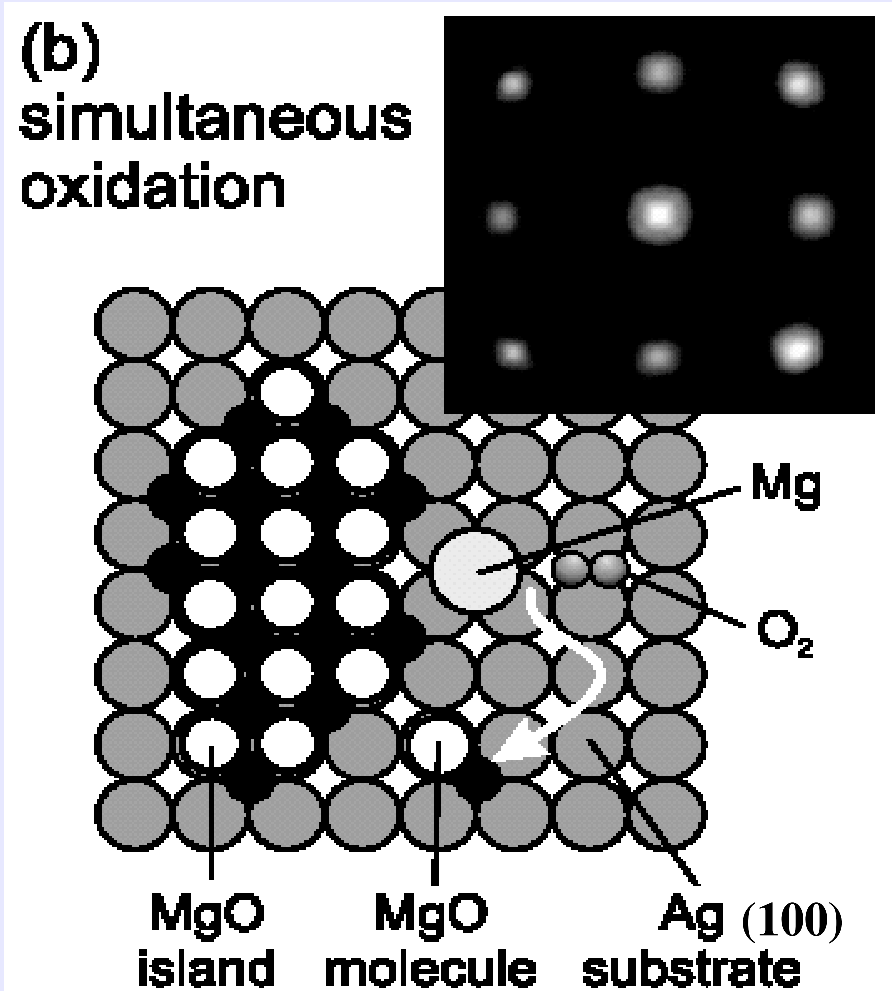
- Growth of ultrathin films: MgO (4.21 Å), Ag (4.09 Å), misfit 2.9 %

  Mg evaporation in 1 x 10^{-6} mbar O_2, Ag(100) substrate @ 500 K
  J. Wollschläger et al., Appl. Surf. Sci. **142**, 129 (1999)

Diffraction patterns



Growth on Mg(111) film



J. Wollschläger et al., Appl. Surf. Sci. **142**, 129 (1999)

MgO(100)/Ag(100)

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  J. Wollschläger et al., Appl. Surf. Sci. **142**, 129 (1999)

- epitaxial stoichiometry: LEED, AES

- electronic structure: XPS, UPS, EELS

- **STS** and **STM** measurements @50 K:
  layer-by-layer investigation of electronic structure and morphology

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    J. Wollschläger et al., Appl. Surf. Sci. **142**, 129 (1999)

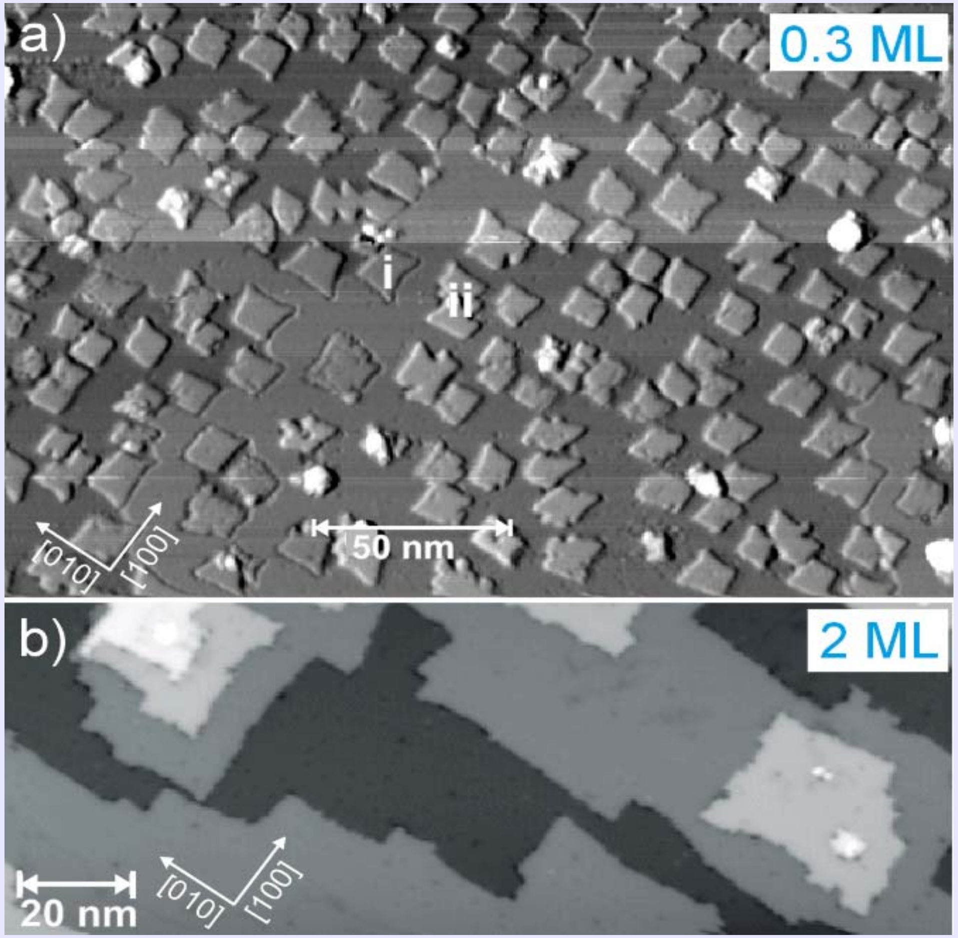
- epitaxial stoichiometry: LEED, AES

- electronic structure: XPS, UPS, EELS

- **STS** and **STM** measurements @50 K:
  layer-by-layer investigation of electronic structure and morphology

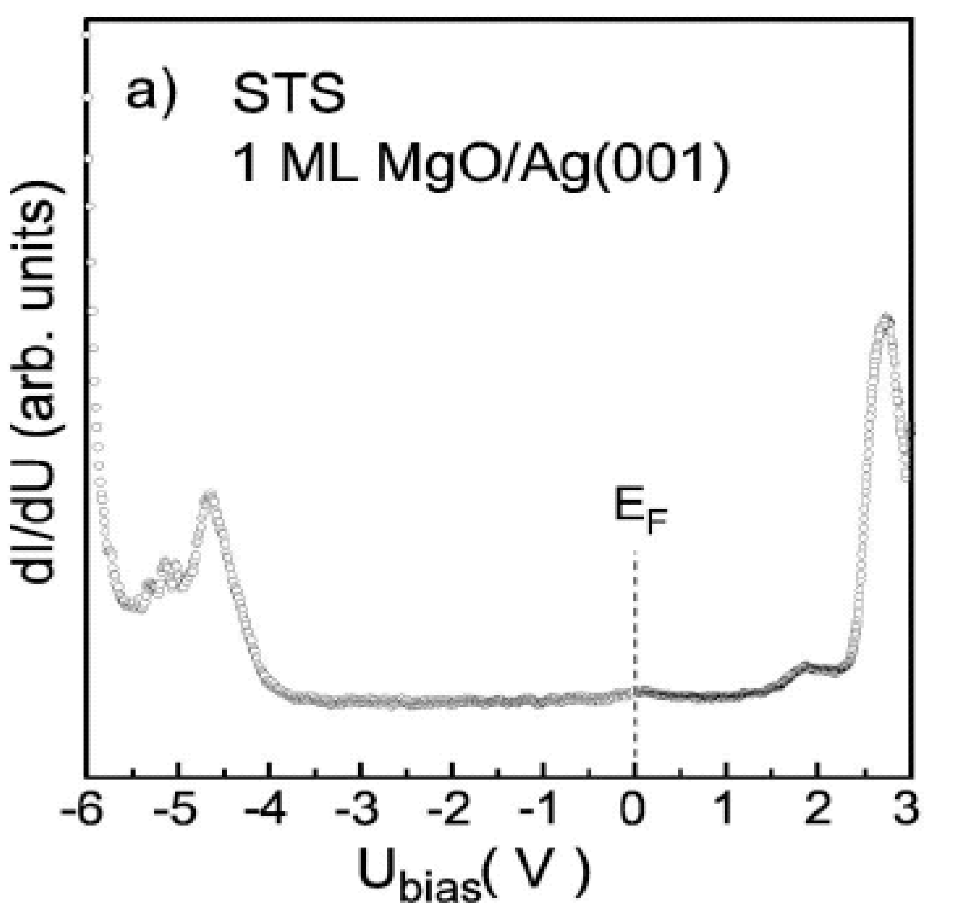
- *ab initio* calulations:
  DFT layer-resolved calculations of the LDOS

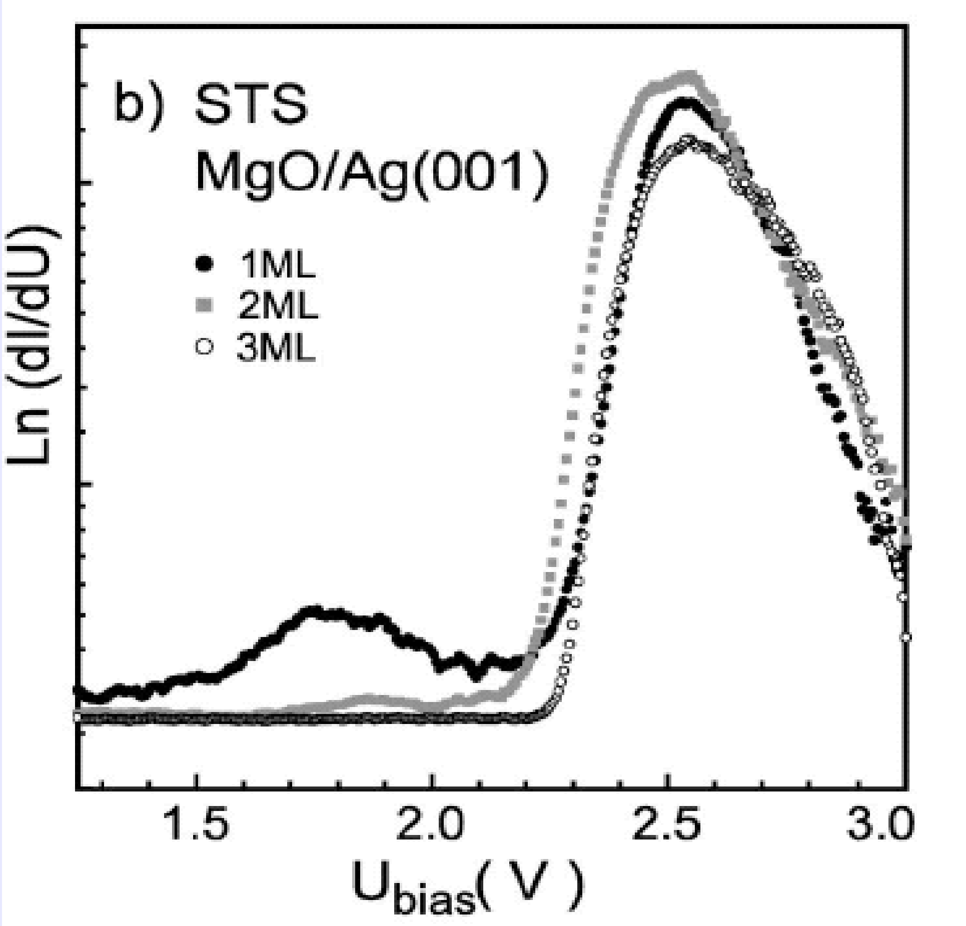
MgO(100)/Ag(100) @ 50 K



S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle,
M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

Insulator at the ultrathin limit





S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle,
M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

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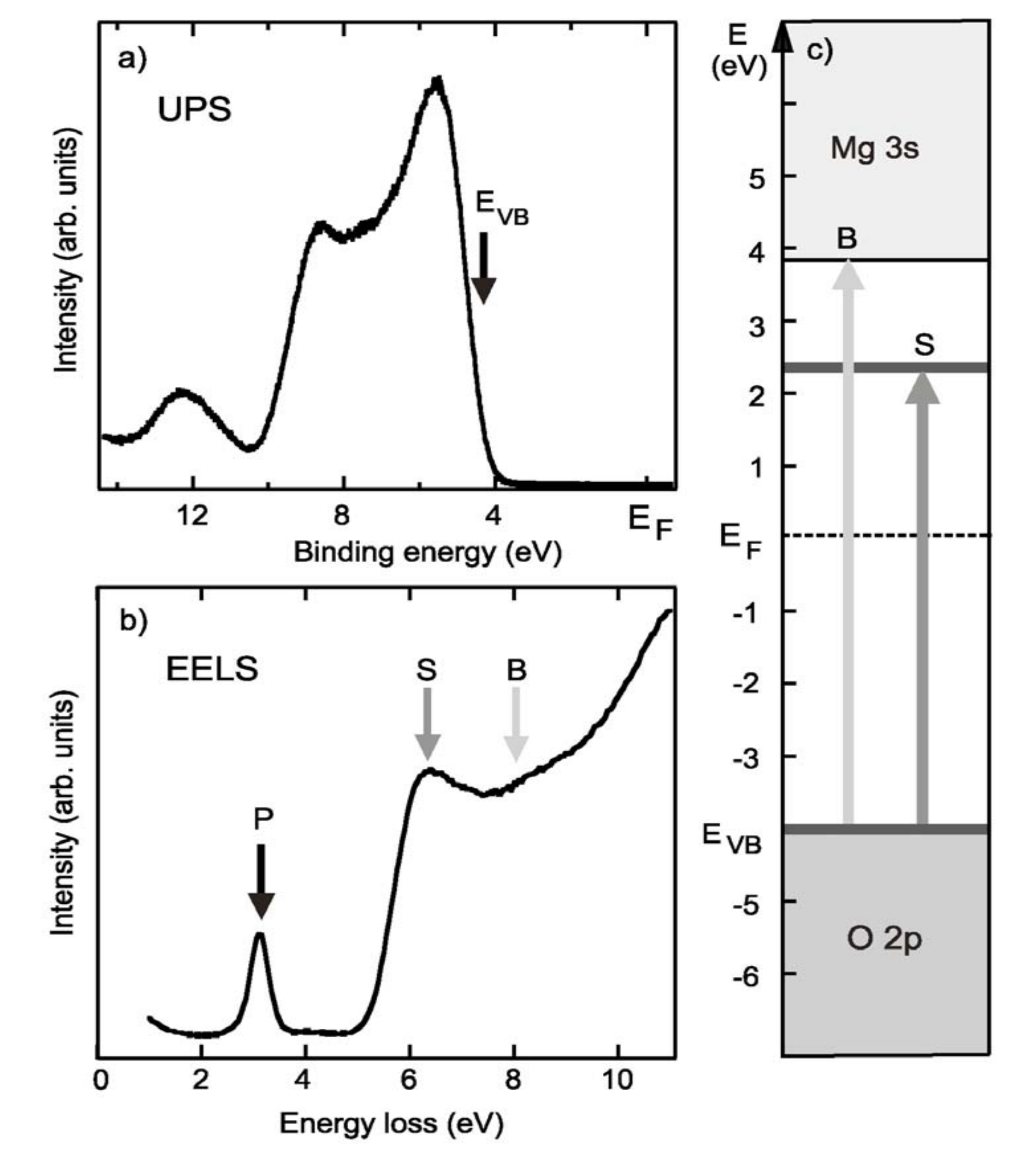

An experimentally derived energy level diagram

10 ML MgO/Ag(100)

S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

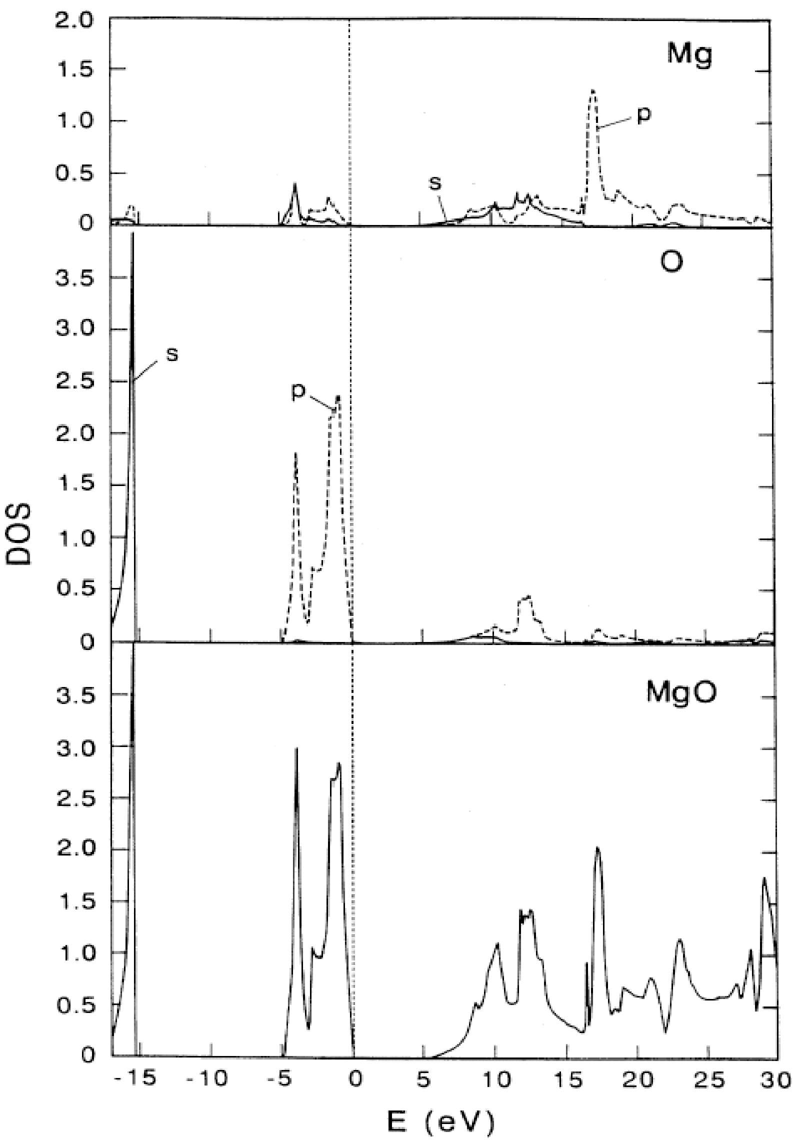

FIG. 2. Total density of states (DOS) of MgO (lower panel) and partial DOS of O (middle panel) and Mg (upper panel).

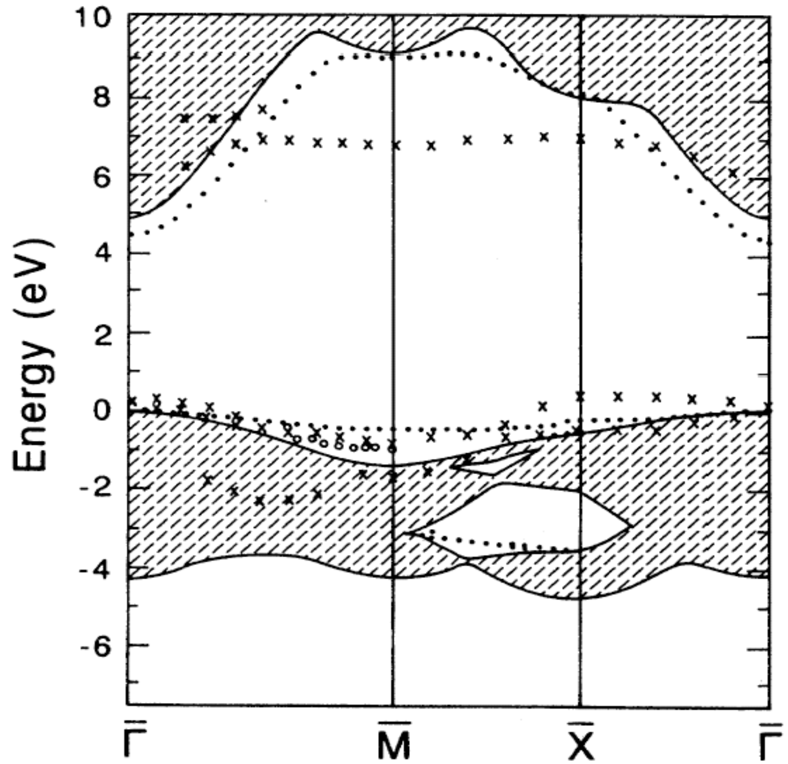

FIG. 4. Surface band structure of MgO(100) (dots). The experimental result of Tjeng, Vos, and Sawatzky (Ref. 28) (open dots) and the theoretical result of Lee and Wong (Ref. 30) (crosses) have been added.

Theory: U. Schönberger et al., PRB **52**, 8788 (1995)

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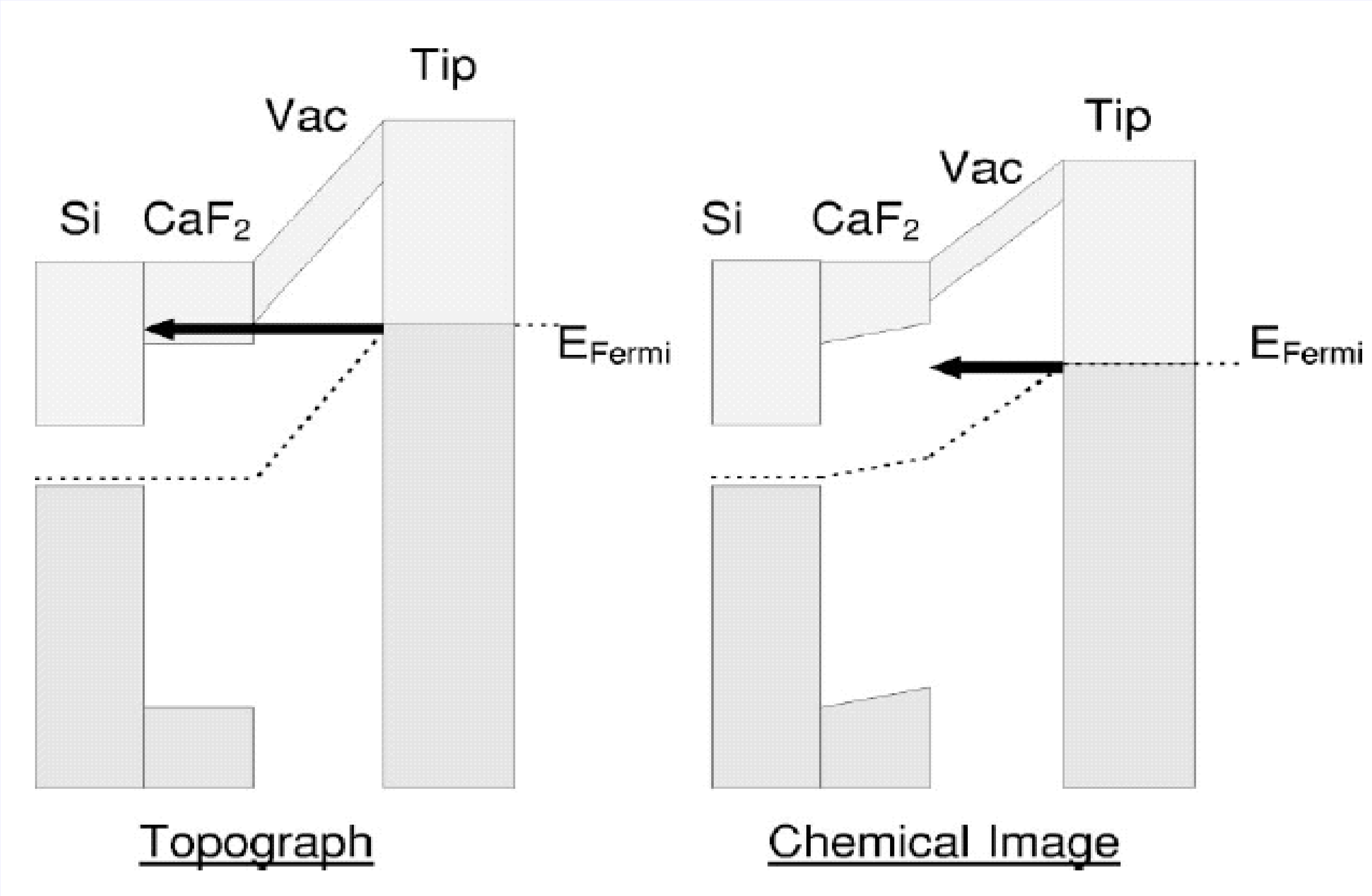
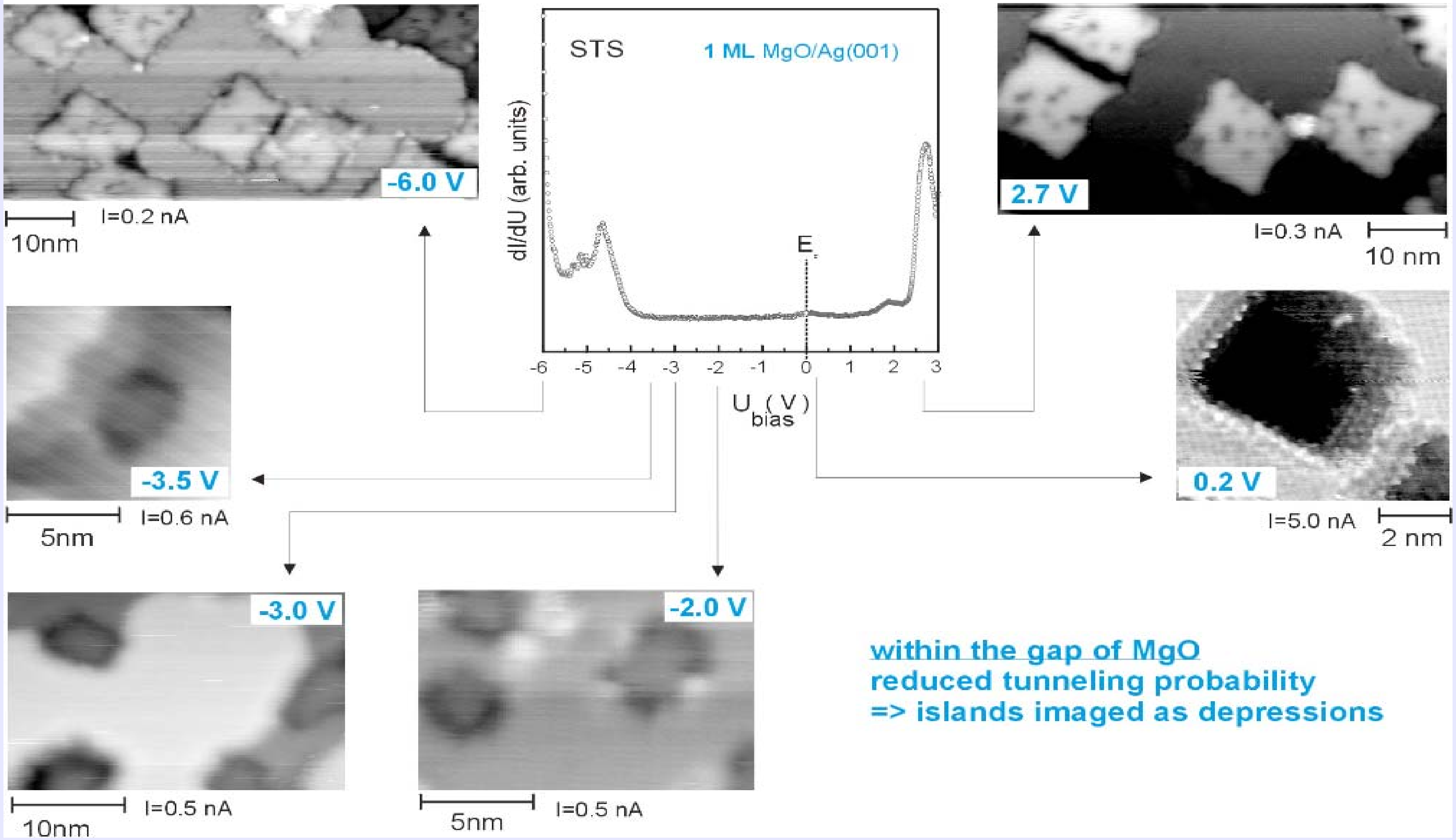
Imaging insulators by STM



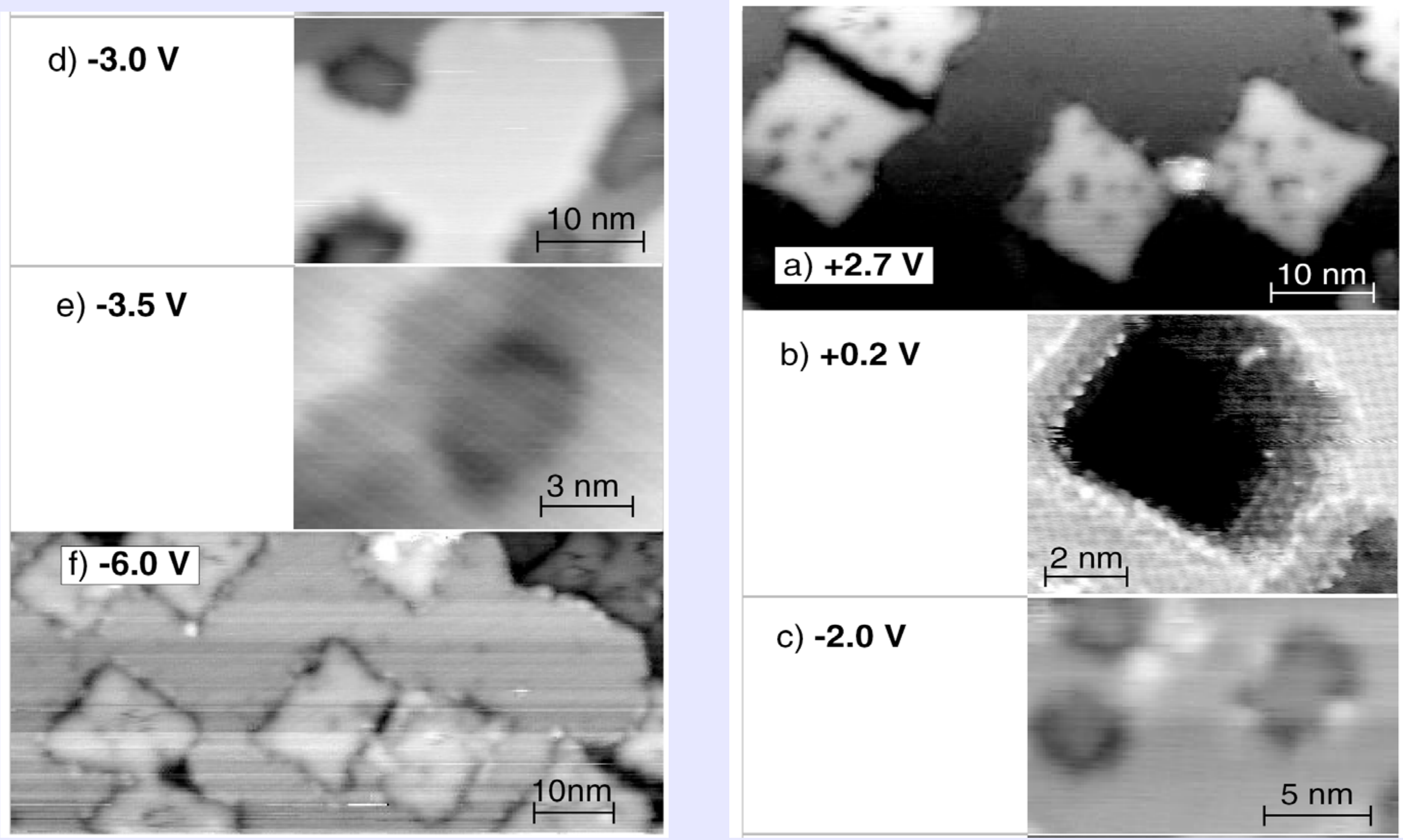
J. Viernow et al., PRB **59**, 10 356 (1999)

STM image contrast of MgO islands

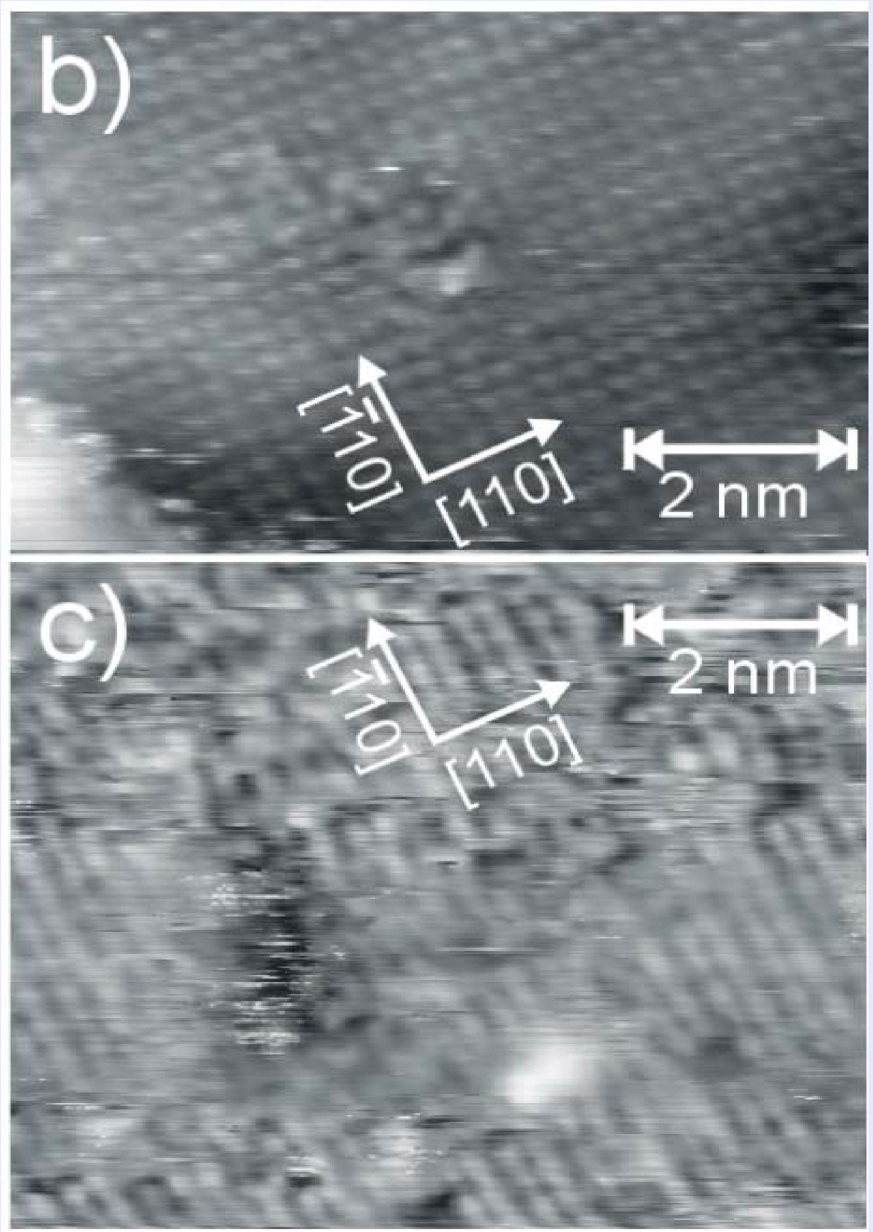


within the gap of MgO
reduced tunneling probability
=> islands imaged as depressions

S. Schintke, PhD thesis, Lausanne (2001)



d) -3.0 V
10 nm
e) -3.5 V
3 nm
f) -6.0 V
10nm
a) +2.7 V
10 nm
b) +0.2 V
2 nm
c) -2.0 V
5 nm



Atomic resolution of the Ag(001) substrate: tunneling through a 1 ML MgO island

(U_t = 30 mV, I_t = 2 pA)

Atomic resolution of 1 ML MgO(001)/Ag(001)

(U_t = 2.5 V, I_t = 50 pA)

S. Schintke et al.,
PRL **87**, 276801 (2001)

EPFL

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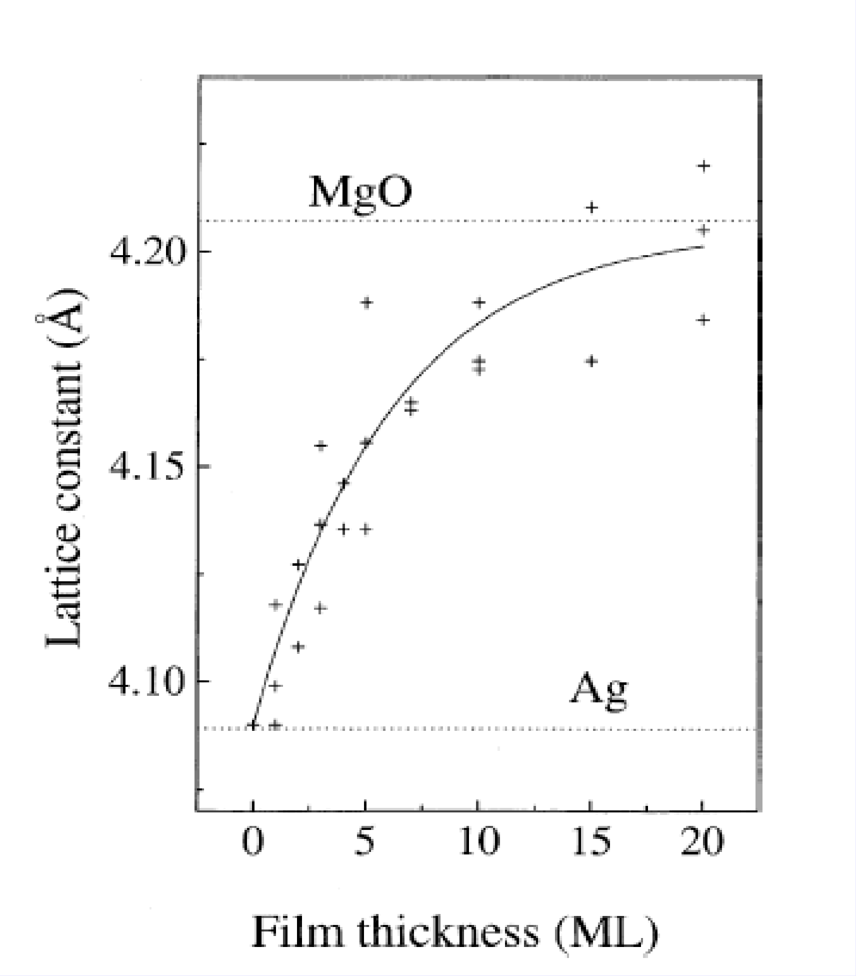
Lattice constant of overgrown MgO films on Ag(001)

MgO: 4.21 Å

Misfit: 2.9%

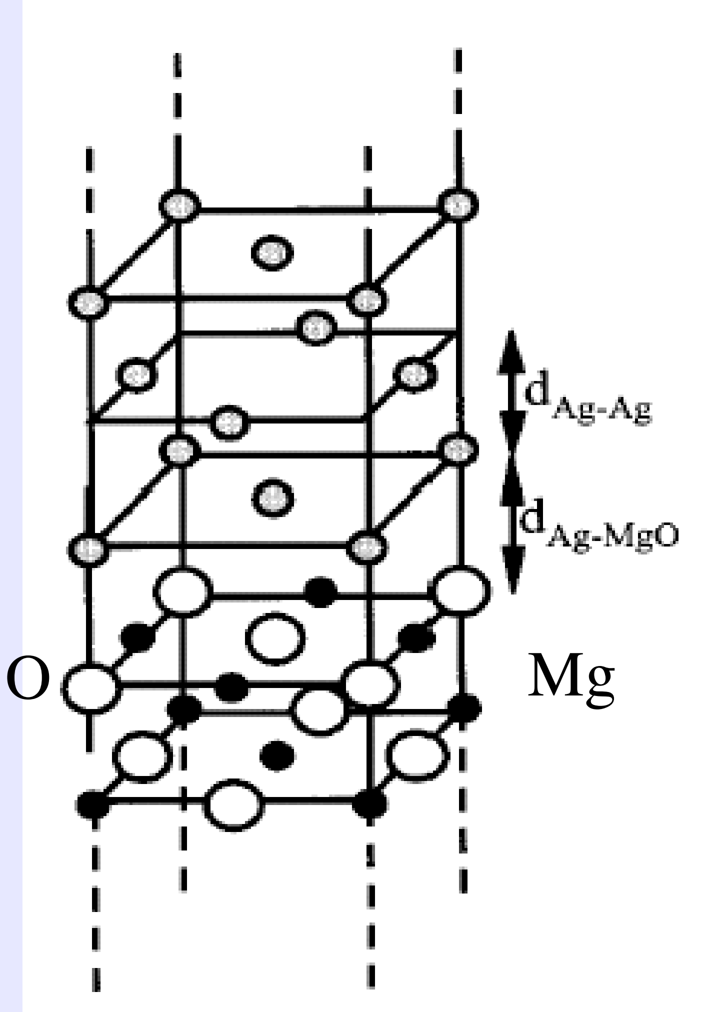
Ag: 4.09 Å



RHEED

M. Kiguchi et al., Surf. Sci. 512, 97 (2002)

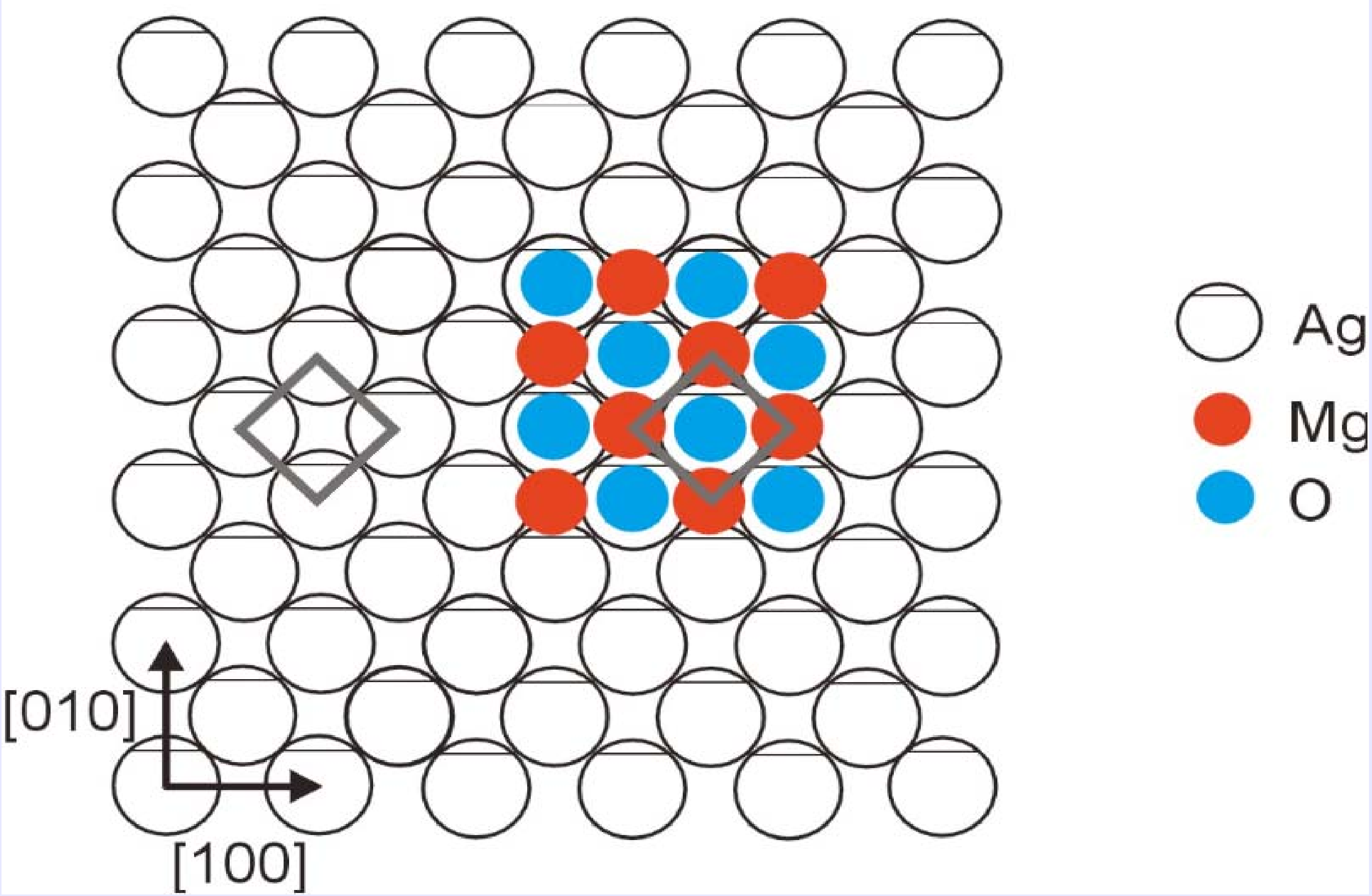
The inverse interface: Ag/MgO(001)



Surface X-ray diffraction, grazing incidence small angle X-ray scattering

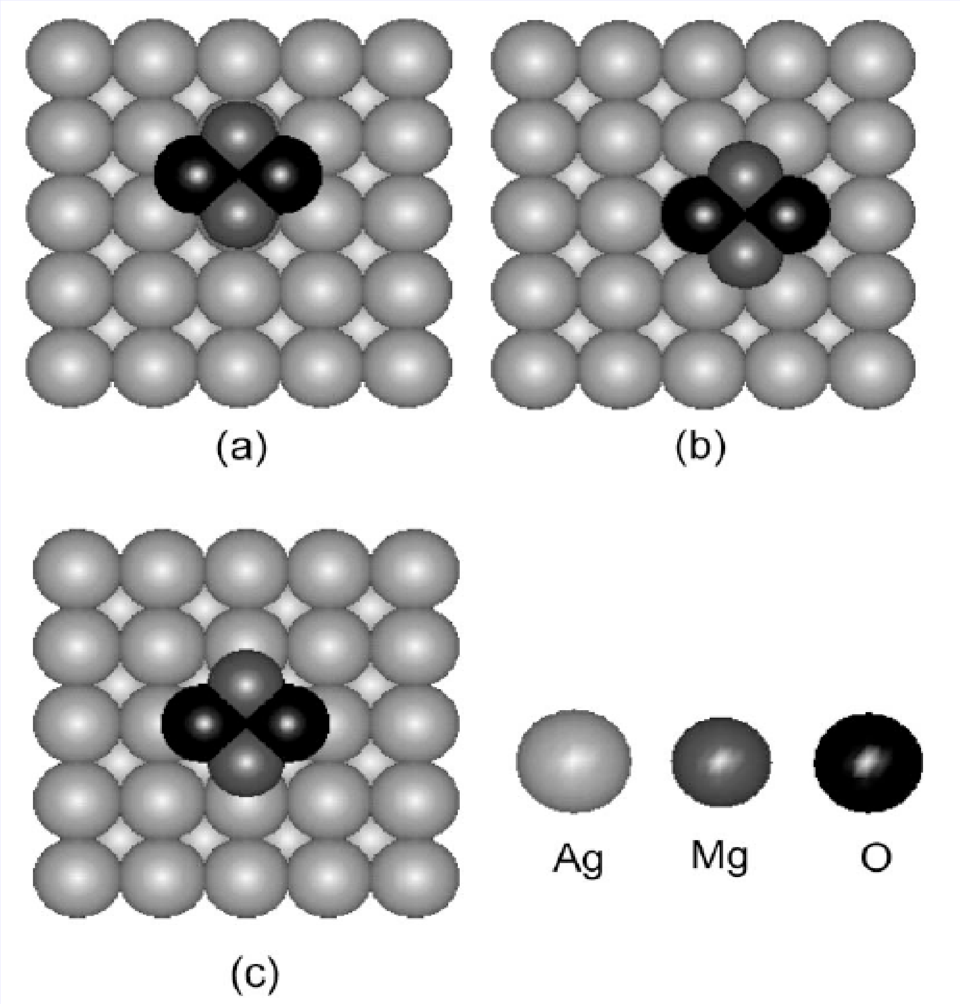
O. Robach et al., PRB **60**, 5858 (1999)

MgO/Ag(001) growth model

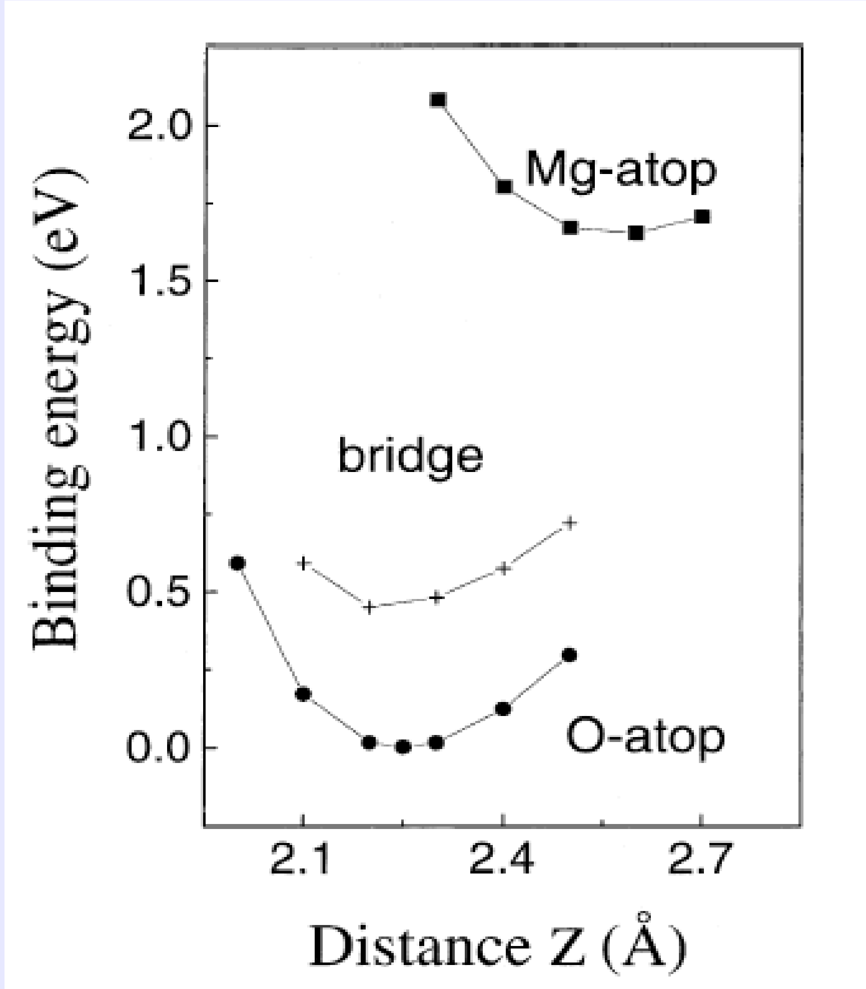


S. Schintke, PhD thesis, Lausanne (2001)

Adsorption geometry



Potential energy



M. Kiguchi et al., Surf. Sci. 512, 97 (2002)

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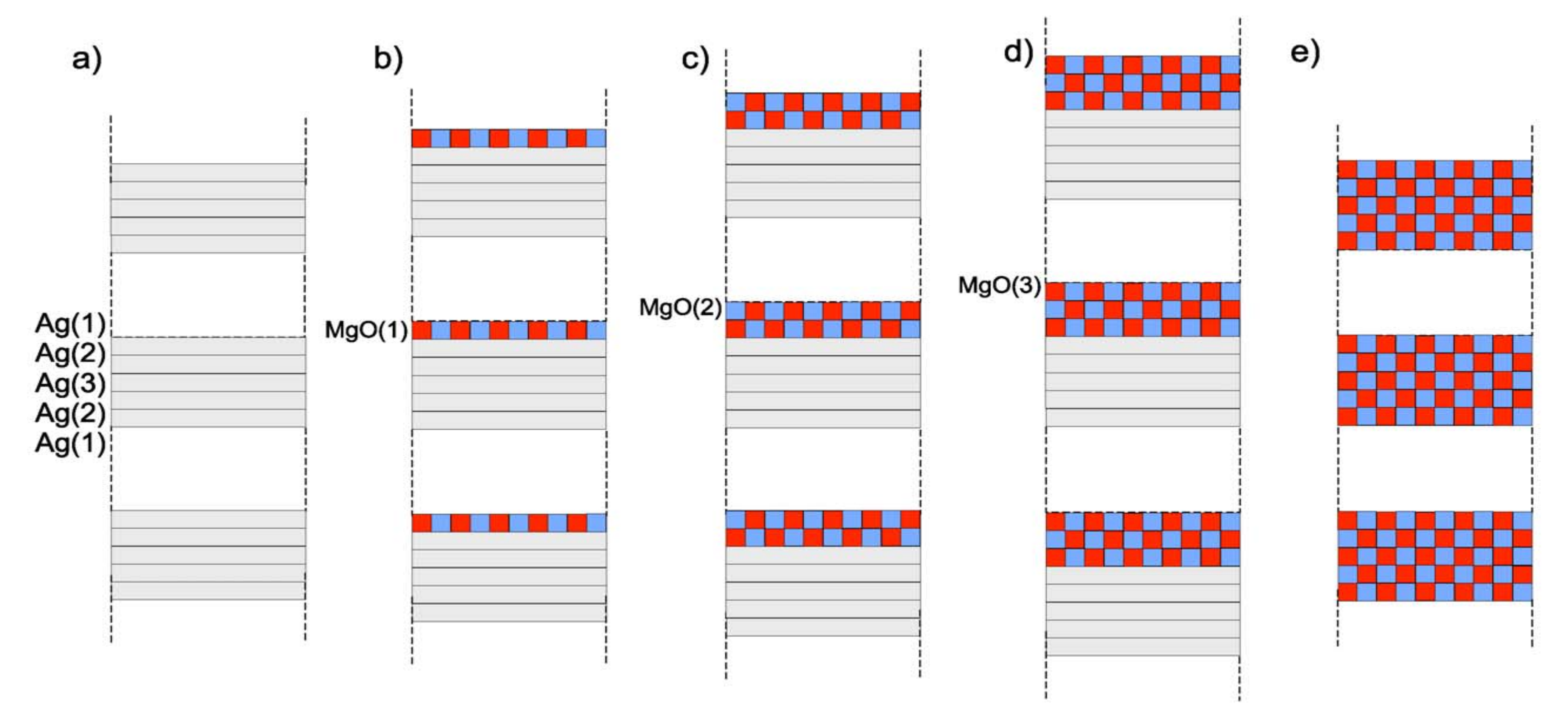
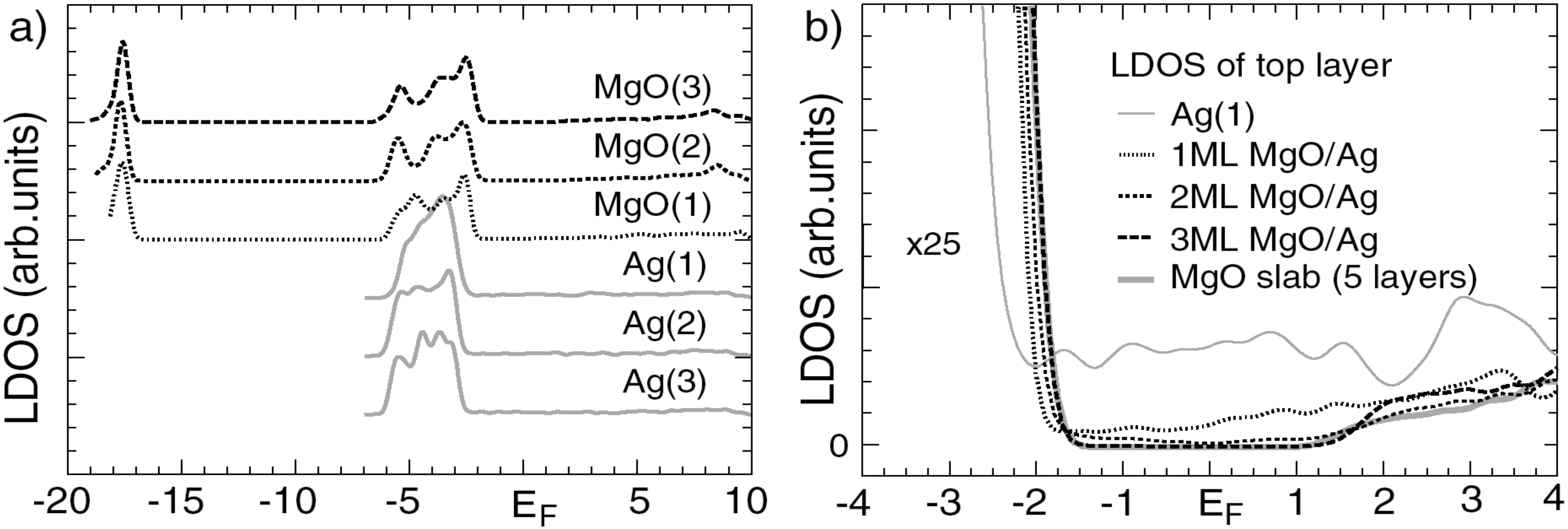
Slab geometries in DFT-calculations with periodic boundary conditions



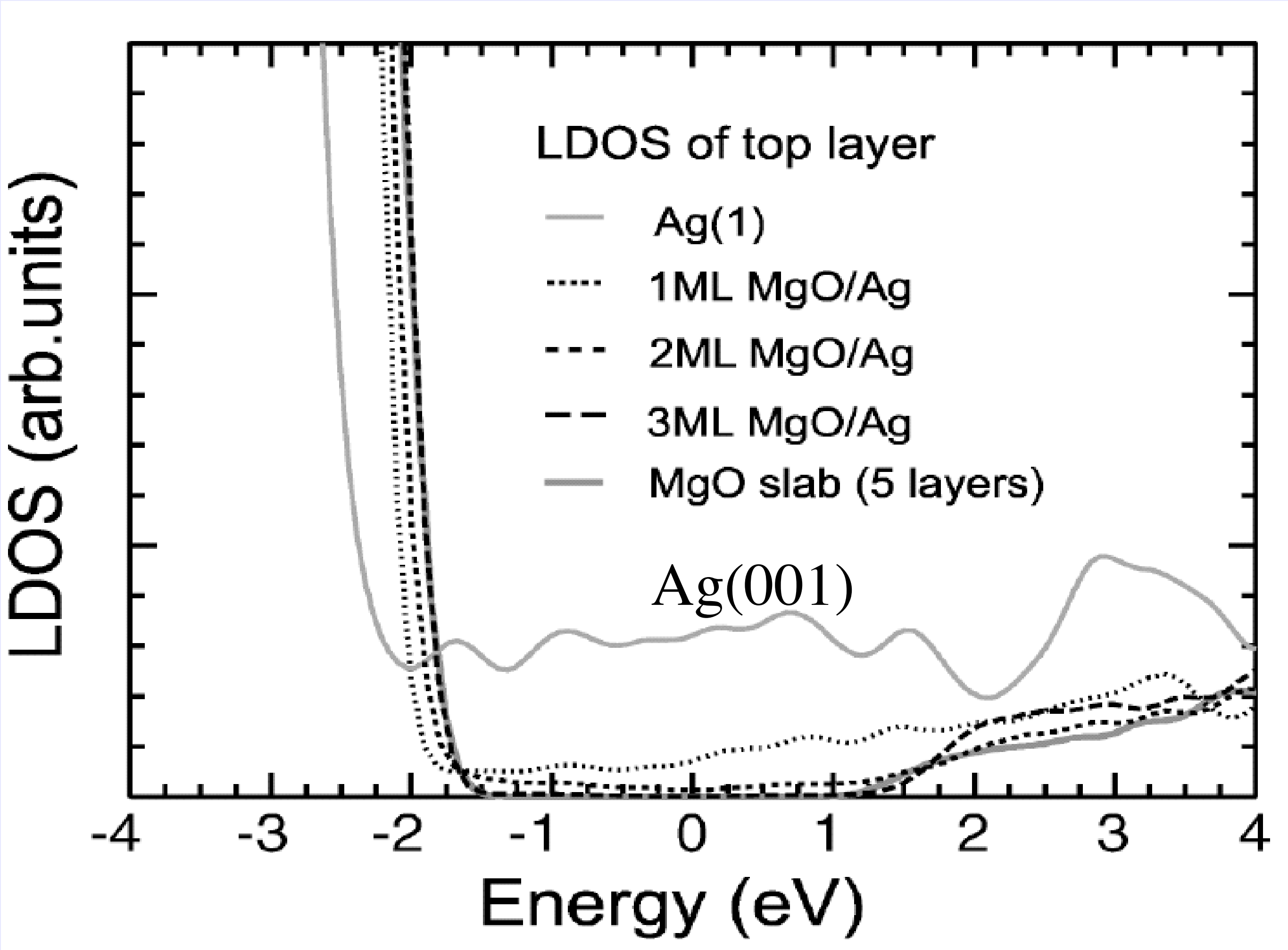
S. Schintke, PhD thesis, Lausanne (2001)

Layer-resolved LDOS calculated within DFT



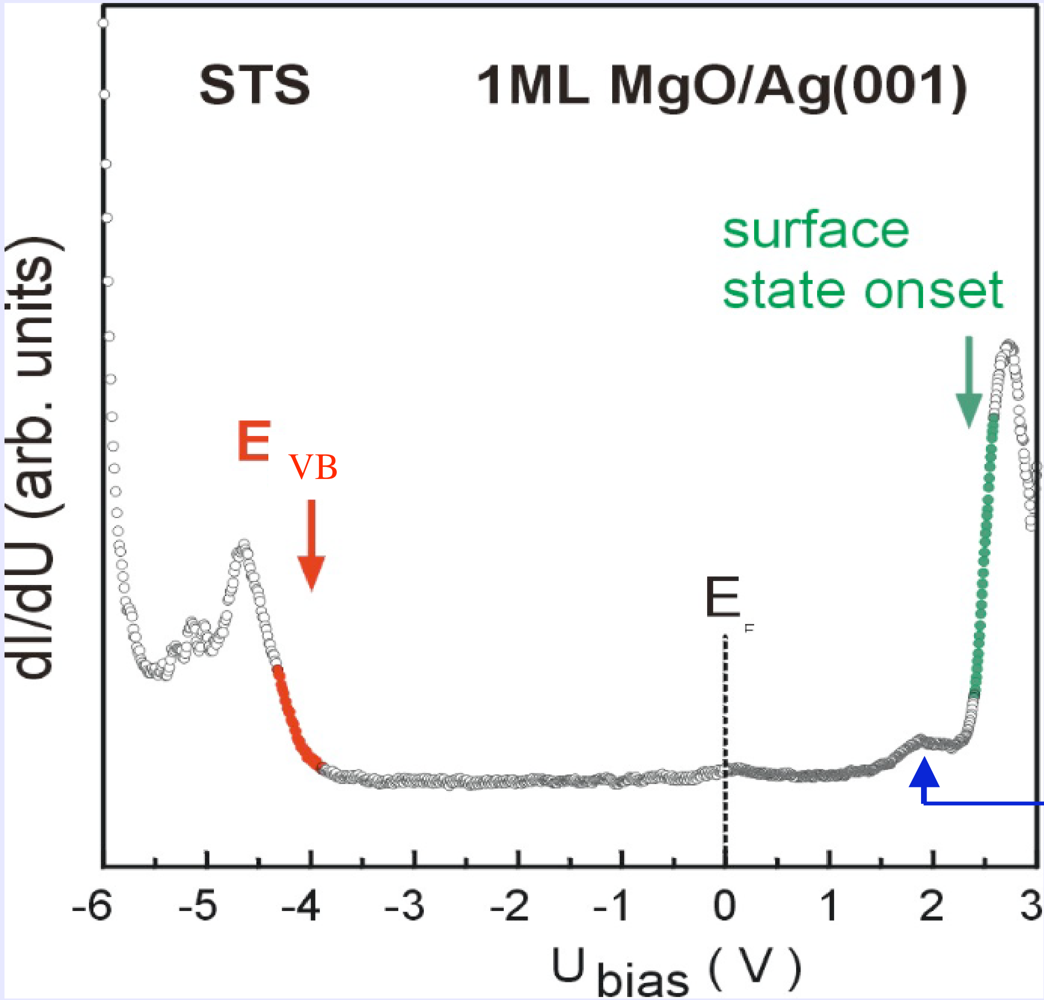
S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

Insulator at the ultrathin limit



S. Schintke et al., PRL **87**, 276801 (2001)

Insulator at the ultrathin limit



interface state

S. Schintke et al., PRL **87**, 276801 (2001)

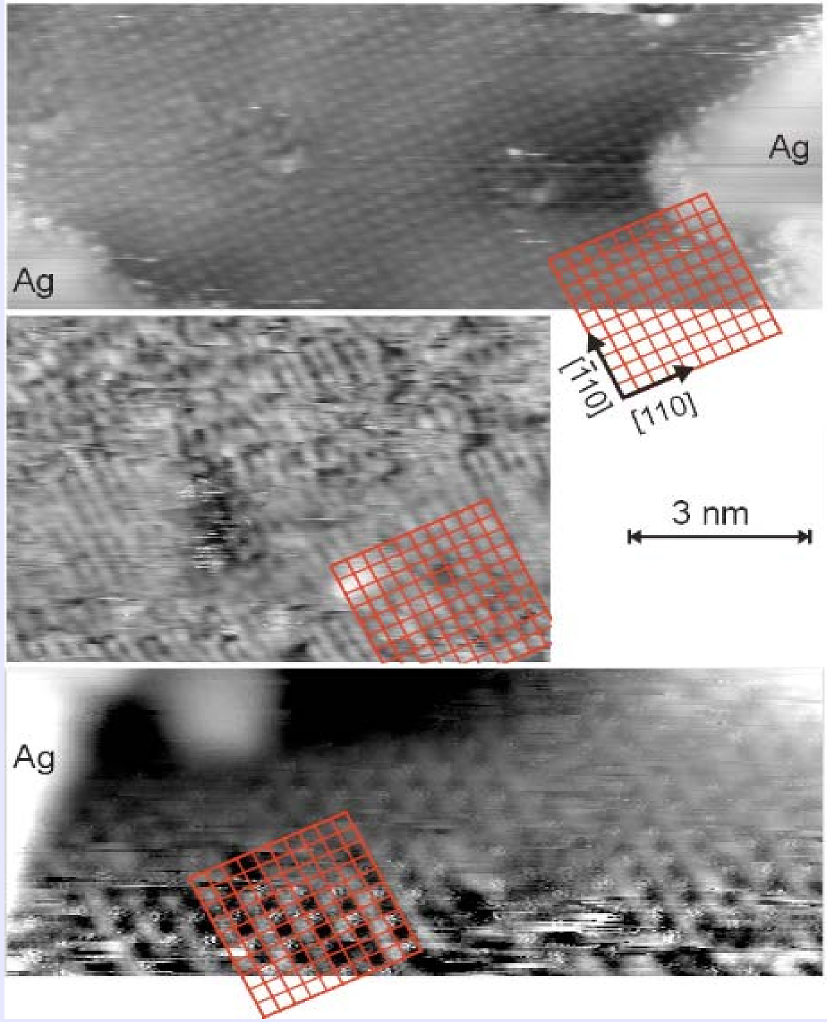
Insulator at the ultrathin limit: MgO

- 1 ML: Gap-structure already present

  Now also seen (EELS) by: M. Kiguchi et al.,
  Surf. Sci. 512, 97 (2002)

- 3ML: Electronic structure identical to the one of the surface terminating bulk MgO

MgO/Ag(001)
High resolution STM images



30 mV
2 pA

underlying metal substrate
Ag(001) atomic resolution <u>through</u> an MgO island

2.5 V
50 pA

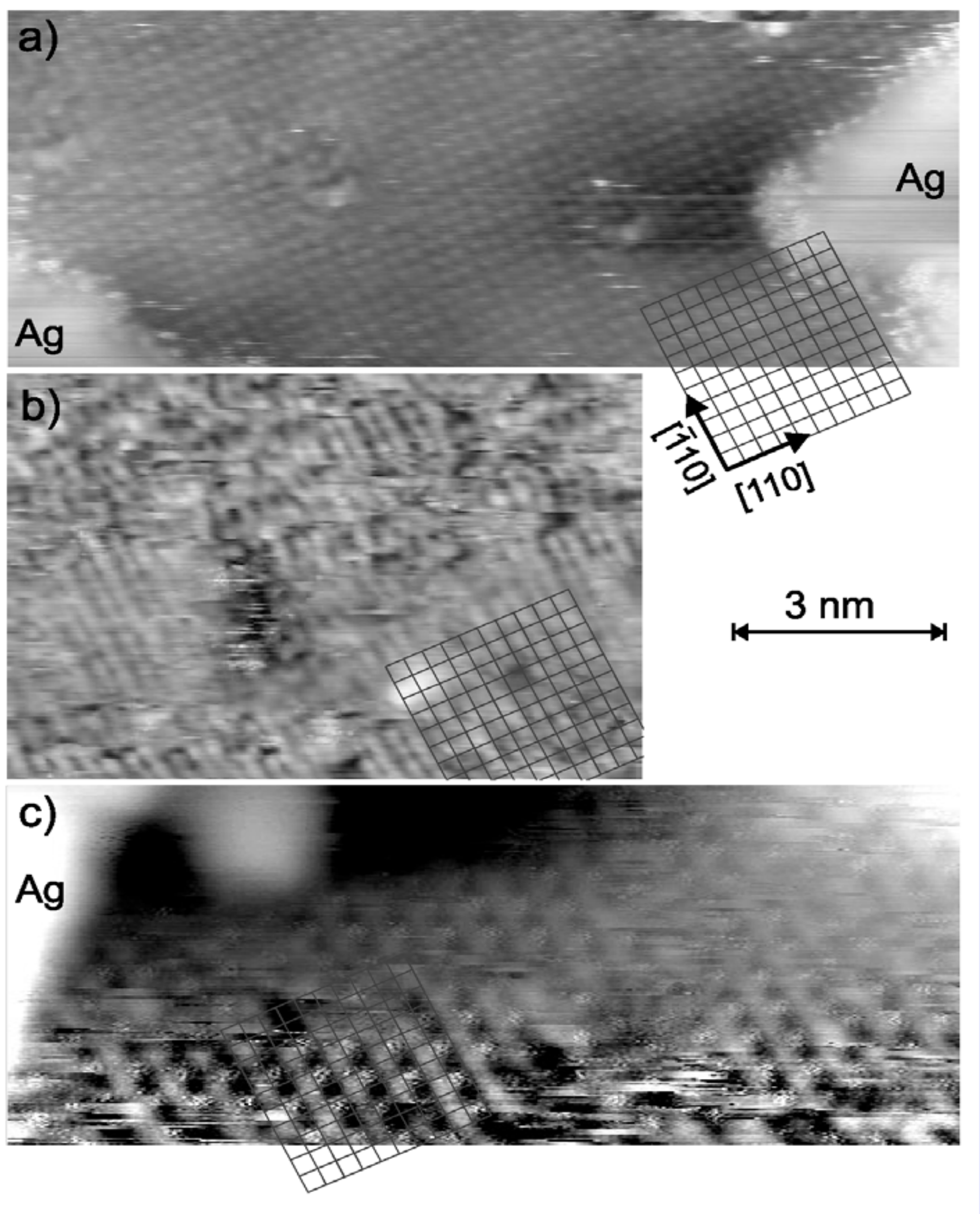
insulating film
atomic resolution of the MgO layer
=> one type of ion resolved

Mg ? or O ?

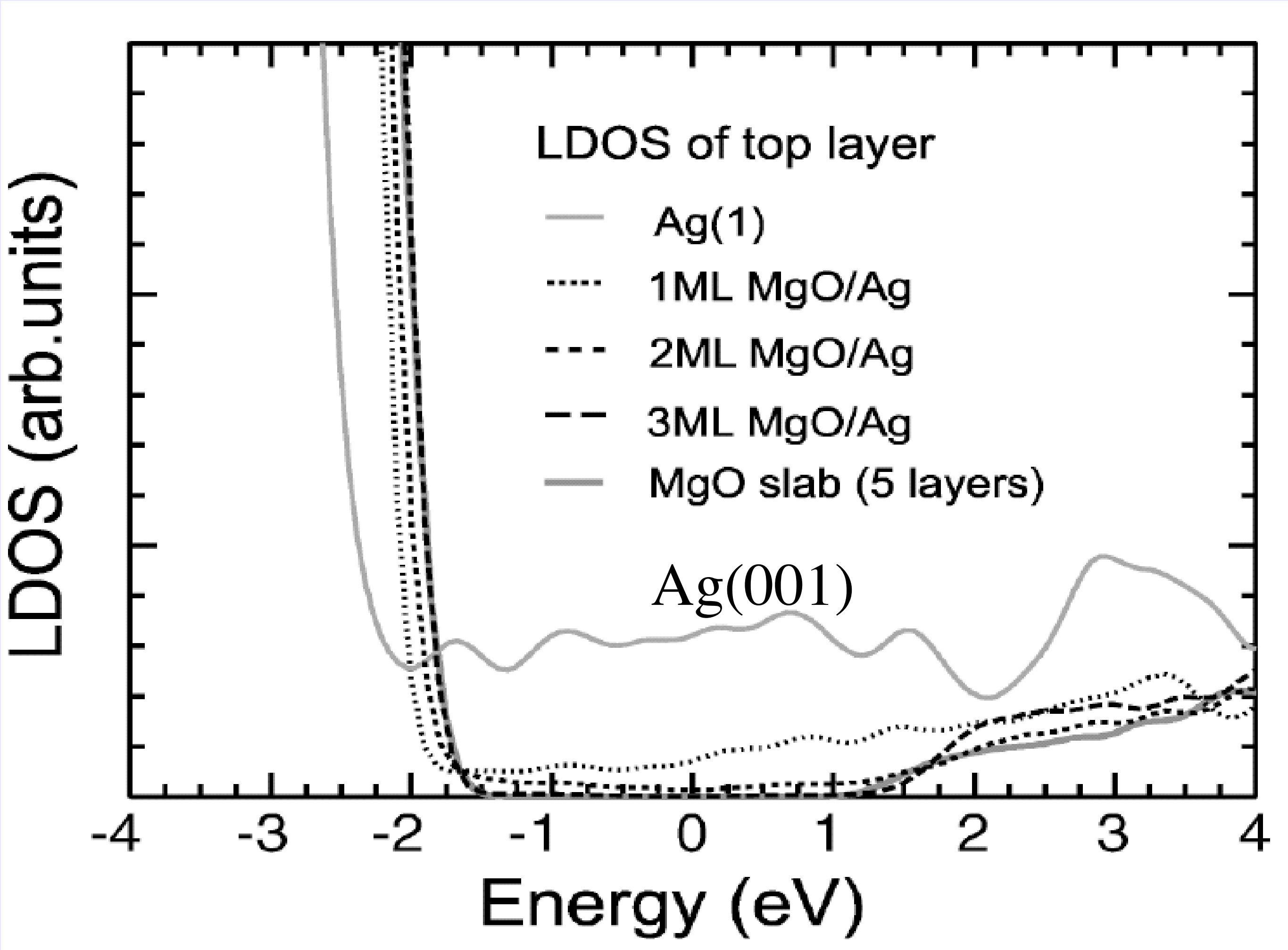
1.7 V
2 pA

interface
c(2x4) superstructur ... on

S. Schintke, PhD thesis, Lausanne (2001)

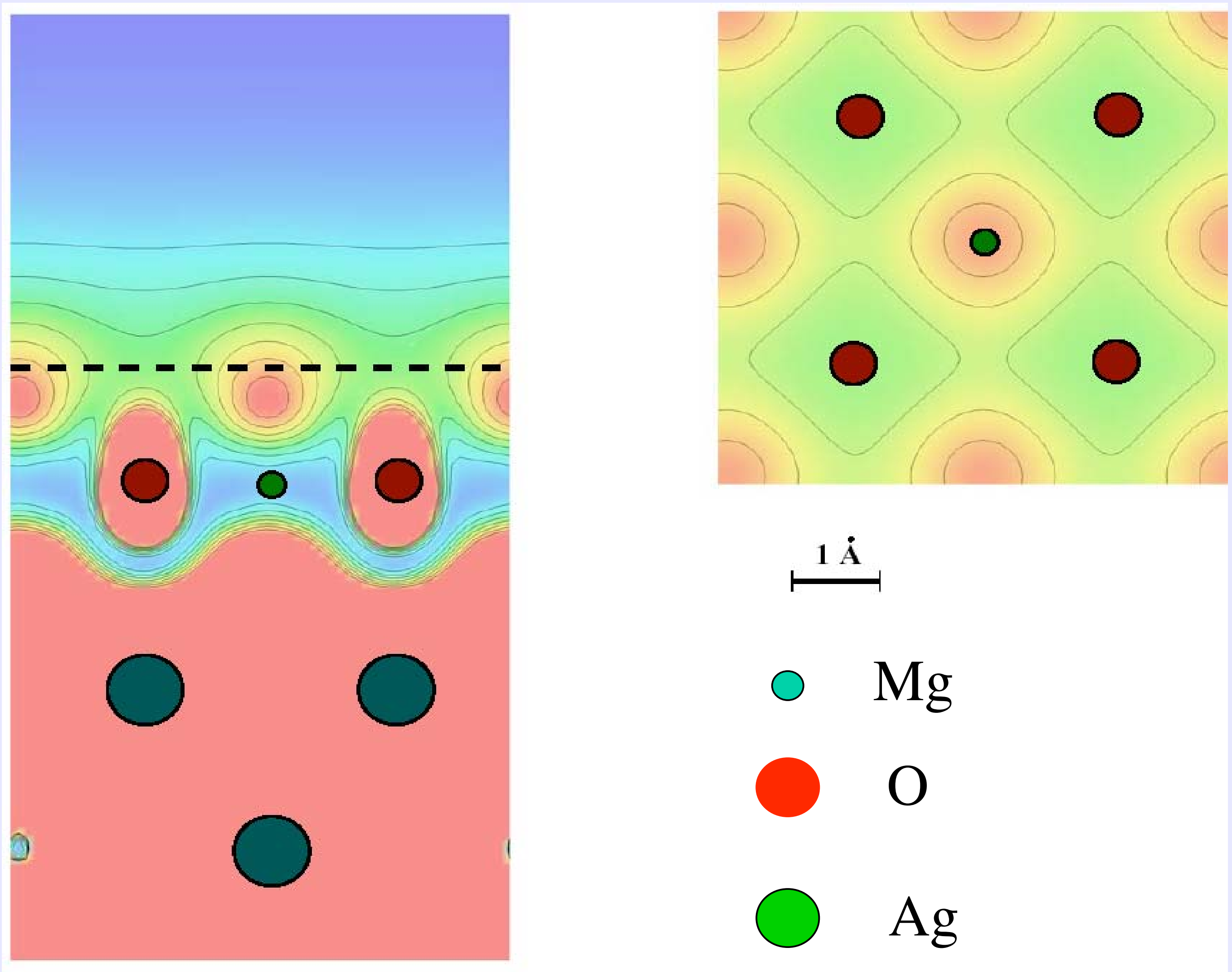

a)
Ag
Ag
b)
[$\bar{1}$10]
[110]
3 nm
c)
Ag

Insulator at the ultrathin limit



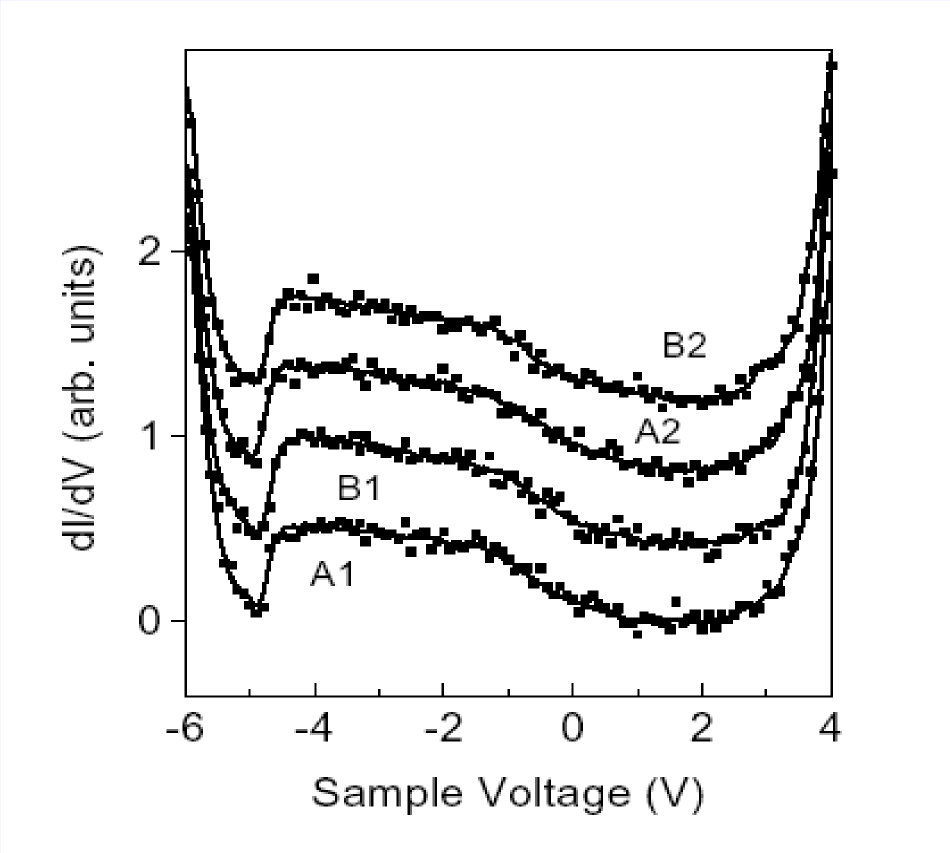
S. Schintke et al., PRL **87**, 276801 (2001)

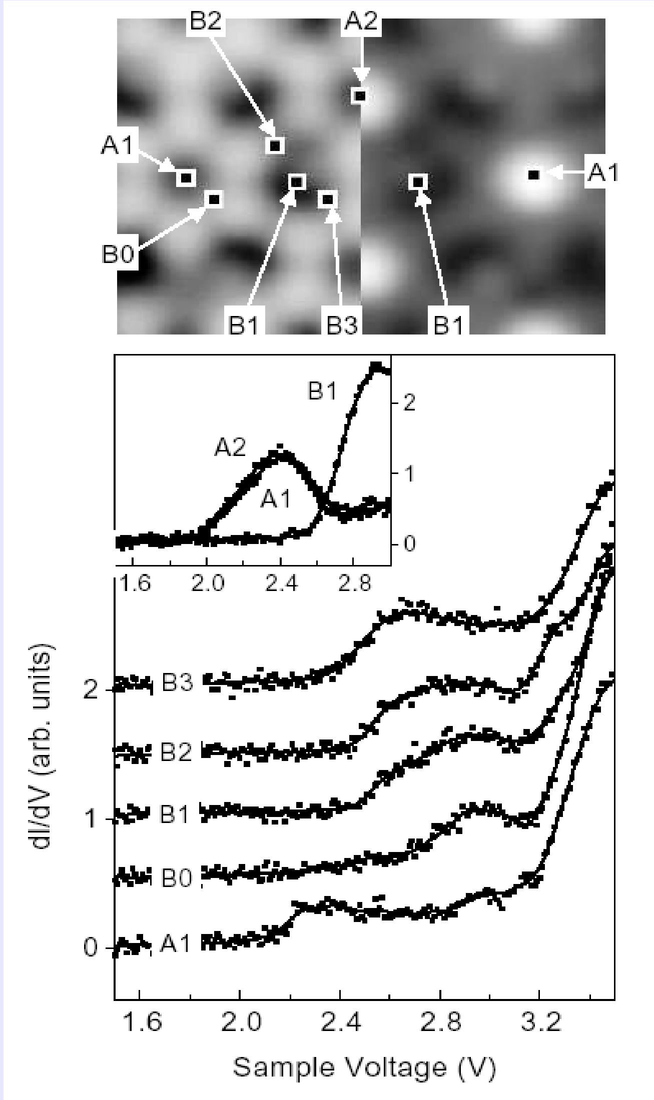
LDOS for 1 ML MgO/Ag(001)



M. Stengel et al., to be published

$Al_2O_3/Ni_3Al(111)$
dI/dV spectra





T. Maroutian, S. Degen, C. Becker, K. Wandelt, R. Berndt, Phys. Rev. B **68**, 155414 (2003)

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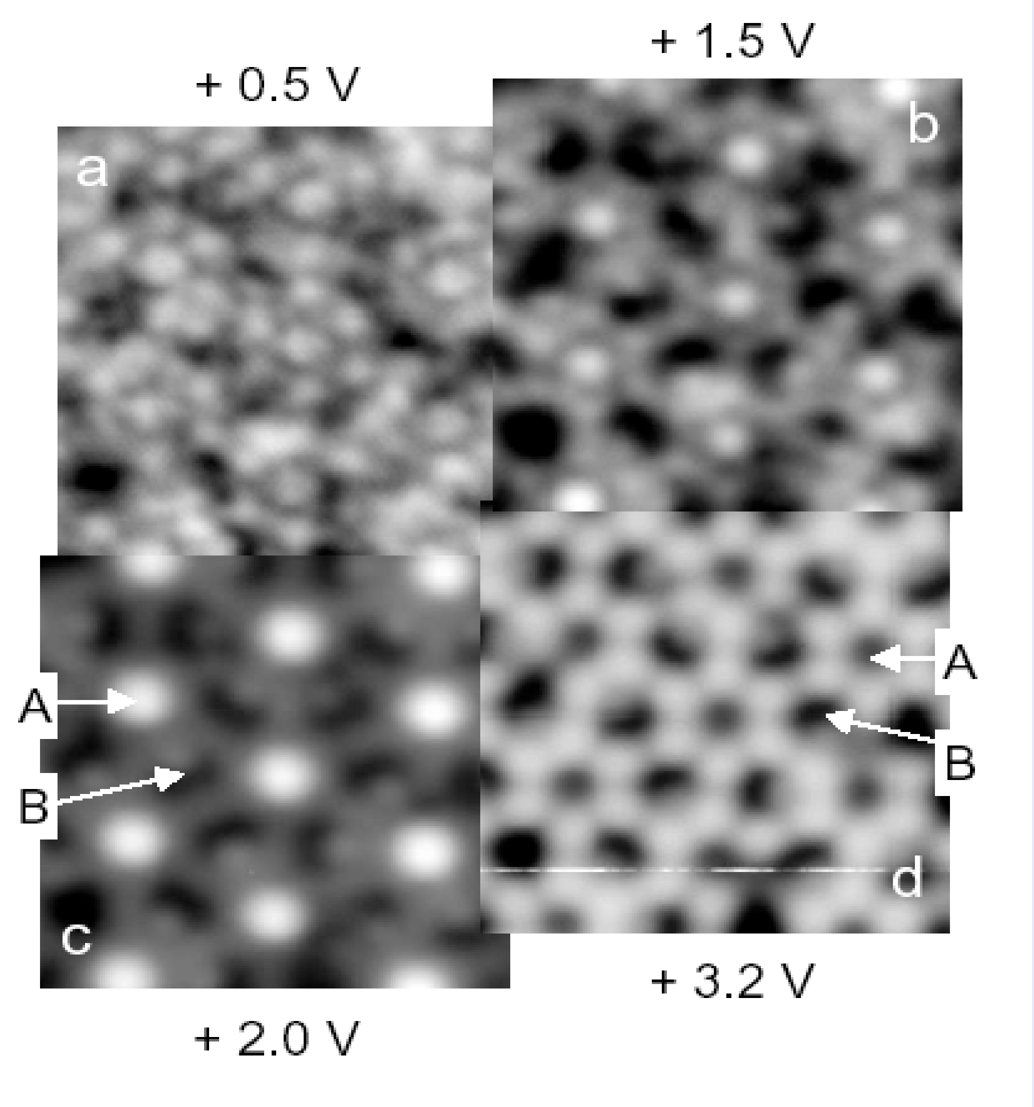
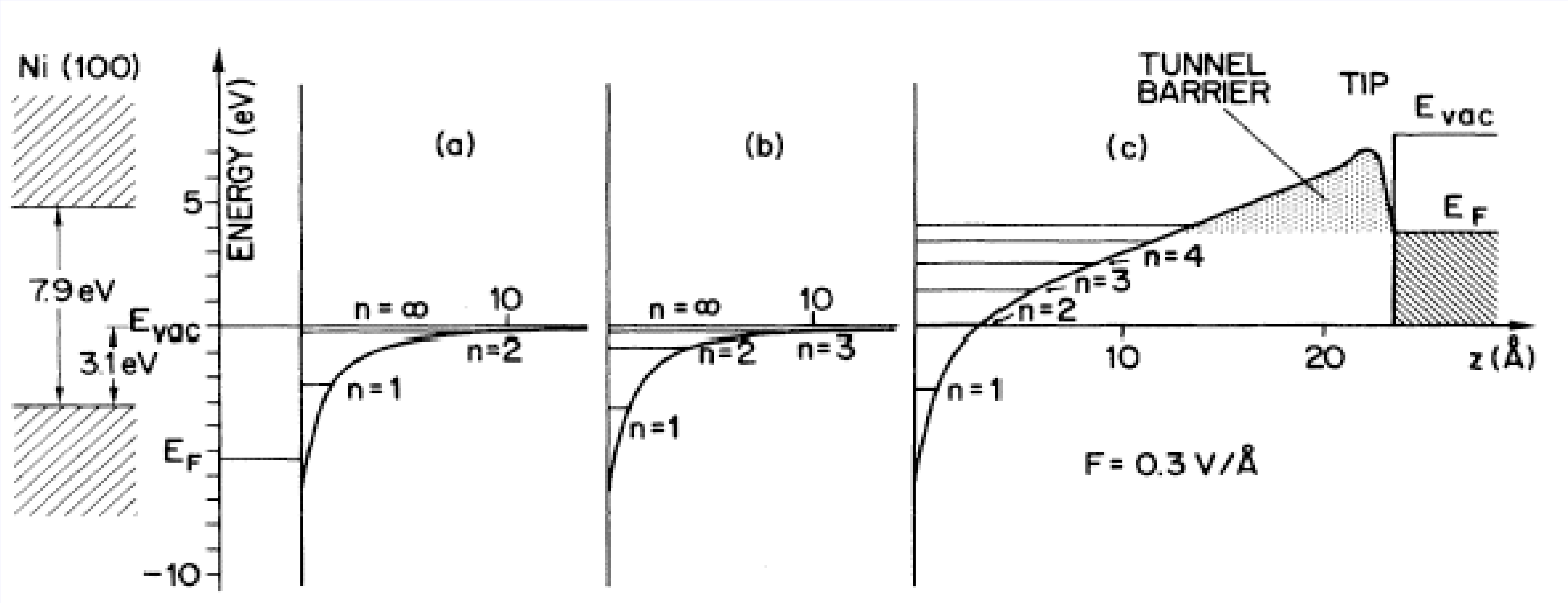
$Al_2O_3/Ni_3Al(111)$

voltage-dependent superstructures



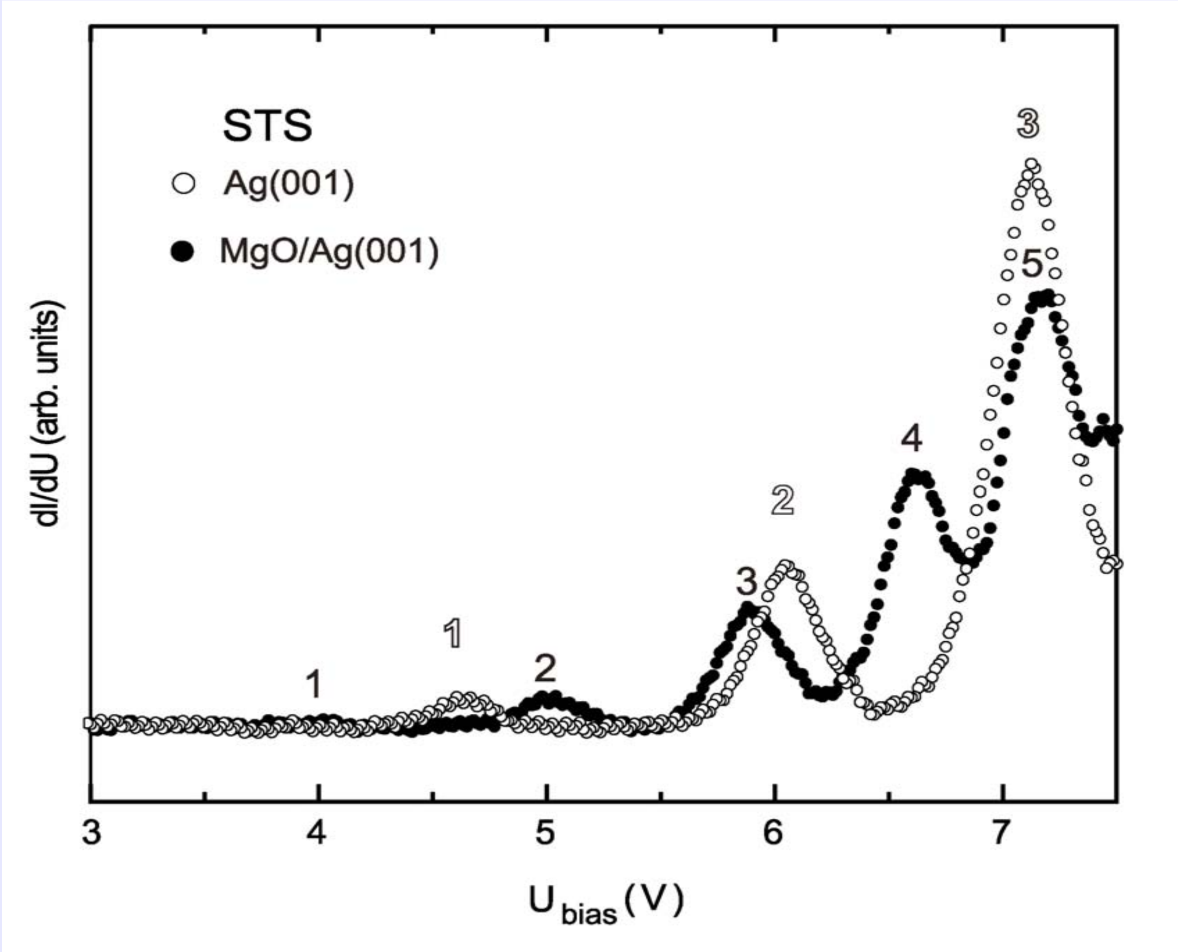
T. Maroutian, S. Degen, C. Becker, K. Wandelt, R. Berndt, Phys. Rev. B **68**, 155414 (2003)

Image and field emission states



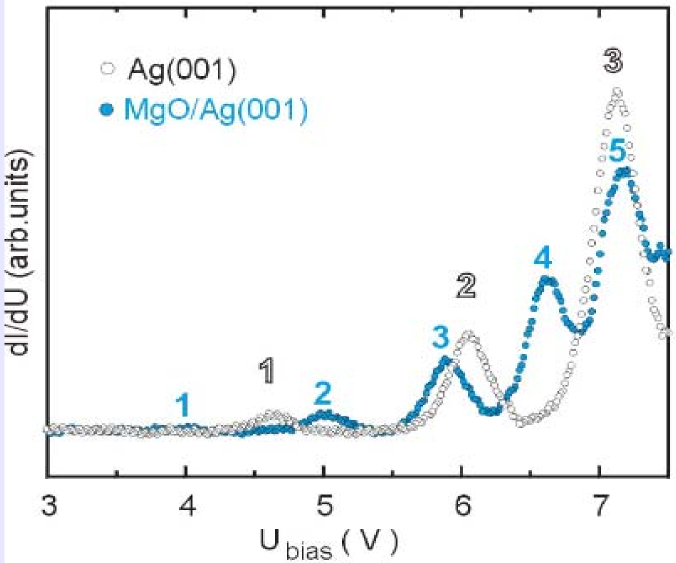
G. Binnig et al., PRL **55**, 991 (1985)

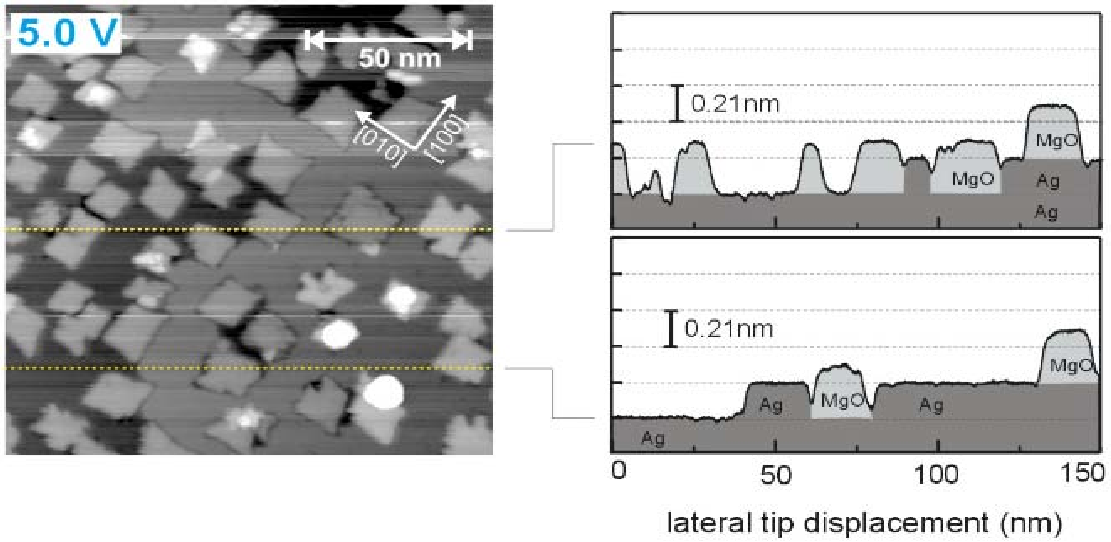
Image and field emission states



S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

MgO/Ag(001): Chemical Contrast via Field Resonances





STM-tip **above an MgO island:**
resonances **shift** to lower energies

- reduced electrical field

- reduced work function

=> STM image contrast
e.g. STM image at **5.0 V**
(resonance when tip above MgO)

=>increased apparent height for 1ML MgO islands:
0.30nm vs. 0.21nm geometric height
(Ag-Ag steps 0.20nm)

S. Schintke, PhD thesis, Lausanne (2001)
S. Schintke and WDS, J. Phys. Condens. Matter **16**, R49 (2004)

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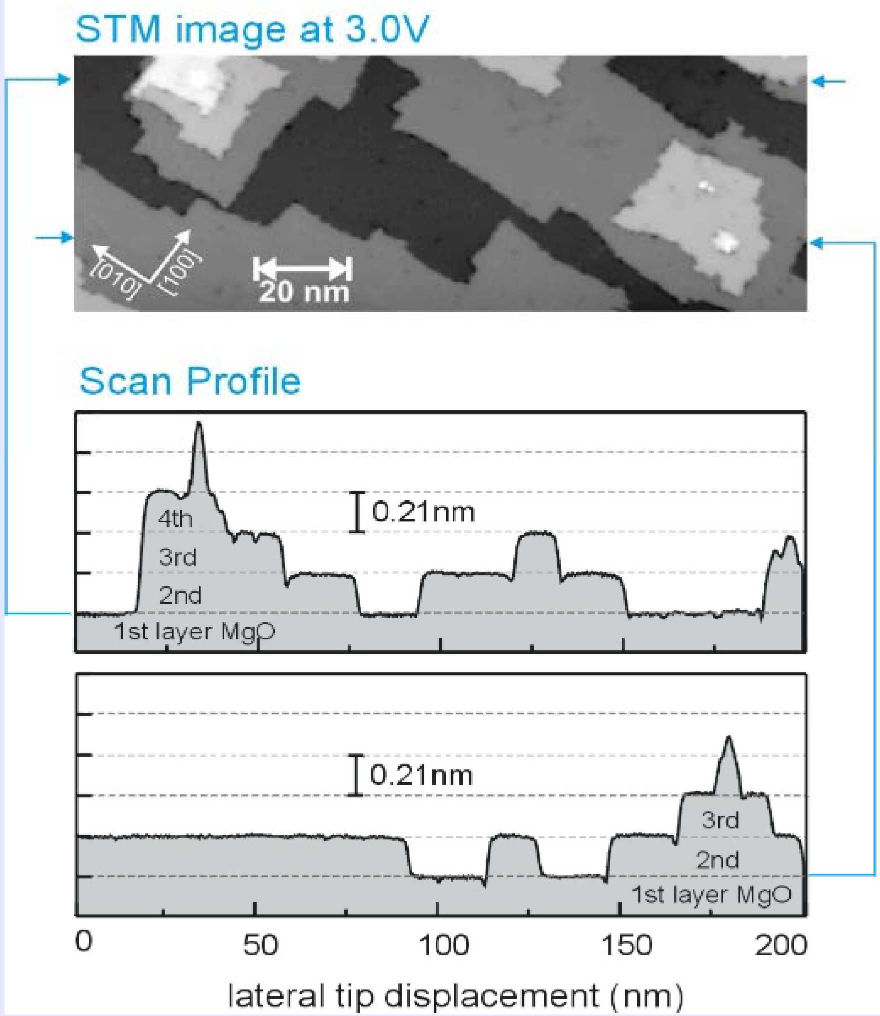
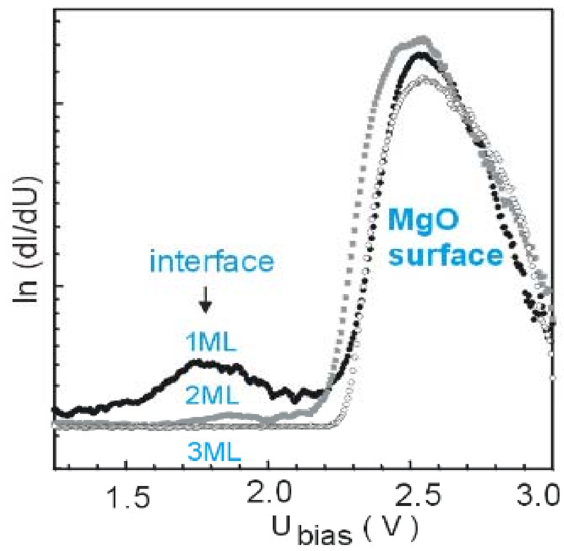
MgO/Ag(001)





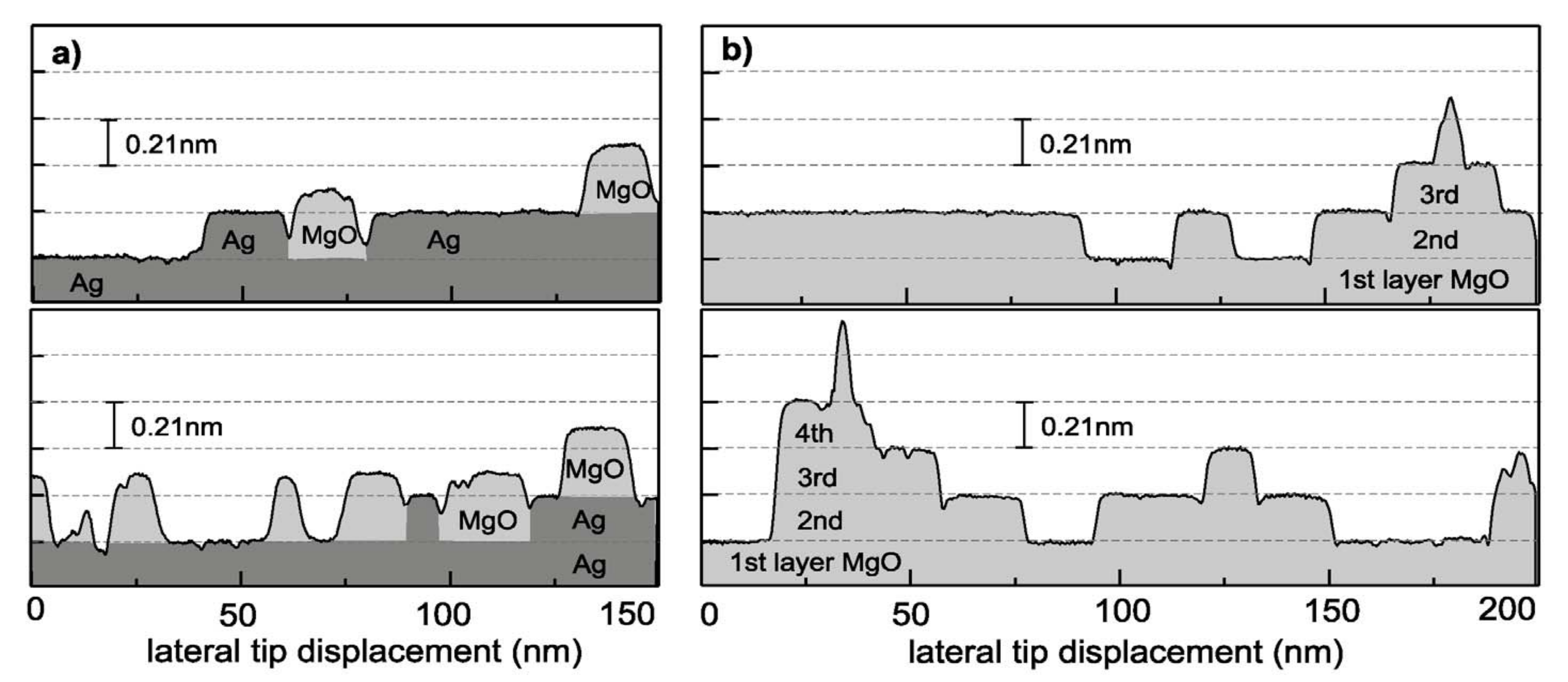
bias outside the gap:
MgO-MgO step heights correspond to their geometric heights

MgO states dominate the tunnel current

S. Schintke, PhD thesis, Lausanne (2001),
S. Schintke and WDS, J. Phys. Condens. Matter **16**, R49 (2004)

Field emission states: Increased step height

Outside band gap: geometrical step height



S. Schintke, PhD thesis, Lausanne (2001),
S. Schintke and WDS, J. Phys. Condens. Matter **16**, R49 (2004)

EPFL

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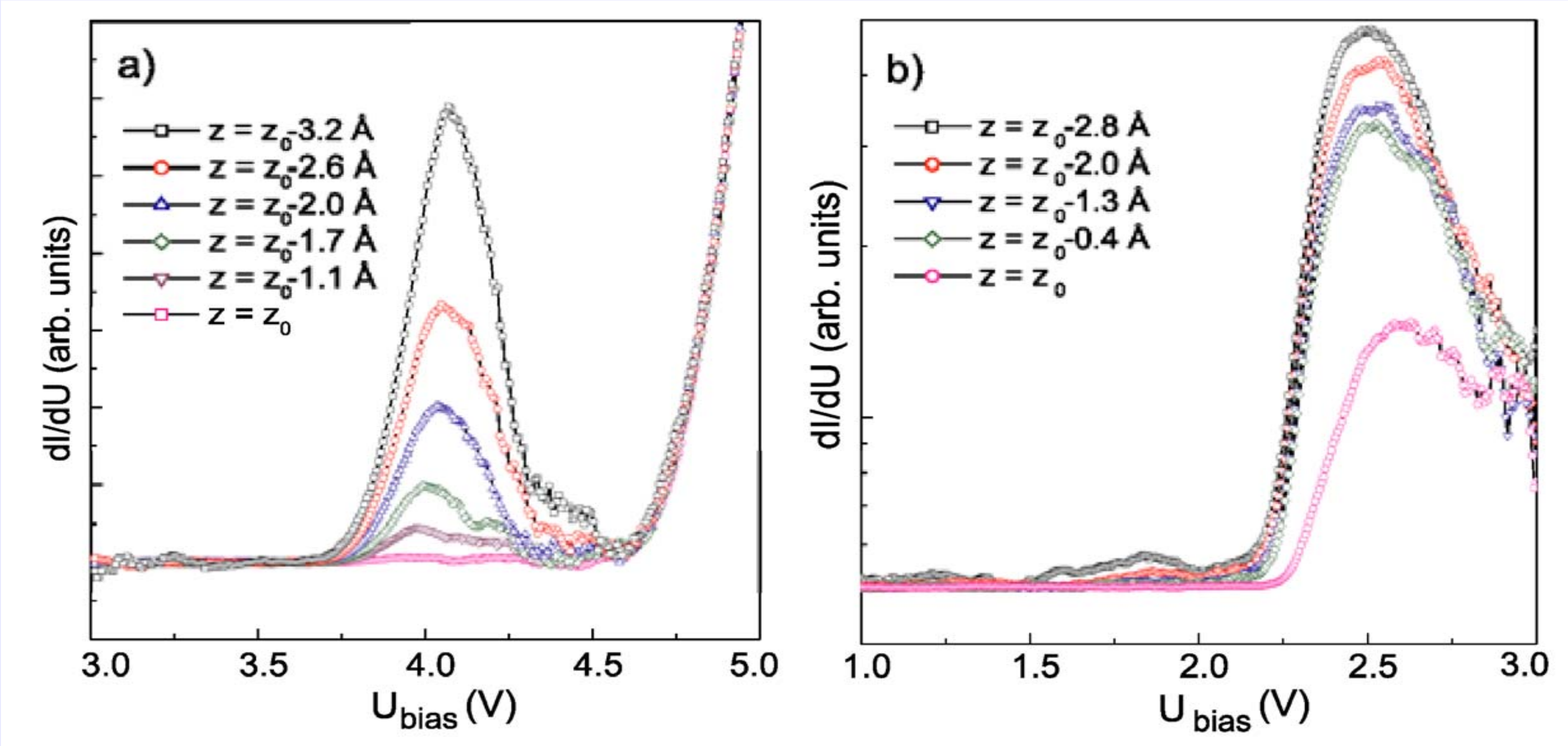
Field dependence of spectral features

Field resonance   Surface state



S. Schintke, PhD thesis, Lausanne (2001),
S. Schintke and WDS, J. Phys. Condens. Matter **16**, R49 (2004)

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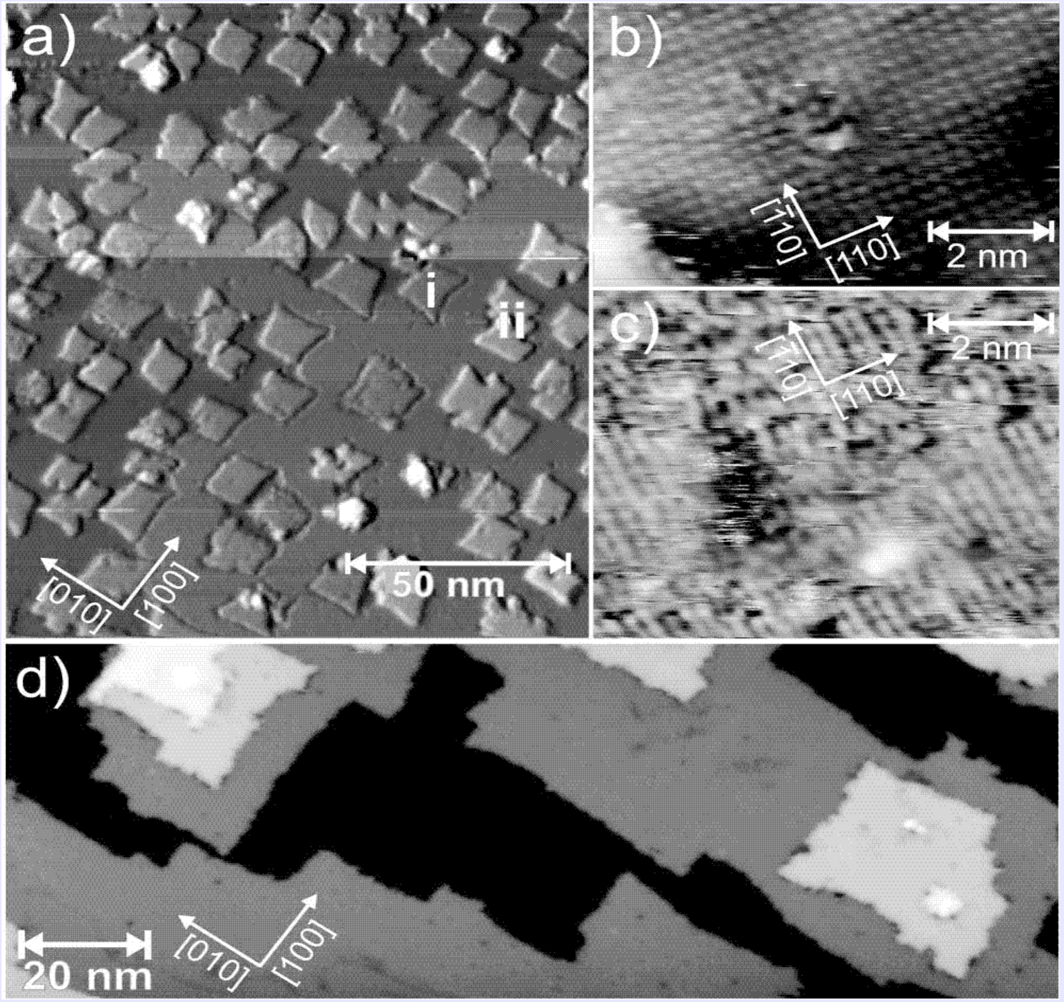
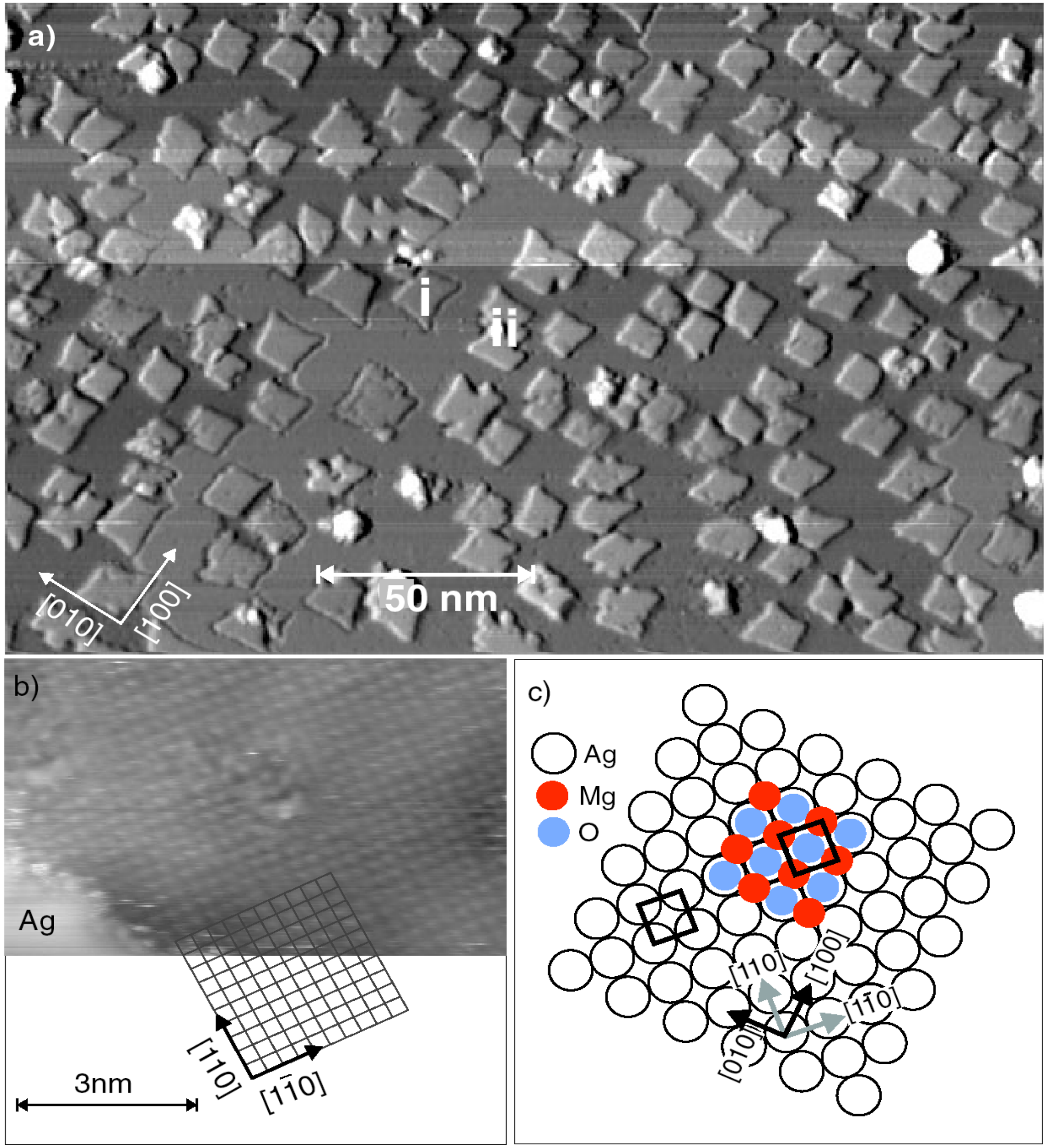
MgO(100)/Ag(100)

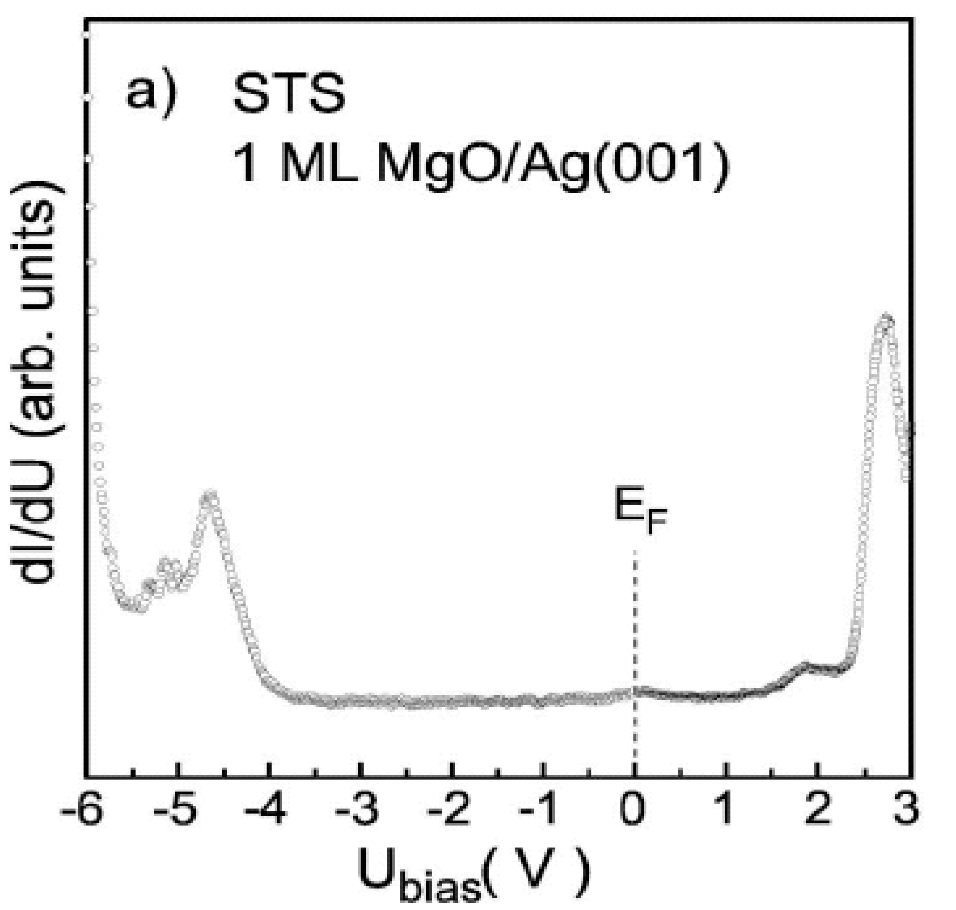


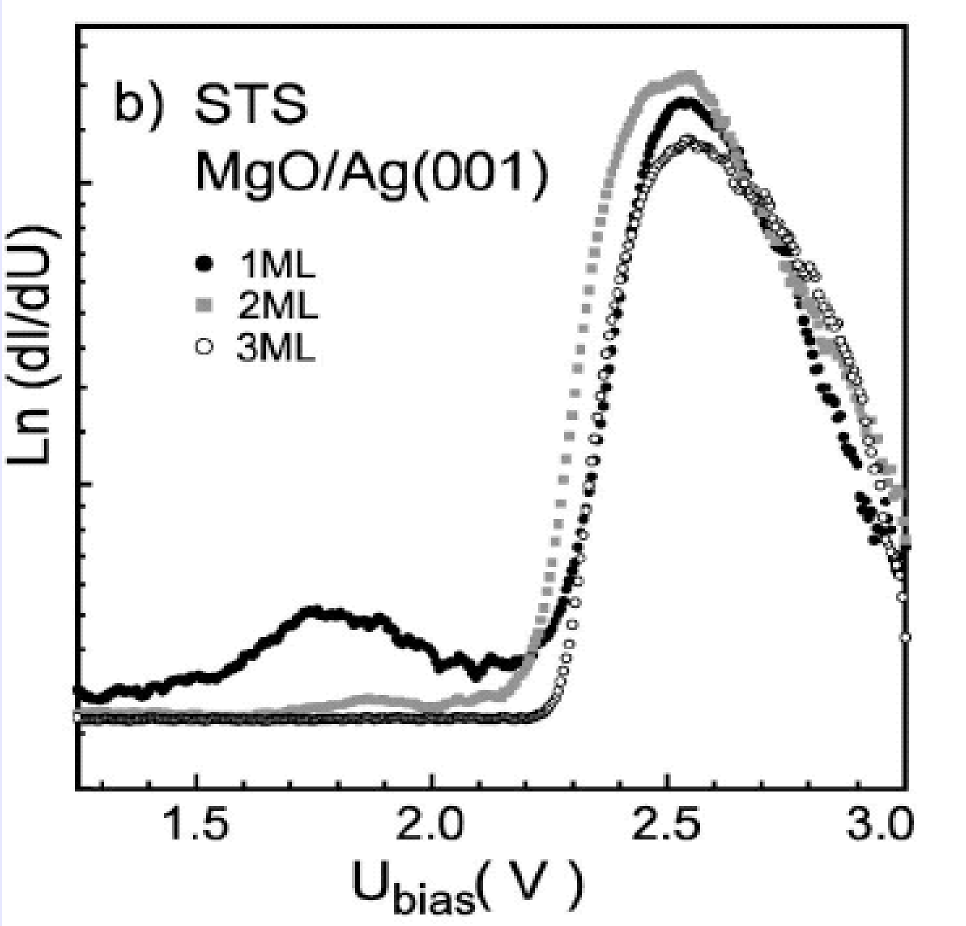
S. Schintke et al., PRL **87**, 276801 (2001)



S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

Insulator at the ultrathin limit





S. Schintke, S. Messerli, M. Pivetta, F. Patthey, L. Libioulle, M. Stengel, A. De Vita, WDS, PRL **87**, 276801 (2001)

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New interpretations:

Structure at 1.7 eV:

Metal induced gap state

M. Stengel, thesis EPFL 2004, to be published

Structure at 2.5 eV:

Image state which is lower than the conduction band onset

M. Rohlfing et al., PRL 91, 256802 (2003),

M. Stengel, thesis EPFL 2004, to be published.

Ultrathin layers of MgO(100)/Ag(100)

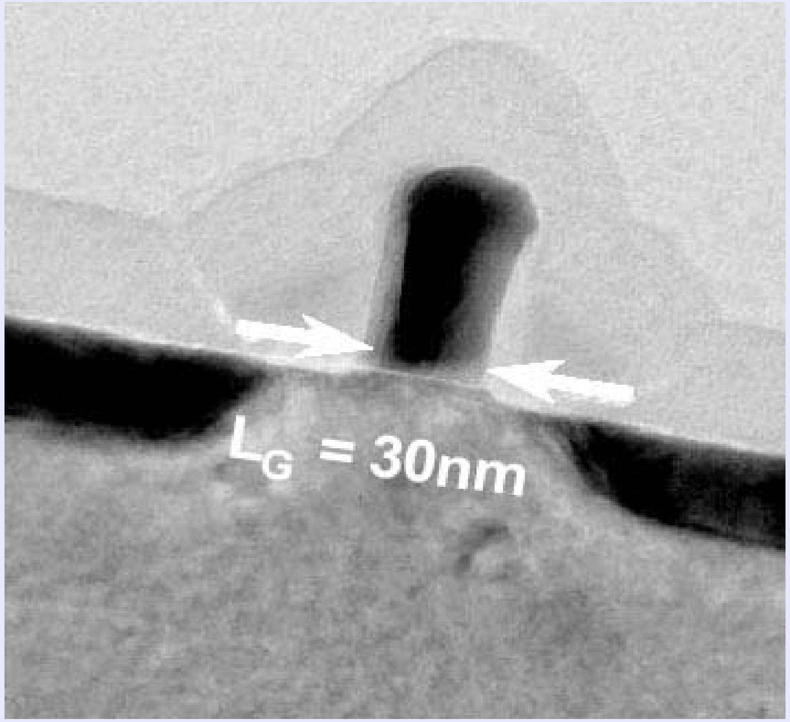
- Model system for wide band gap insulators
- Layer-resolved morphology on the atomic scale
- Layer-resolved electronic structure
- Minimum usable thickness for insulating MgO: 3 ML

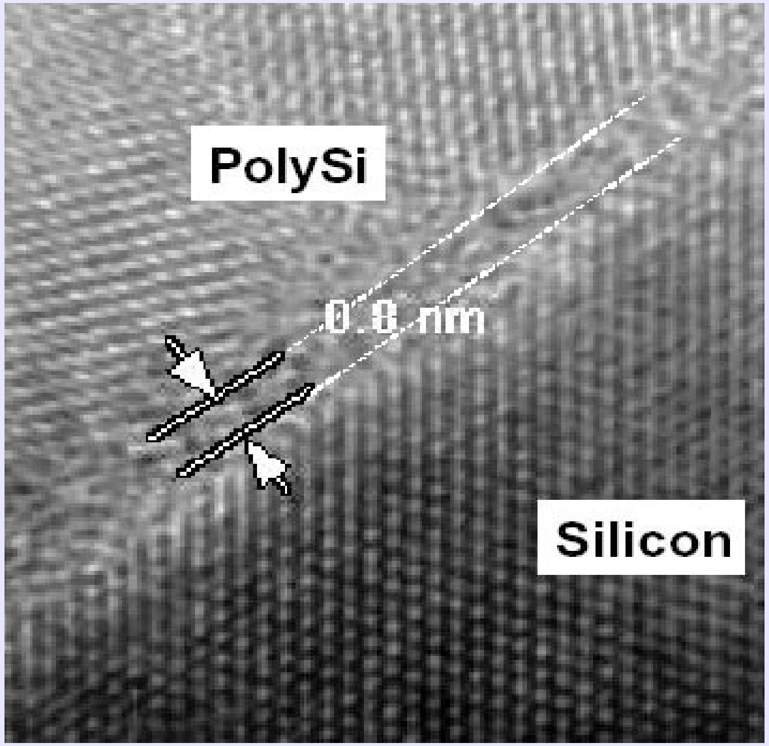
- **Control** of the number of dielectric layers on a metal substrate

↓

- **Tuning** of the electronic, magnetic, and chemical properties of the resulting surface

CMOS-transistor
with 0.8 nm gate - oxide thickness





intel.com/labs/ (2001)

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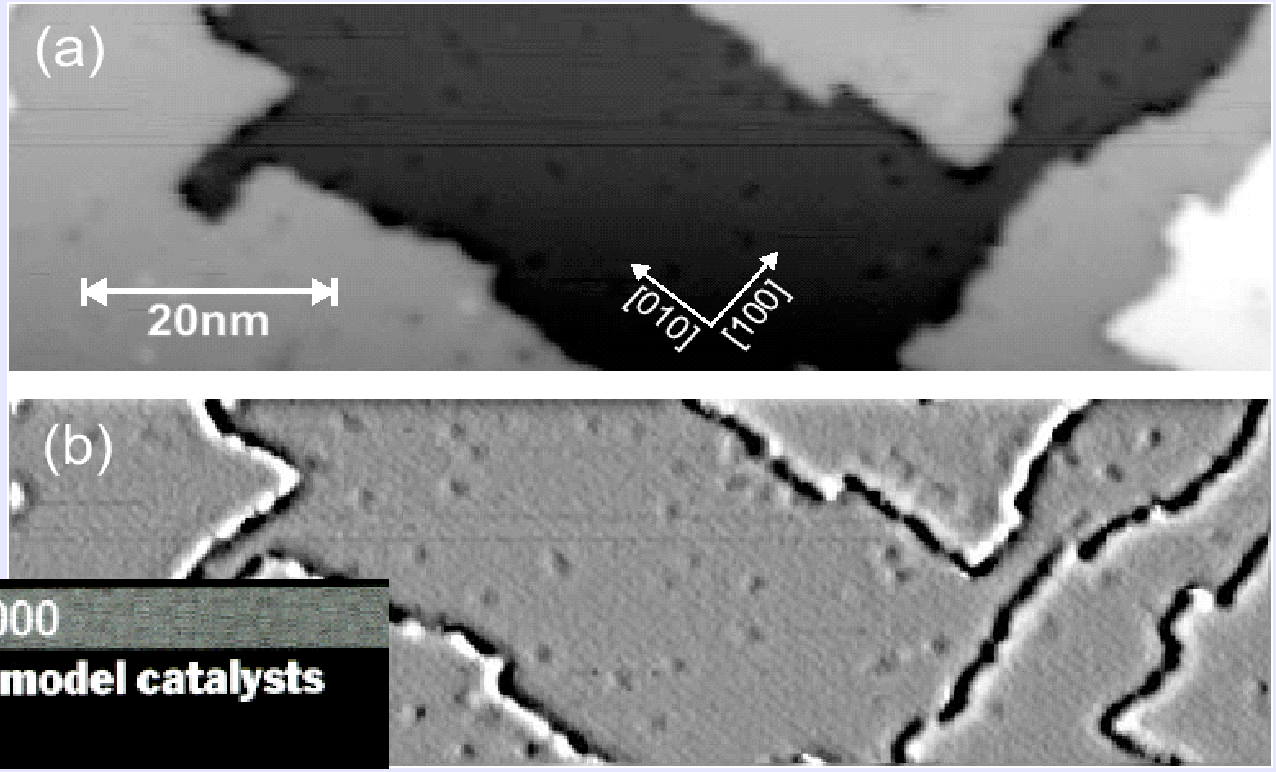
Applied Physics



Defect density < 0.1 %

Volume 33 Number 11 7 June 2000
Review article: Nanoassembled model catalysts
U Heiz and W-D Schneider

Atomic-scale imaging of insulating diamond through resonant electron injection

Kirill Bobrov, Andrew J. Mayne & Gérald Dujardin

Laboratoire de Photophysique Moléculaire, Bât. 210, Université Paris-Sud, 91405, Orsay, France

Nature **413**, 616 (2001)

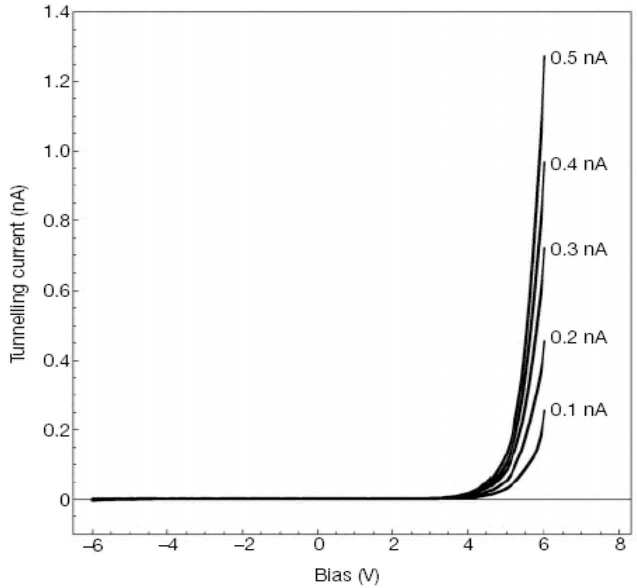


Figure 1 Current–voltage (*I*–*V*) spectroscopy of the clean C(100)–(2 × 1) surface as a function of tunnelling current. The *I*–*V* curves were recorded simultaneously with the scanning tunnelling microscope (STM) topography at $U_{bias} = +5.9$ eV. During normal imaging, the tunnel current (marked on the curve) is constant and gives an indication of the tip–sample separation. In *I*–*V* spectroscopy, the distance is fixed for each curve so that the current (*y* axis) varies as a function of *V* during the acquisition.

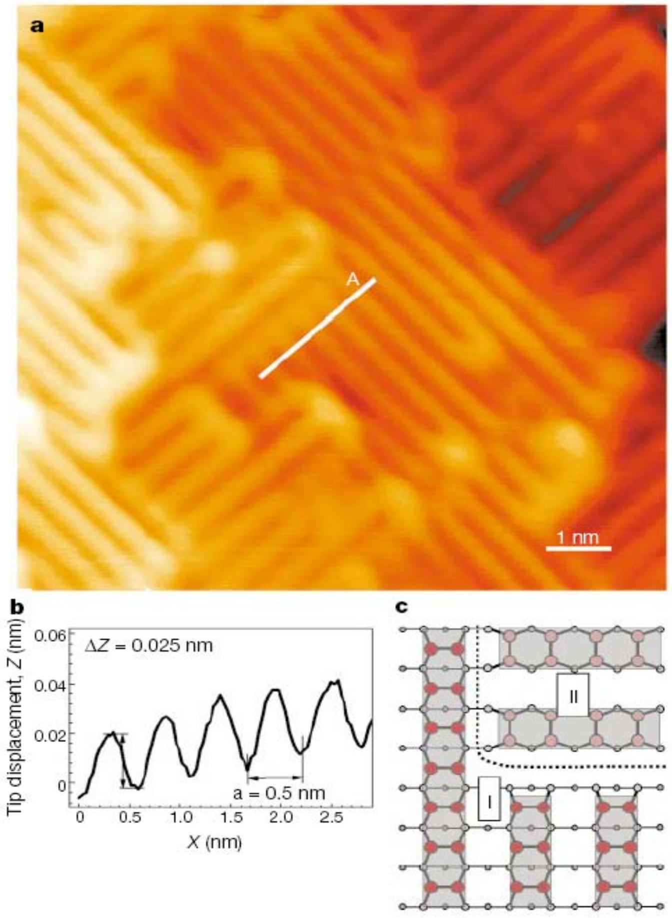


Figure 2 Clean diamond C(100)–(2×1) surface. **a**, The STM topography (10 nm × 10 nm) of the clean diamond surface recorded in the near-field emission regime ($U_{bias} = 5.9$ V, $I = 1.1$ nA). **b**, Height variation of the STM tip along the line A. **c**, Top-view of a monoatomic step on the two-domain (2×1) reconstructed surface. The coloured circles represent the carbon atoms belonging to the top four surface layers; the biggest circles represent the carbon–carbon dimers. The domains labelled as I and II represent the upper and lower terrace, respectively. The dimer rows are highlighted by shading, whereas the troughs between them are unfilled. The dashed line shows schematically the boundary between the domains.

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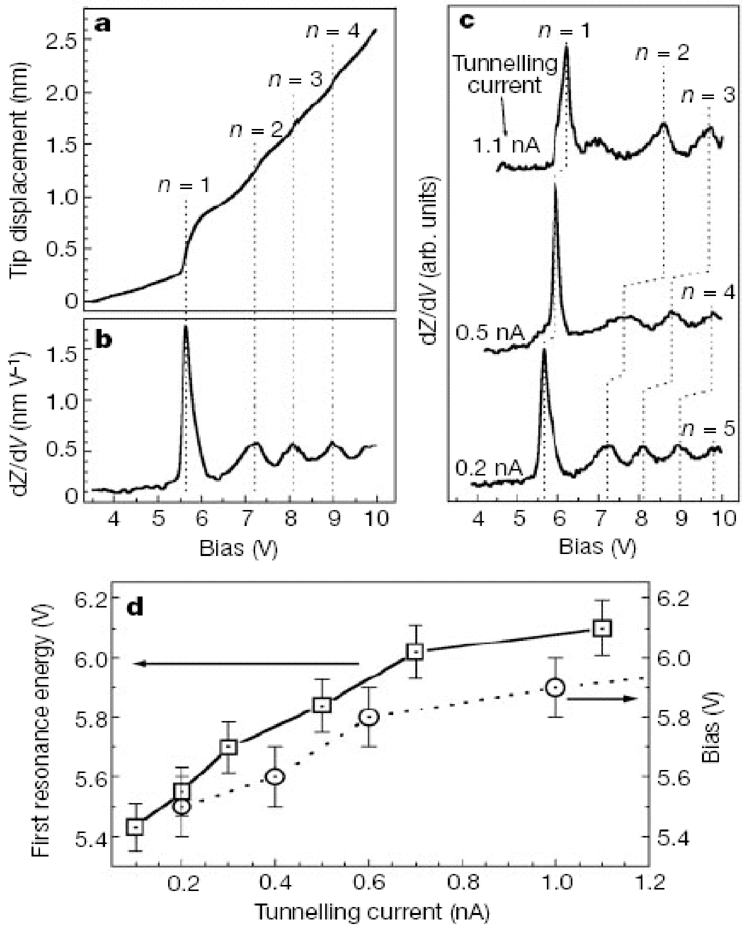


Figure 3 Distance–voltage z–V spectroscopy of the clean diamond C(100)–(2 × 1) surface. **a**, A typical spectroscopy curve recorded at $I = 0.2$ nA in the 3.5–10.0 V bias range; n is the resonance number. **b**, The numerical derivation dz/dV of the z–V spectroscopy curve shown in **a**. The energies of the barrier resonances (dotted lines) were taken at the maxima on the dz/dV curve. **c**, dz/dV curves as a function of the tunnelling current. The shift of the barrier resonance towards higher energies is shown by the dotted lines. **d**, The correlation between the bias at which atomically resolved STM topographies were obtained (dotted circles with error bars) and the first barrier resonance energy (dotted squares with error bars) as a function of the tunnelling current.

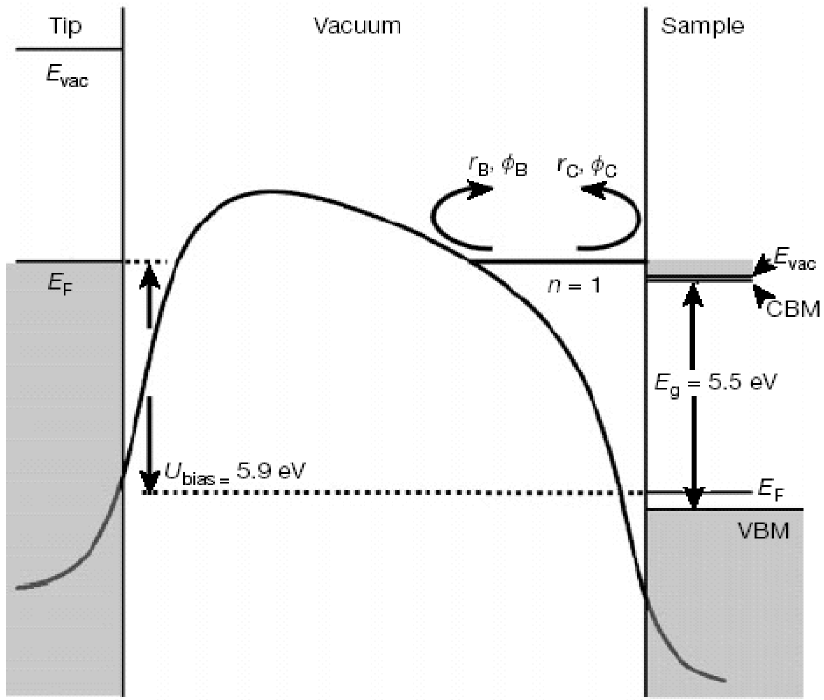


Figure 4 Potential well for the electrons scattered on the diamond surface. The potential barrier in the vacuum gap was constructed assuming a 10 Å tip–sample separation and a 0.4 V Å^{-1} electrostatic field in the vacuum gap. The actual shape of the potential barrier was obtained by a superposition of the electric field and the image potential of the surface, modified to include the surface potential contribution. For both the tip and the sample, the positions of the vacuum level, E_{vac}, and the Fermi level, E_F, are indicated. In addition, the surface gap E_g, the positions of the valence band maximum, VBM, and the conduction band minimum, CBM, are labelled. In the potential well, the reflection coefficients, r_B, r_C, and the dephasing, ϕ_B, ϕ_C, of the barrier and the diamond surface respectively, are noted at the first resonance, $n = 1$.

K. Bobrow et al., Nature **413**, 616 (2001)

Ultrathin dielectric layers: MgO, NaCl

- Model systems for wide band gap insulators
- Layer-resolved morphology on the atomic scale
- Layer-resolved electronic structure
- Minimum usable thickness for insulating MgO: 3 ML

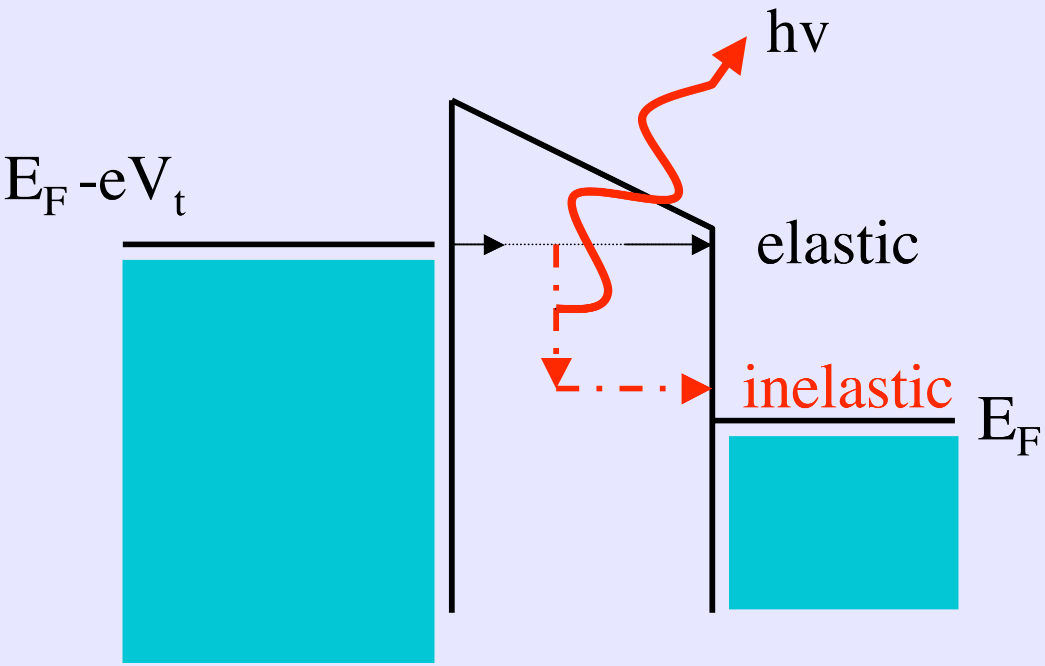
- **Control** of the number of dielectric layers on a metal substrate

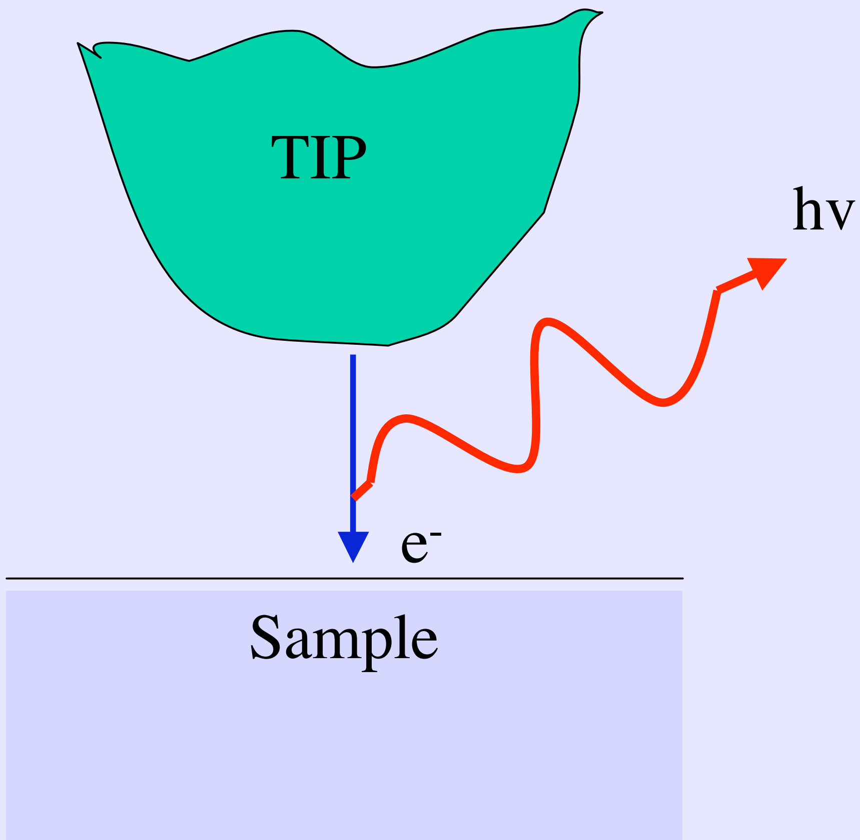
↓

- **Tuning** of the electronic, magnetic, and chemical properties of the resulting surface

Photonemission induced by an STM-tip

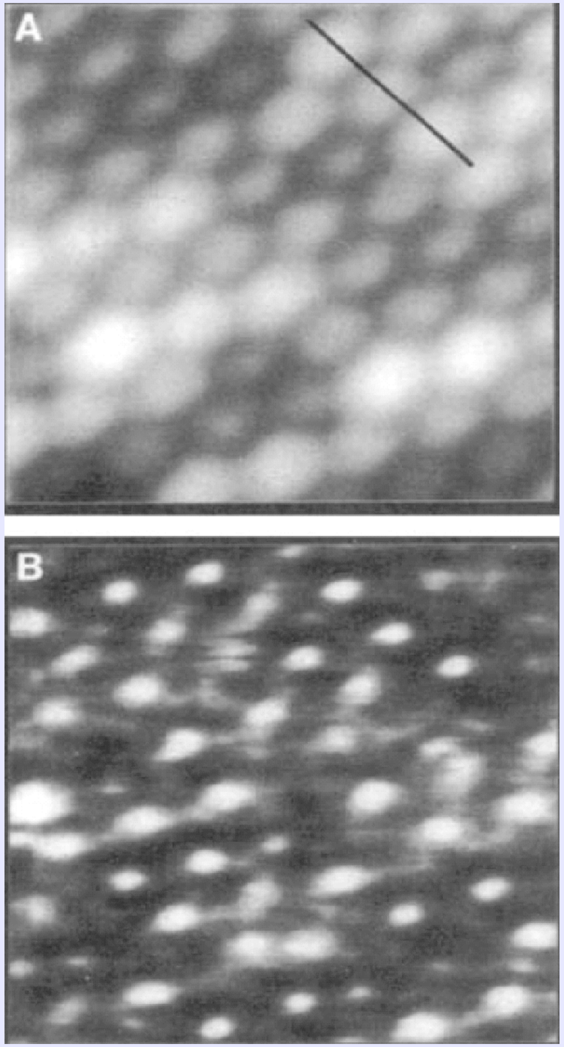
J. K. Gimzewski et al., Z. Phys. B 72, 497 (1988)

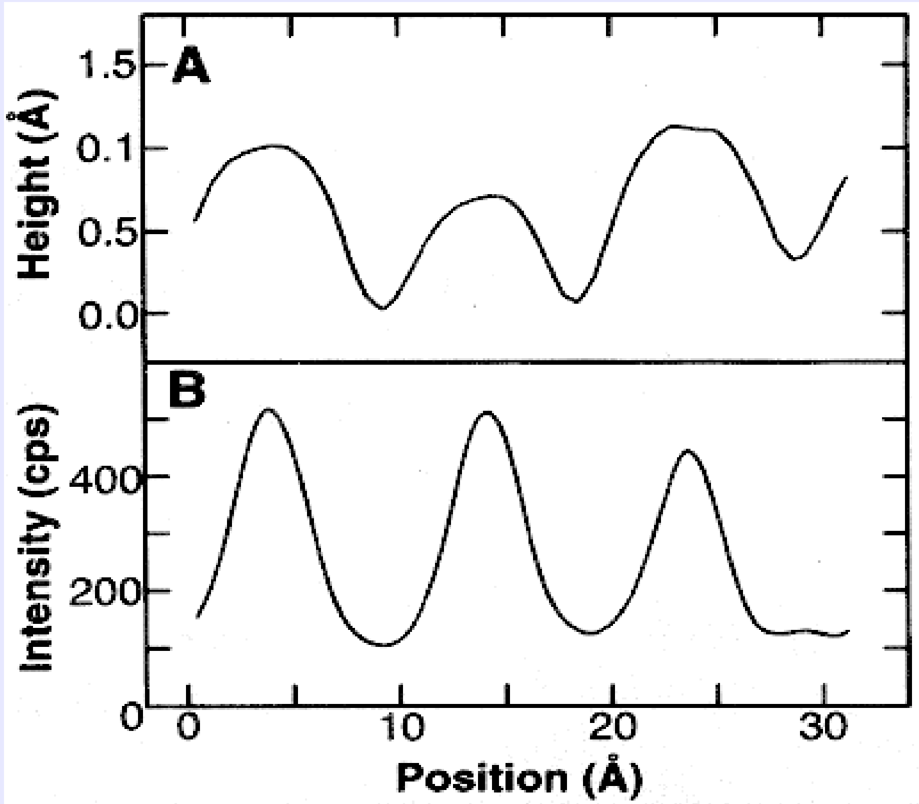




- Inelastic process
- $P \approx 10^{-4}$ photons/electron

Photon emission from C_{60} on Au(110)





R. Berndt et al., Science **262**, 1425 (1993)

Growth model of MgO(100)/Ag(100)

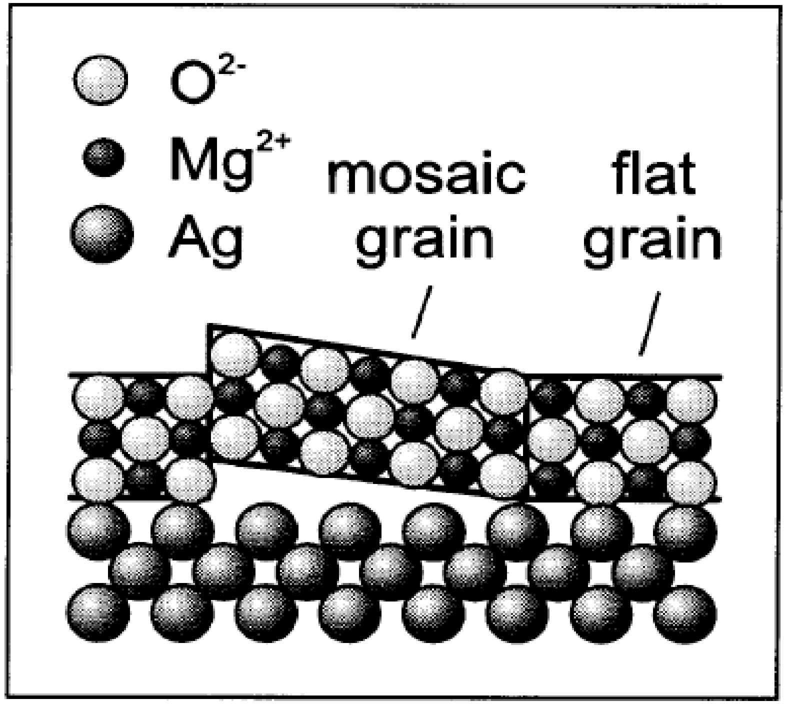
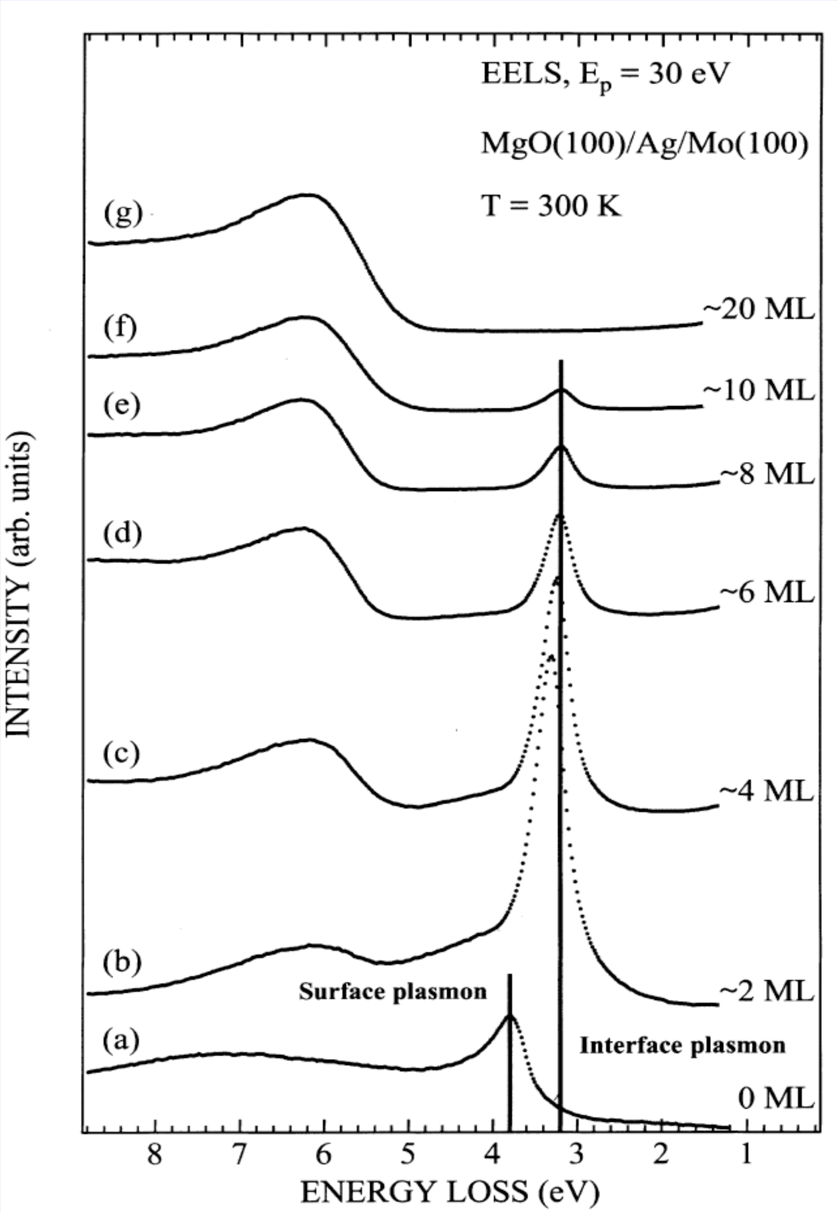


Fig. 3. Model of one misoriented tilted mosaic grain embedded into grains that are perfectly well aligned with respect to the substrate. At the grain boundaries, the configuration of the MgO molecules is almost identical to the bulk configuration. Within the mosaic, the lattice is slightly strained.

J. Wollschläger et al., Surf. Sci. **402 - 404**, 272 (1998)



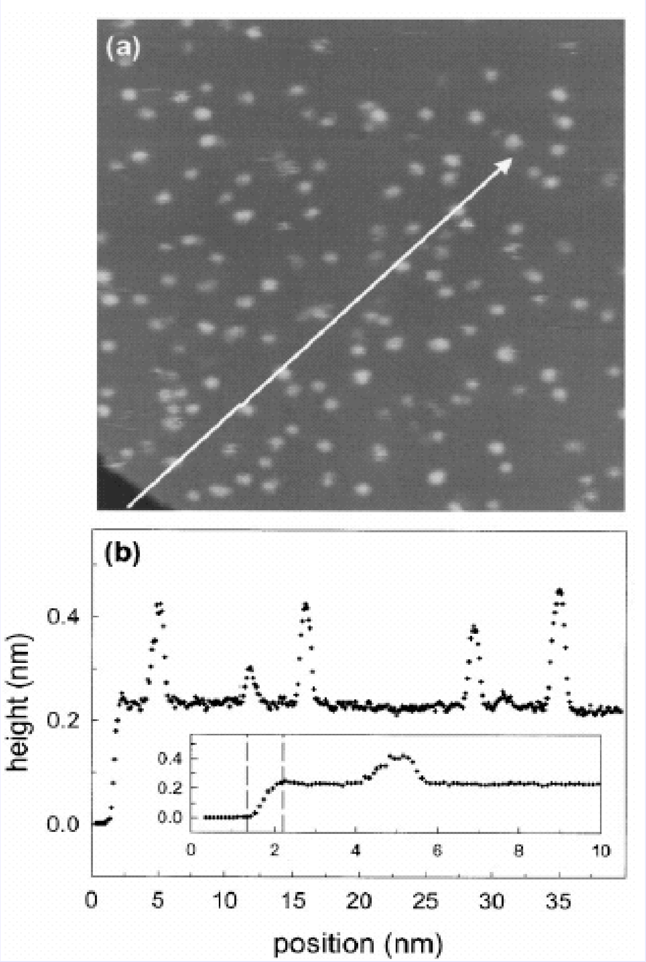
Ag - MgO interface plasmon

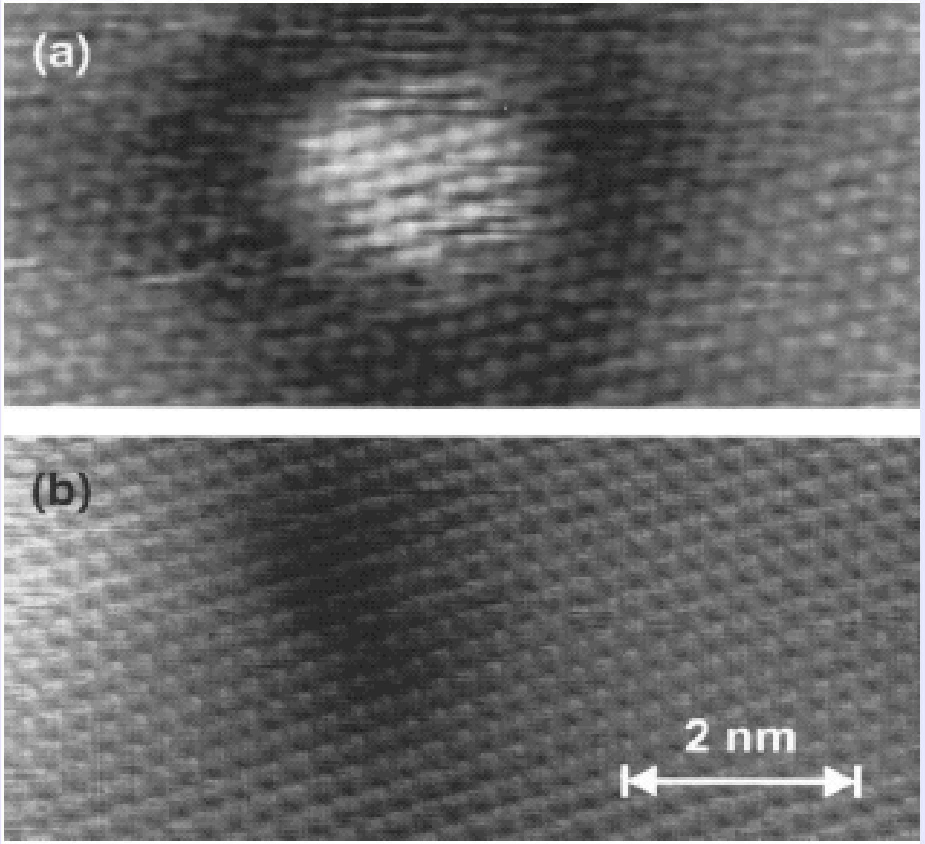
(F. Didier et al., Surf. Sci. 307 - 309, 587 (1994))

M.-H. . Schaffner et al., Surf. Sci. **417**, 159 (1998)

Now it’s really enough!

Si_{39} clusters on Ag(111) @ 50 K





S. Messerli et al., Surf. Sci. **465**, 331 (2000)