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Spring College on Computational Nanoscience

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From Supported Clusters to Nanocatalysis
Part III

Gianfranco PACCHIONI
Dipt. Scienze dei Materiali
Univ. Milano Bicocca
Italy

Spring College on Computational Nanoscience, Trieste, May 21, 2010

FROM SUPPORTED CLUSTERS TO NANOCATALYSIS

New phenomena: metal clusters on ultra-thin oxide films

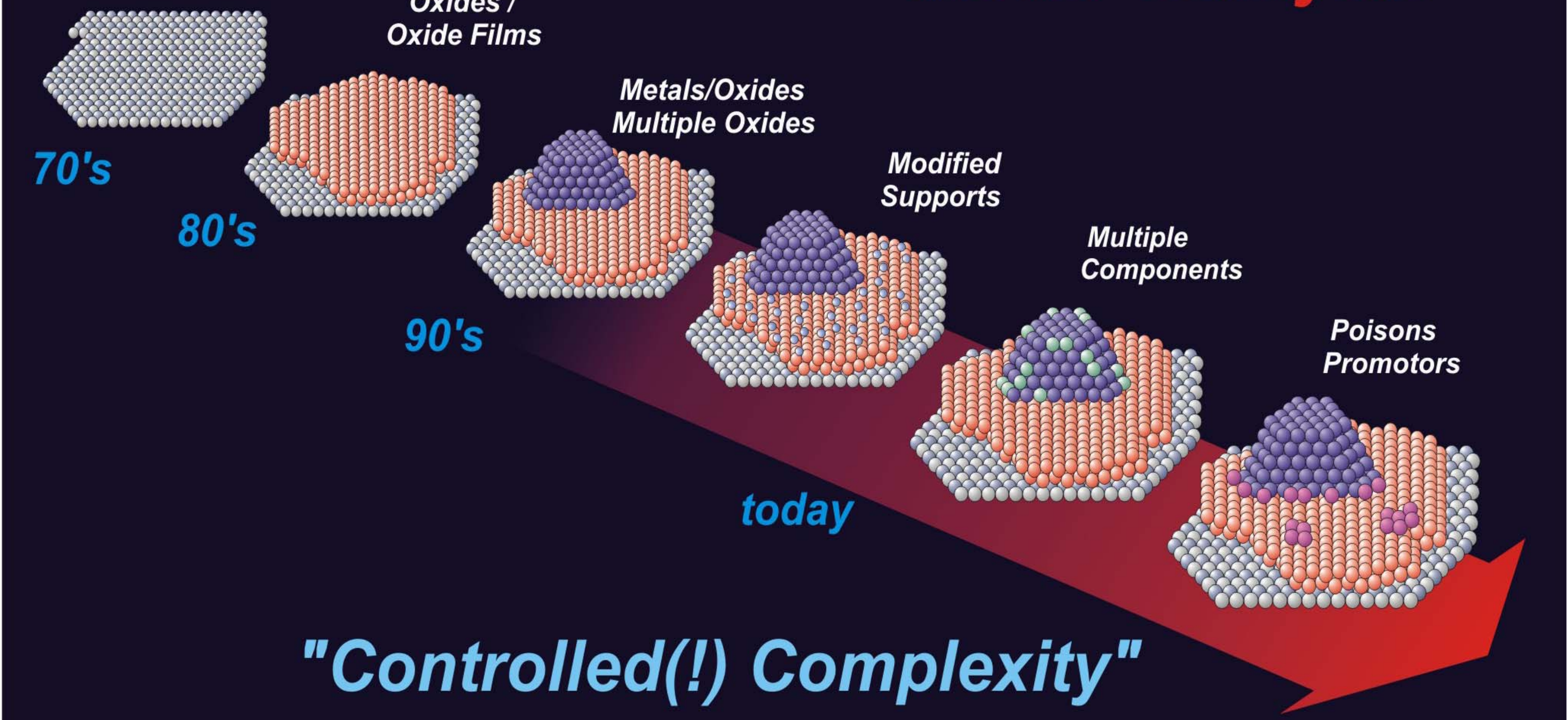
Gianfranco Pacchioni
Dipartimento di Scienza dei Materiali
Università Milano-Bicocca

Part I – Nanocatalysis: supported clusters, particles, and model systems

Part II - CO on MgO: lessons from 25 years of interplay between theory and experiment

Part III – New phenomena: metal clusters on ultra-thin oxide films

Supported Model Catalysts



Metal Single Crystals

70's

Oxides / Oxide Films

80's

Metals/Oxides Multiple Oxides

90's

Modified Supports

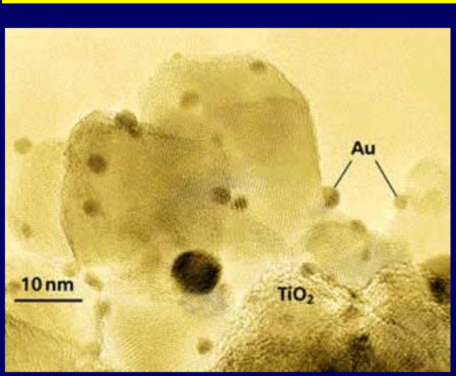
Multiple Components

today

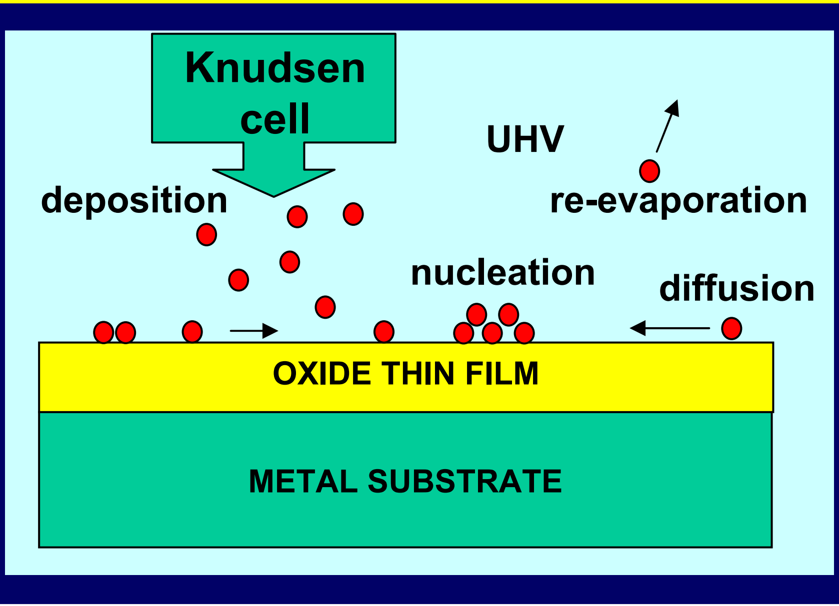
Poisons Promotors

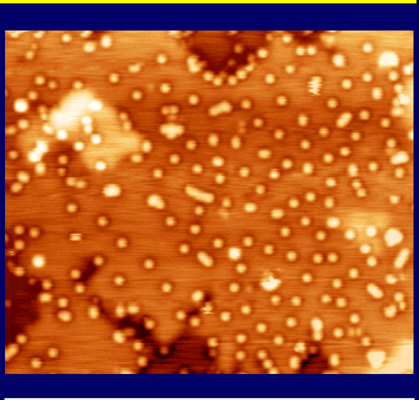
"Controlled(!) Complexity"

METAL CLUSTERS ON OXIDE SURFACES AND THIN FILMS



Real system: Au nanocatalyst on TiO_2

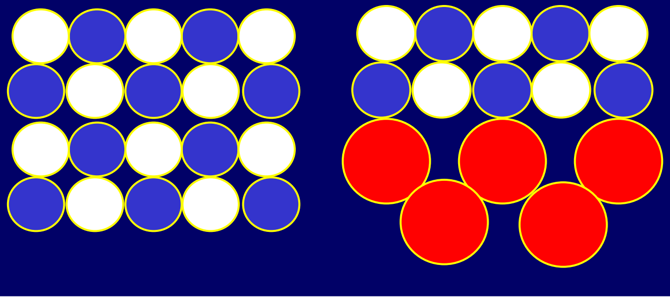




Model system: Au nanoclusters on MgO/Ag(100)

thin oxide films (<10 layers) grown on a metal substrate in UHV allow use of STM, electron spectroscopies, etc. Full characterization of oxide substrate

Clusters produced from metal vapor deposition (self-assembling)



Bulk oxides versus thin films: same behavior? Strain in epitaxial films - Oscillation of properties with number of layers - Bonding at metal-oxide interface, etc.

ATOMS AND NANOPARTICLES ON OXIDE ULTRA-THIN FILMS (<1 nm)

Supercell calculations

Plane wave basis set

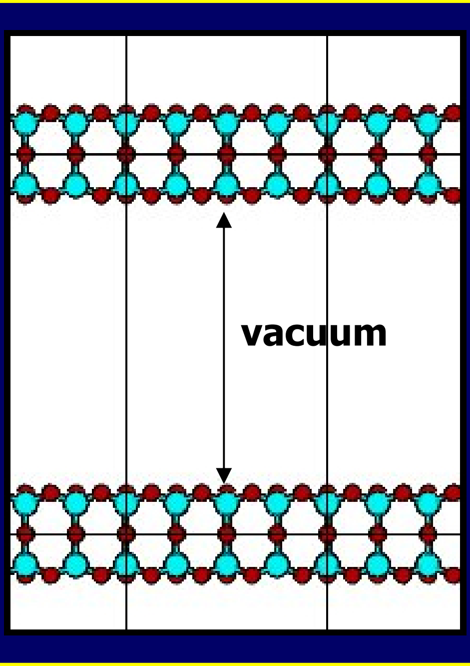
Pseudopotentials + Projector Augmented Wave (PAW, Blöchl)

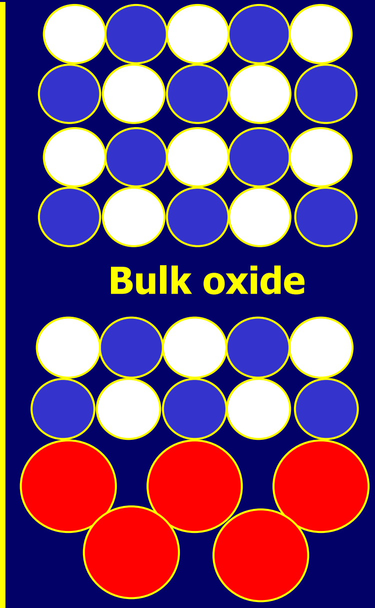
Perdew-Wang GGA exchange-correlation functional (PW91)

1-5 oxide layers, >10 Å vacuum

large unit cells, ≈100 atoms/cell

VASP (G. Kresse, Vienna)





HJ Freund

M Heyde

N Nilius

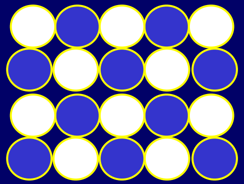
T Risse

M Sterrer

Shaikutdinov

Fritz-Haber Institut der Max Planck Gesellshaft, Berlin

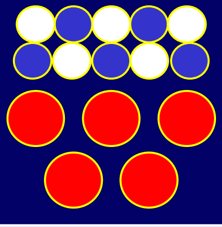
Pd atoms adsorbed on MgO and MgO/Mo(100)



Pd/MgO(100)

	on-top O		on-top Mg	
	E(eV)	r, Å	E(eV)	r, Å
1L	1.87	2.03	0.68	2.49
2L	1.50	2.05	0.58	2.54
3L	1.53	2.05	0.58	2.54
4L	1.52	2.05	0.58	2.54

- Unsupported MgO films – results converged after three layers (3L)
- Adsorption on O preferred over adsorption on Mg by a factor 3



Pd/MgO/Mo(100)

	on-top O		on-top Mg	
	E(eV)	r, Å	E(eV)	r, Å
1L	1.52	2.15	1.06	2.49
2L	1.69	2.11	0.99	2.55
3L	1.55	2.07	0.80	2.57
4L	1.54	2.07	0.73	2.57

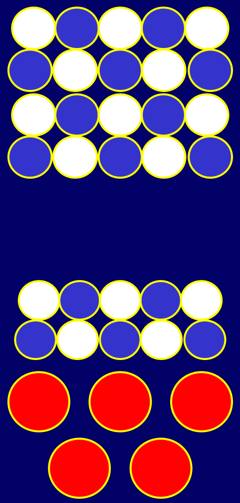
- Supported MgO films on Mo(100) - results converged after 4L
- MgO(100) and MgO/Mo(100): similar bonding propertes

Au atoms adsorbed on MgO and MgO/Mo(100)

Au/MgO(100)				
	on-top O		on-top Mg	
	E(eV)	r, Å	E(eV)	r, Å
1L	1.35	2.24	0.63	2.63
2L	0.98	2.24	0.48	2.69
3L	1.01	2.24	0.49	2.70
4L	1.01	2.24	0.49	2.70

Au/MgO/Mo(100)				
	on-top O		on-top Mg	
	E(eV)	r, Å	E(eV)	r, Å
1L	2.00	2.68	2.27	2.55
2L	2.06	2.76	2.21	2.58
3L	1.64	2.76	1.87	2.57
4L	1.42	2.70	1.61	2.61
5L	1.29	2.63	1.44	2.64

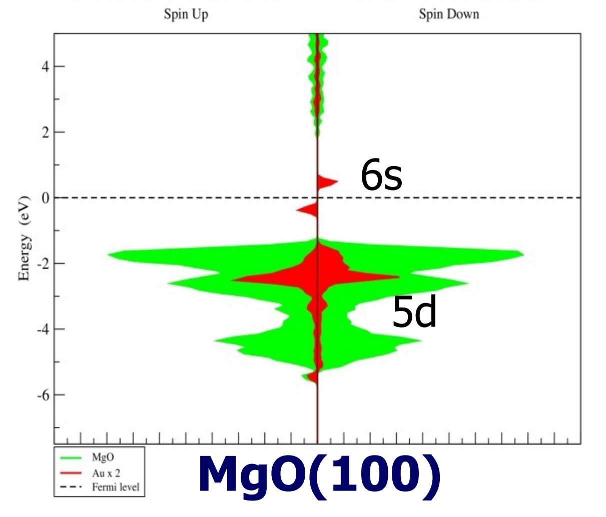
- **Unsupported MgO films – results converged after three layers (3L)**
- **Adsorption on O preferred over Mg**
- **Au-MgO bonding weaker than Pd-MgO**



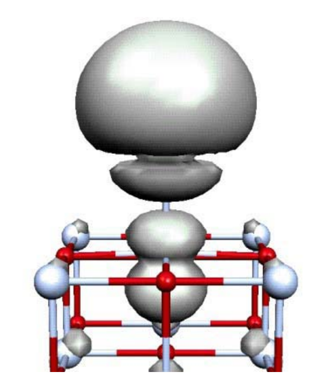
- **Supported MgO films - even after 5L of MgO on Mo(100) results not fully converged**
- **Adsorption on Mg preferred over adsorption on O !**
- **Adsorption on MgO/Mo very different from MgO(100)**

WHY IS Au DIFFERENT FROM Pd?

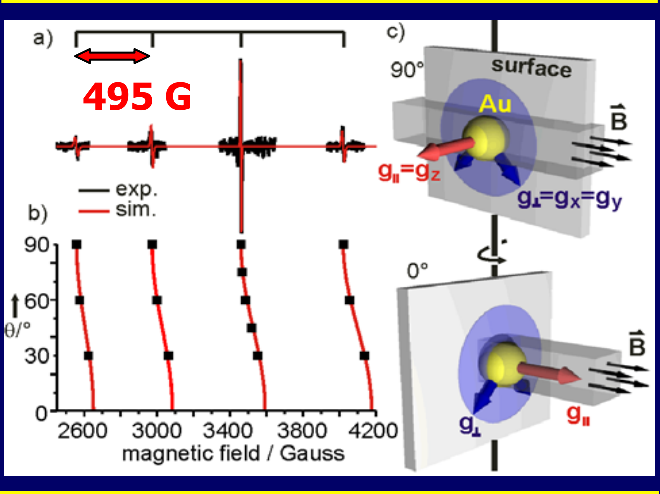
Au ATOM ON BULK MgO(100) SURFACE



- **Au 6s level: α component filled, β component empty**
- **Au $(6s)^1$ is paramagnetic**
- **Proven by Electron Paramagnetic Resonance (EPR)**



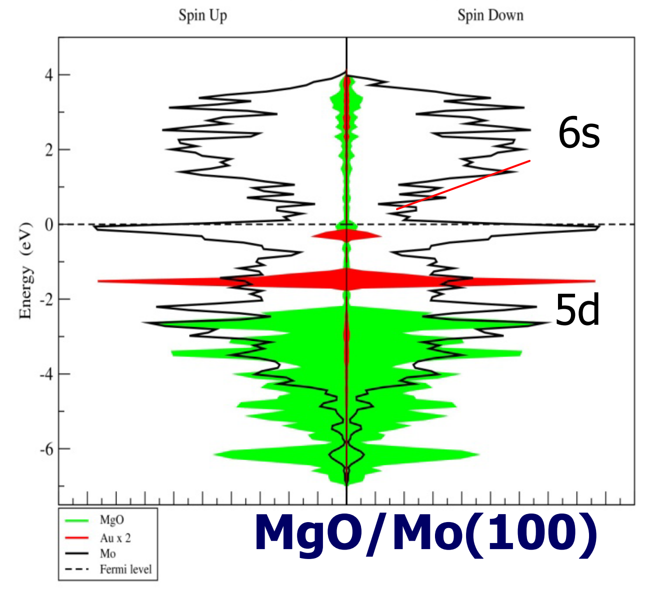
Spin density on Au = 0.8



On bulk MgO the Au atom is neutral

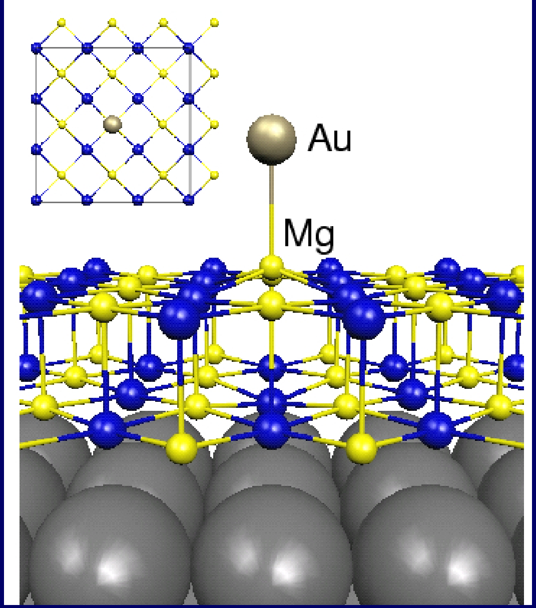
Yulikov, Sterrer, Heyde, Rust, Risse, Freund, GP, Scagnelli, PRL 96, 146804 (2006)

Au ATOM ON Au/MgO/Mo(100) FILMS



Au/MgO/metal

- **Au 6s level is below E_F (Mo)**
- **Net charge transfer makes Au negatively charged, Au^-**

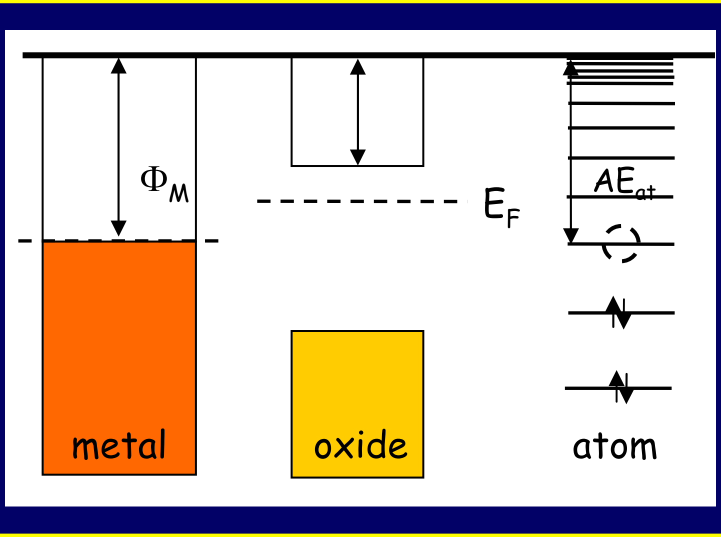


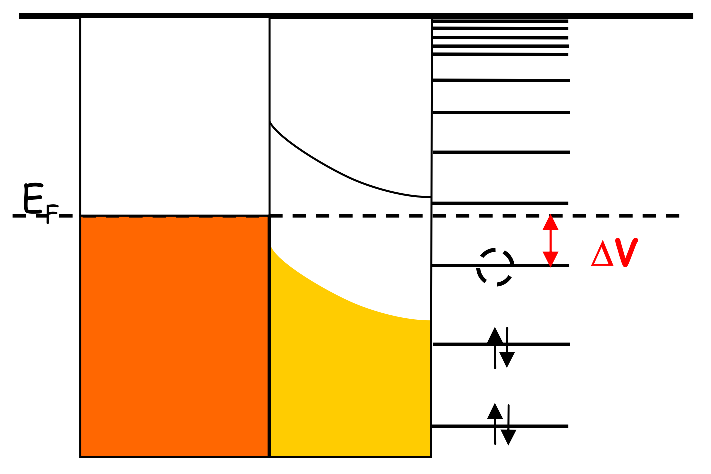
MgO/Mo(100) or MgO/Ag(100): Au is a full anion
Different behavior of Pd atom (always neutral)

GP, Giordano, Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005)

Giordano, GP, Phys. Chem. Chem. Phys. 8, 3335 (2006)

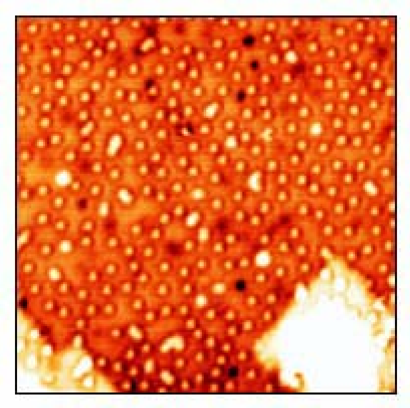
CHARGING OF ADSORBATES ON OXIDE THIN FILMS

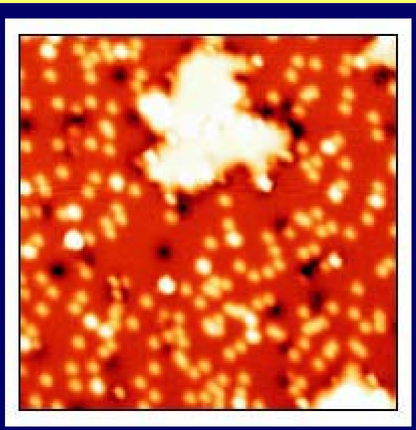


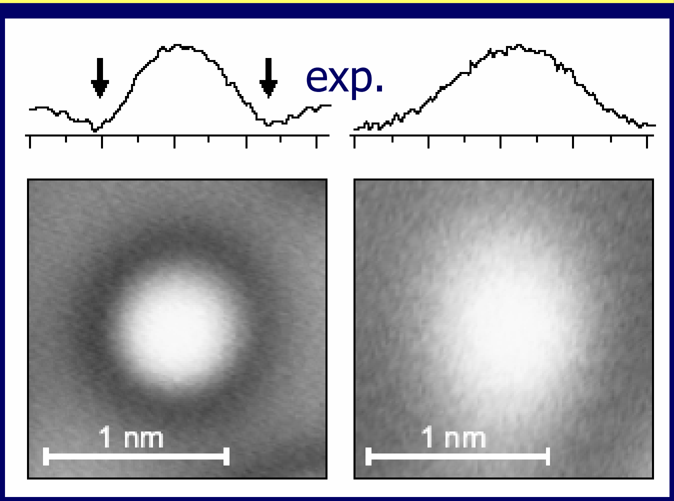


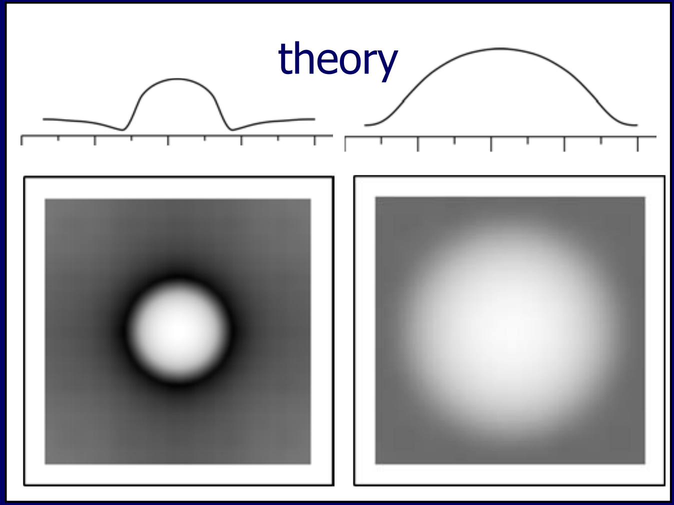
- metal clusters, molecules or defects on MgO/metal thin films: empty levels may fall below (above) metal E_F
- charge flow through a dielectric barrier not possible for thick insulating films but possible by direct tunneling in ultrathin films (< 1 nm)

Au/MgO(3L)/Ag(100): charging proven by STM

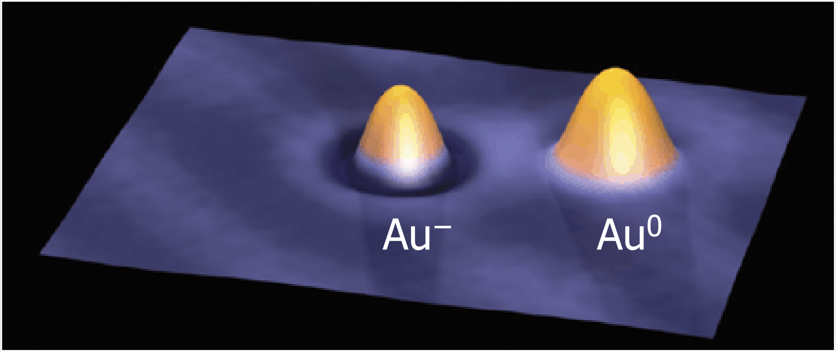

Au/MgO(3L)/Ag(100)


Pd/MgO(3L)/Ag(100)





Au atom Pd atom



Au atoms on NaCl/Cu(111). Au^- shows typical “sombrero” shape (charged state)

Repp et al. *Science* 305, 493, (2004)

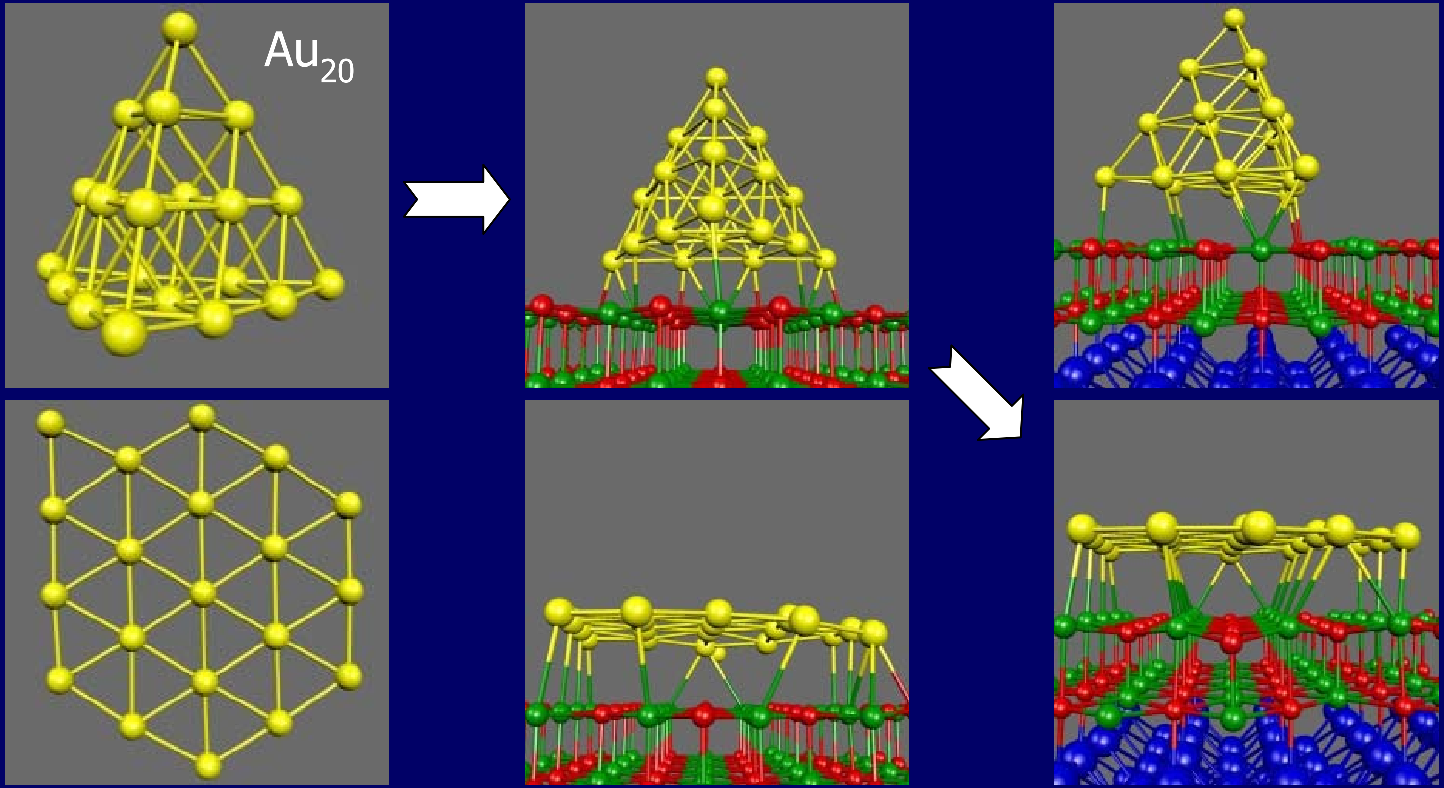
Sterrer, Risse, Martinez, Giordano, Heyde, Rust, GP, Freund, Phys. Rev. Lett. 98, 096107 (2007)

Au_n clusters: gas-phase ⇒ MgO(100) ⇒ MgO/Mo(100)

Gas-phase | MgO(100) | MgO/Mo(100)

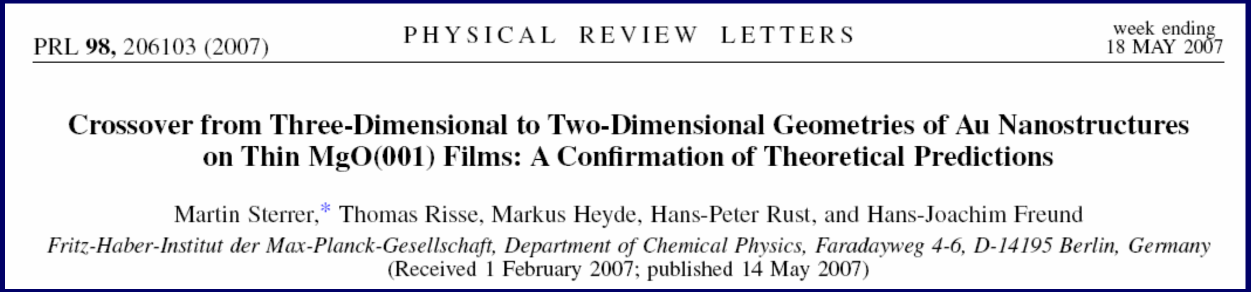
3D

2D



Gas-phase	MgO(100)	MgO/Mo(100)
$E_{3D} > E_{2D}$ ΔE **= 1.9 eV**	$E_{3D} > E_{2D}$ $\Delta E =$ **1.2** eV	$E_{2D} > E_{3D}$ $\Delta E = -$**3.3** eV

Ricci, Bongiorno, GP, Landman, Phys. Rev. Lett. 97, 036106 (2006)

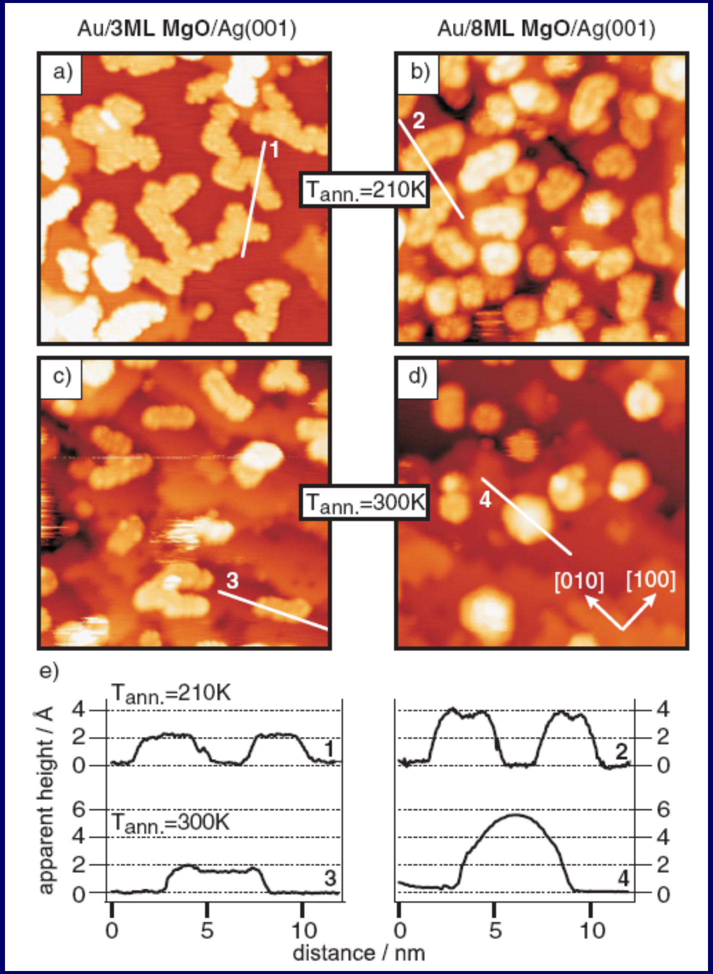


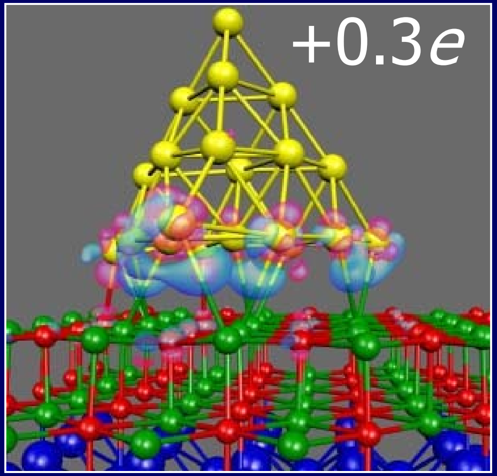
PRL **98,** 206103 (2007)
PHYSICAL REVIEW LETTERS
week ending
18 MAY 2007

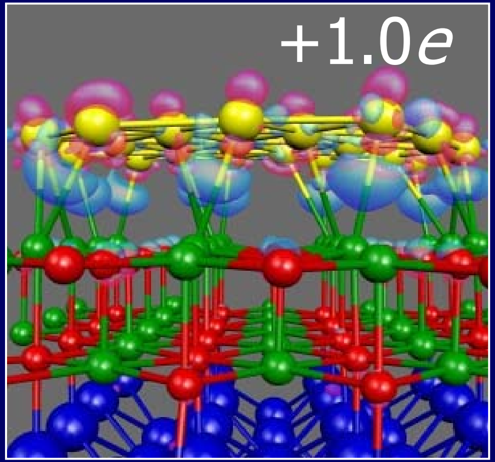
Crossover from Three-Dimensional to Two-Dimensional Geometries of Au Nanostructures on Thin MgO(001) Films: A Confirmation of Theoretical Predictions

Martin Sterrer,* Thomas Risse, Markus Heyde, Hans-Peter Rust, and Hans-Joachim Freund
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, D-14195 Berlin, Germany

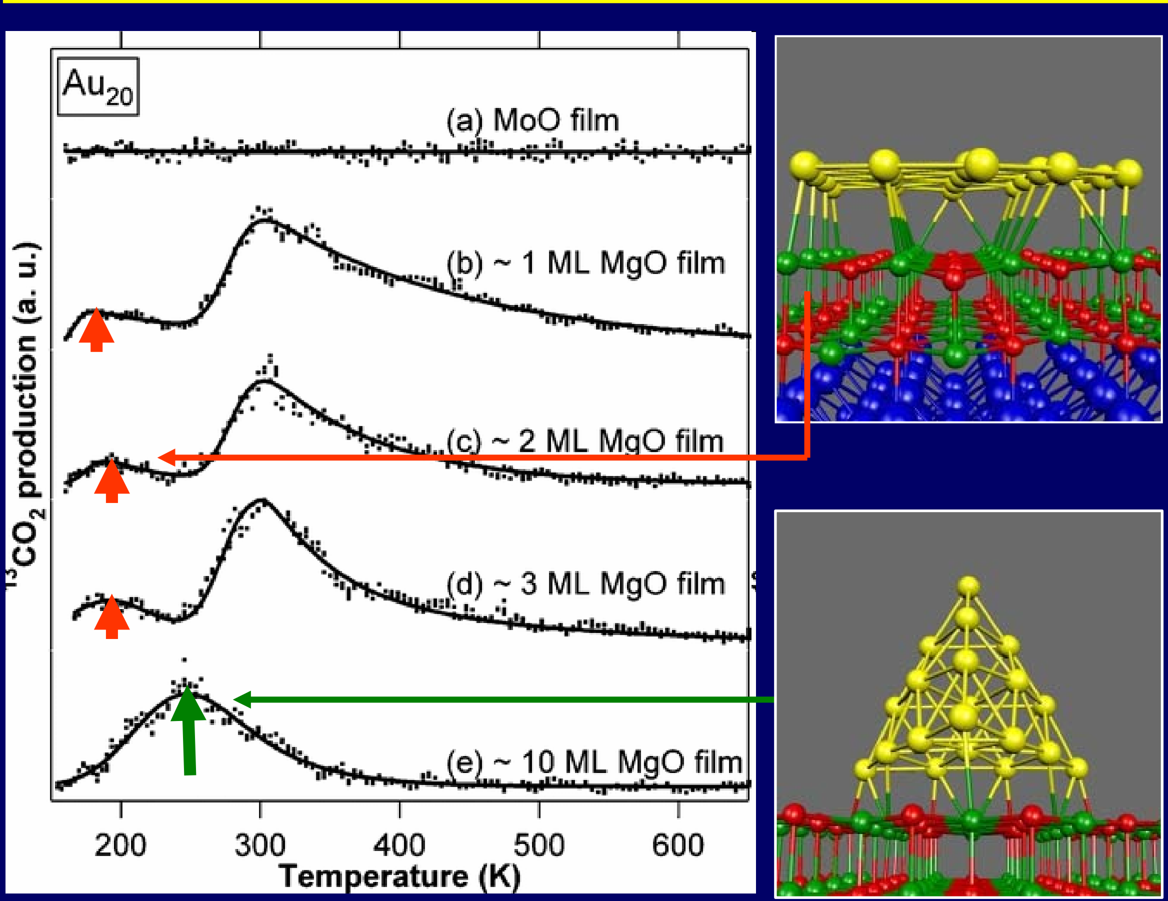
(Received 1 February 2007; published 14 May 2007)

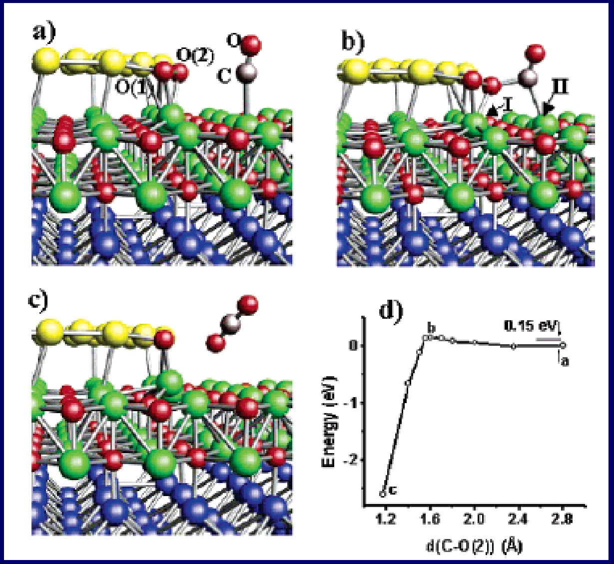






NANOCATALYSIS: Au ON MgO/Mo FILMS





Au_{20}/MgO/Mo: Au_{20} 2D more active than 3D in CO oxidation (DFT)

Zhang, Yoon, Landman J. Am. Chem. Soc. 129, 2228, 2007

- **Au clusters on thick (10ML) and thin (1-3 ML) MgO/Mo films: different activity in CO oxidation**
- **Thin films: CO_2 forms at 180 K; thick films: CO_2 forms at 250 K (TPD)**
- **Different reaction mechanism**

Harding, Habibpour, Kunz, Farnbacher, Heiz, Yoon, Landman J. Am. Chem. Soc. 131, 538, 2009

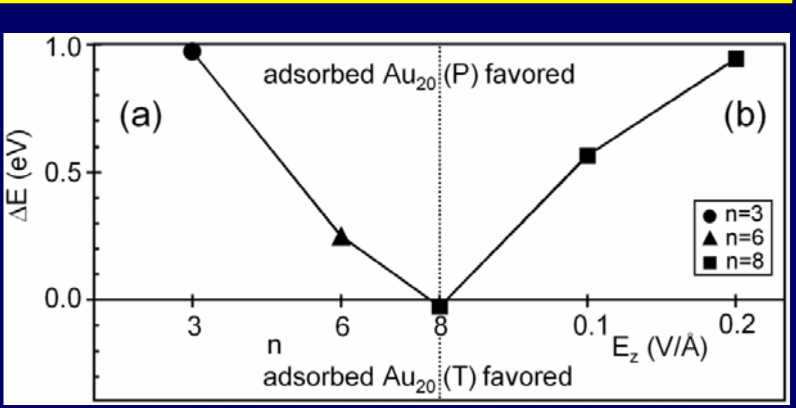
ELECTRIC FIELD EFFECT ON THE SHAPE OF GOLD NANOPARTICLES ON MgO/Ag(100) FILMS

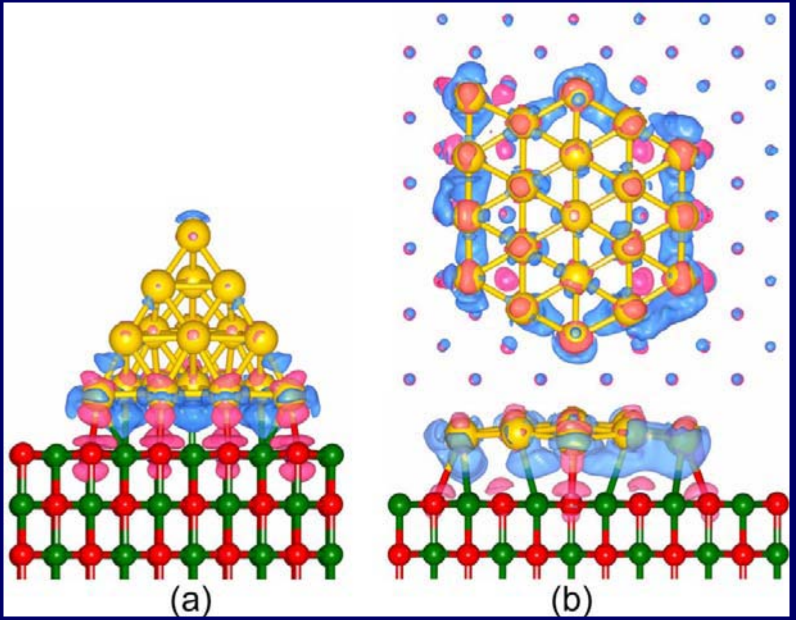
- **MgO(8 layers) /Ag(100): Au_{20} 3D (tetrahedral) is preferred (as for bulk MgO)**

- **Apply an electric field of 1 V/nm: Au_{20} 2D (planar) becomes more stable**

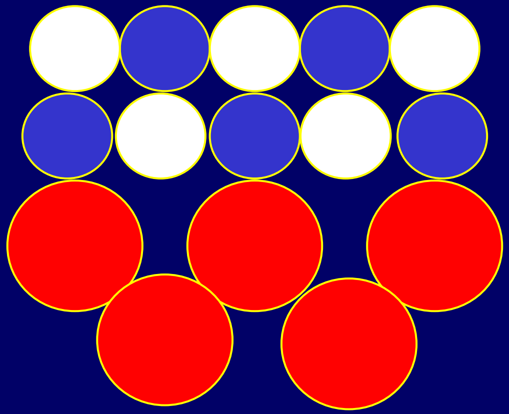
- **Reason: electric field moves charge from the Ag support to the interface resulting in stronger adhesion of 2D structure**

Yoon and Landman, Phys. Rev. Lett. 100, 056102, 2008

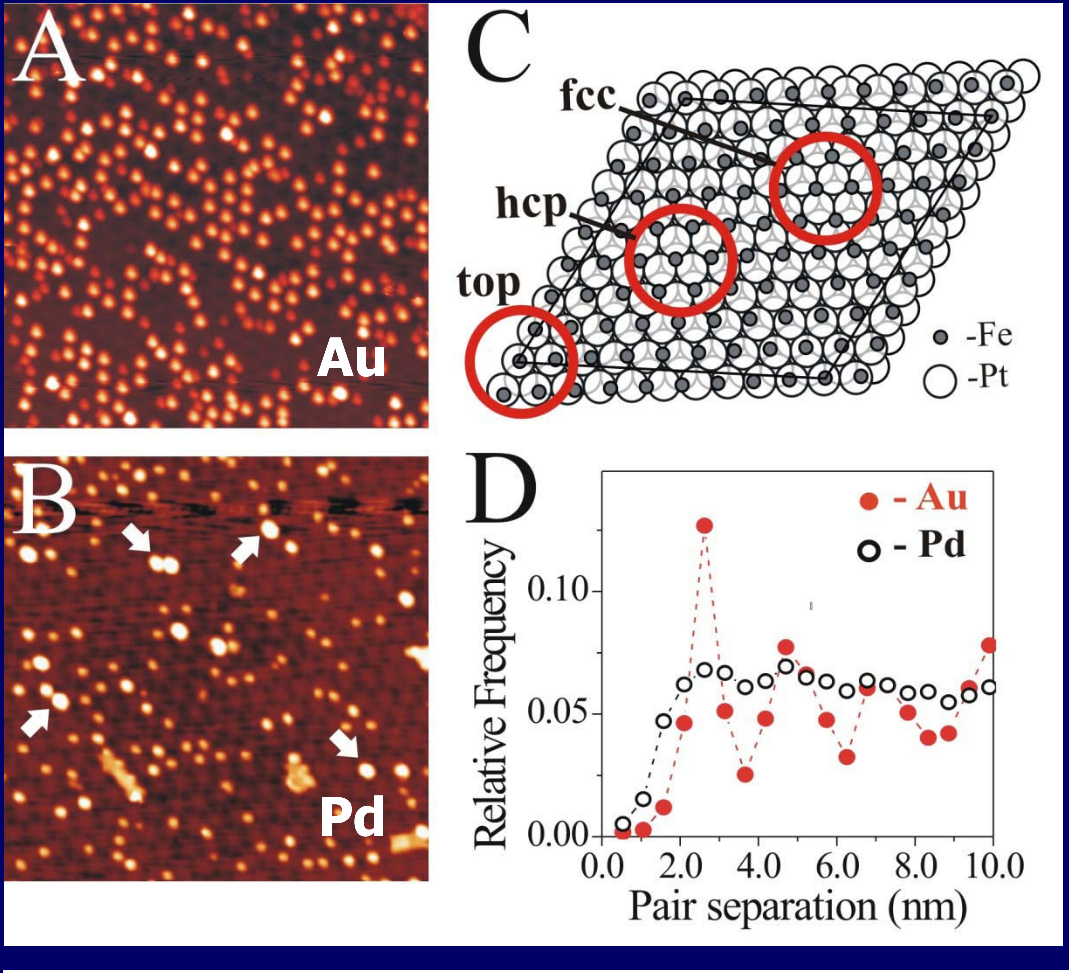




IS CHARGING OF METALS ON ULTRA-THIN FILMS UNIVERSAL?



Au AND Pd ATOMS ON FeO/Pt(111)



- **FeO/Pt(111): Au atoms deposited at 10K: adsorption on hcp domains**
- **Self-organization of adsorbed Au atoms**
- **Not observed for Pd atoms (random distribution)**
- **Similar as for Au and Pd on MgO/Ag(100)**

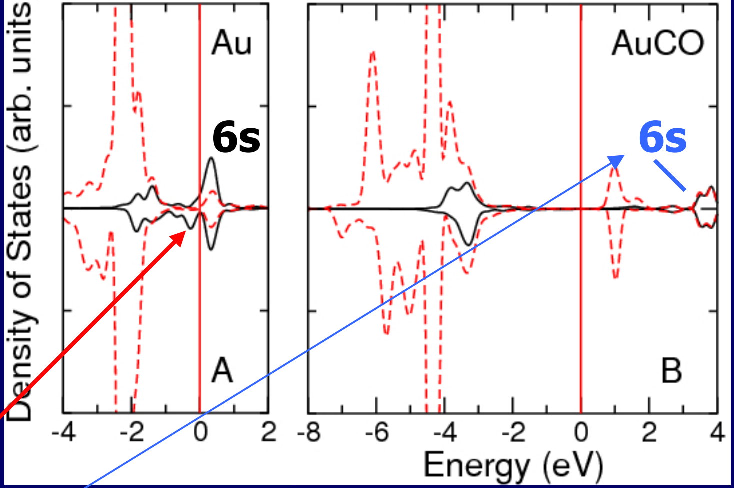
Are Au atoms negatively charged as on MgO/Ag(100)?

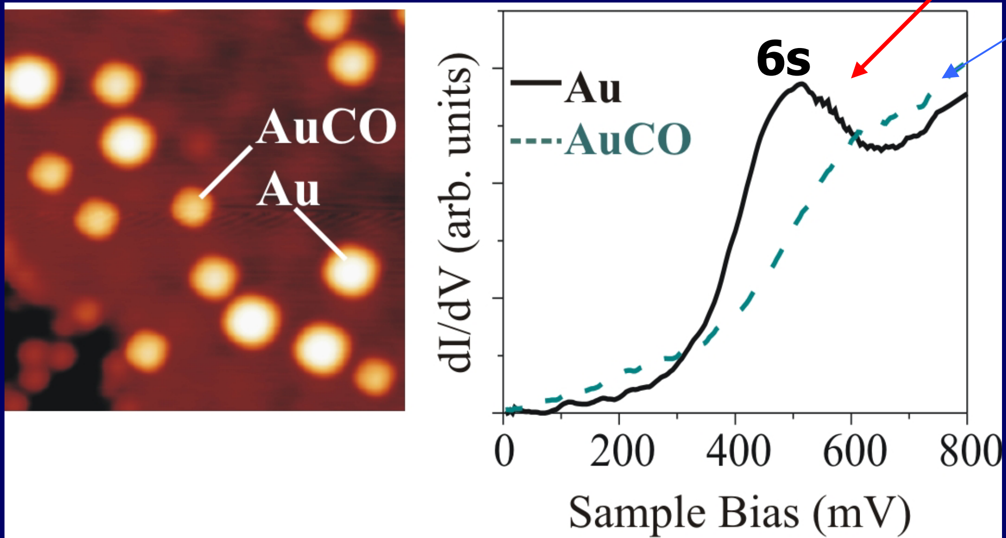
Au ATOMS ON FeO/Pt(111)

- **DFT calculations: Au atoms in hcp domains (adsorption on-top of O): 6s level above E_F (empty)**

- **Au is formally Au^+**

- **Consistent with dI/dV curves (empty state on Au 0.5 eV above E_F)**



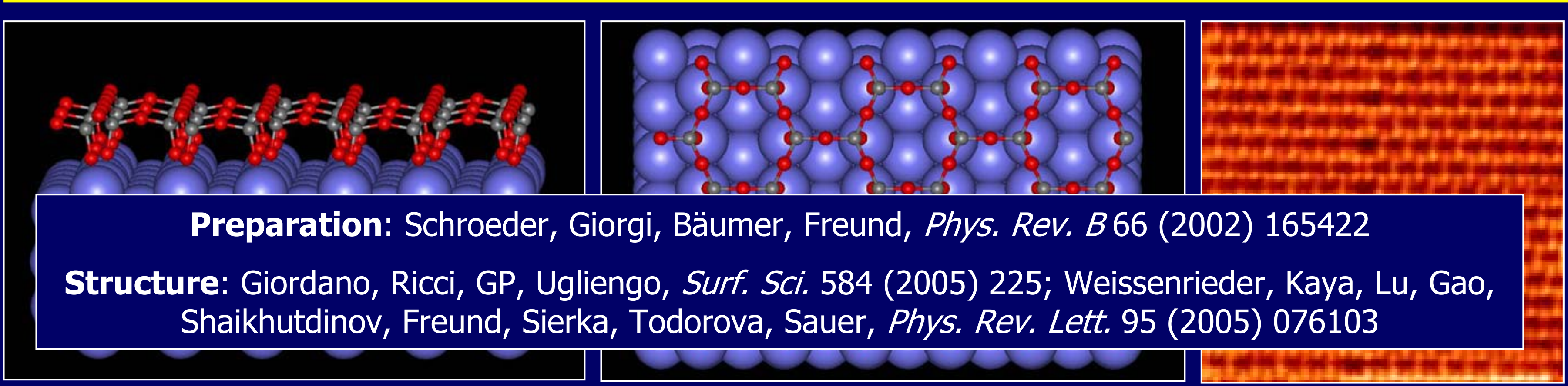


- **Additional proof: CO adsorption shifts empty 6s state to higher energies**
- **CO forms strong bond with Au (typical of $AuCO^+$ complexes)**

Au is positively charged!

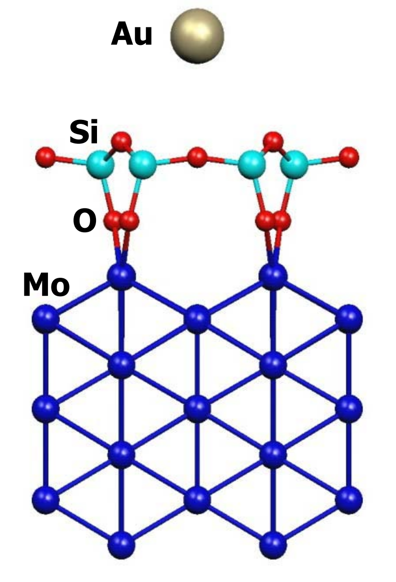
Giordano, GP, Goniakowski, Nilius, Rienks, Freund,
Phys. Rev. Lett. 101, 026102 (2008)

Au ATOMS ON SiO_2/Mo(112)



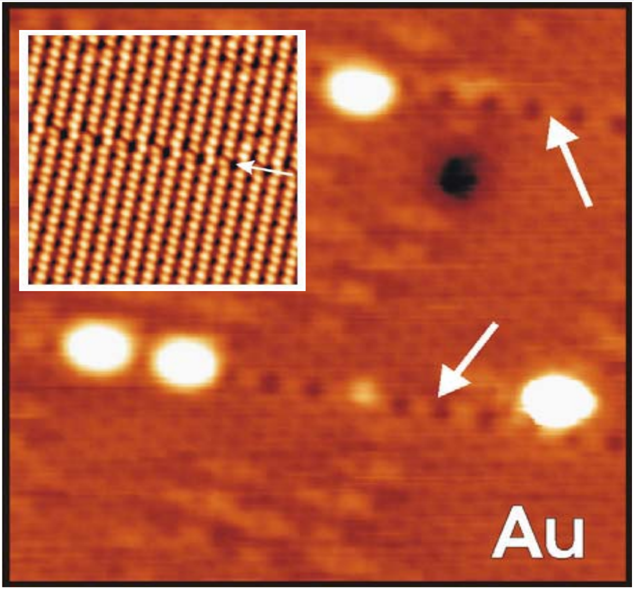
Preparation: Schroeder, Giorgi, Bäumer, Freund, *Phys. Rev. B* 66 (2002) 165422

Structure: Giordano, Ricci, GP, Ugliengo, *Surf. Sci.* 584 (2005) 225; Weissenrieder, Kaya, Lu, Gao, Shaikhutdinov, Freund, Sierka, Todorova, Sauer, *Phys. Rev. Lett.* 95 (2005) 076103



- Au atom very weakly adsorbed on all sites ($D_e < 0.1$ eV)
- DOS curves show that Au keeps $6s^1$ configuration

Au is neutral, NO CHARGE TRANSFER!



Martinez, Giordano, GP, J. Phys. Chem. B 110, 17015 (2006)

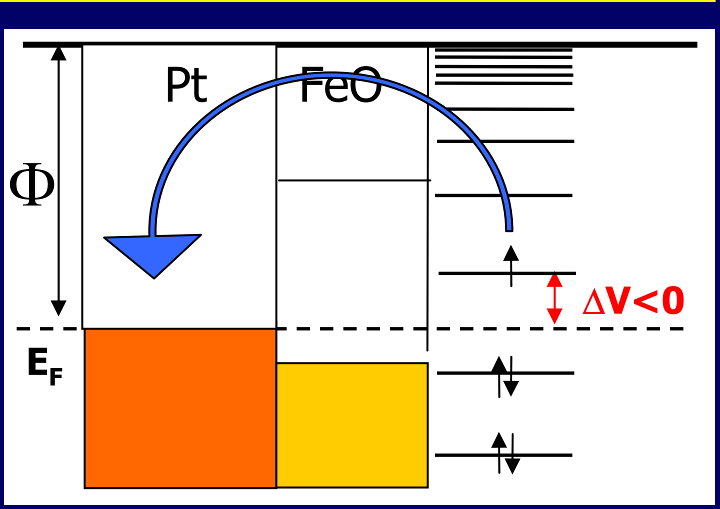
Au ATOMS ON OXIDE THIN FILMS

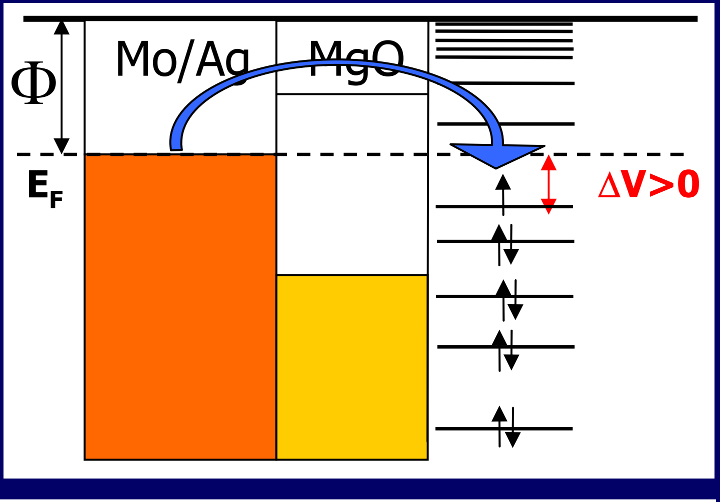
MgO/Ag(100)	Au is negatively charged, Au^-
FeO/Pt(111)	Au is positively charged, Au^+
SiO_2/Mo(112)	Au is neutral, Au^0

Charge transfer is not universal. Why?

Oxide films on metal supports: role of work function

Oxide/Metal	$\phi_{O/M}$ eV	ϕ_M eV
FeO/Pt(111)	6.0-5.6	5.8
TiO_2/Pt(111)	5.6	5.8
SiO_2/Mo(112)	4.9	4.2
TiO_3/Mo(112)	4.6	4.2
NiO/Ag(100)	3.9	4.3
MgO/Ag(100)	3.3	4.3
BaO/Au(100)	2.3	5.1
MgO/Mo(100)	2.1	4.2
BaO/Ag(100)	2.0	4.3
BaO/Pd(100)	2.0	5.2





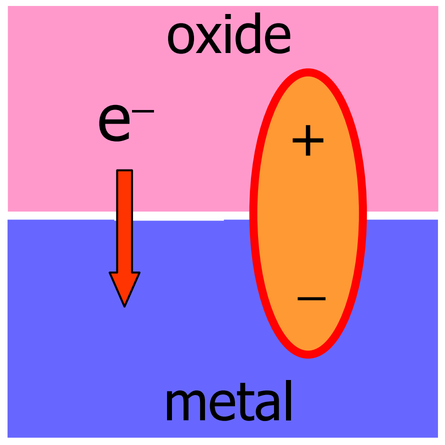
FeO/Pt(111) high work function (high electron affinity)
MgO/Ag(100) low work function (low ionization potential)

WHAT IS THE ORIGIN OF WORK FUNCTION CHANGES ?

Charge transfer at the interface

oxide ⇒ metal CT

BaO/Ag(100)



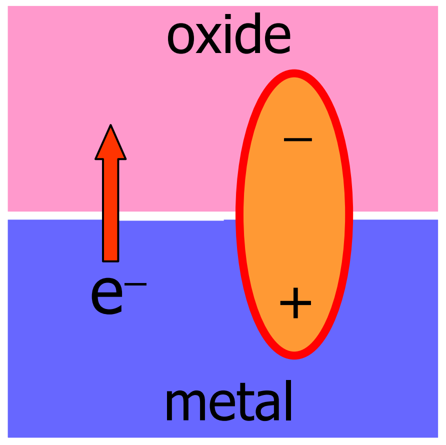
positive dipole

$\Delta\mu > 0$

lowers Φ_{eff}

metal ⇒ oxide CT

SiO_2/Mo(112)



negative dipole

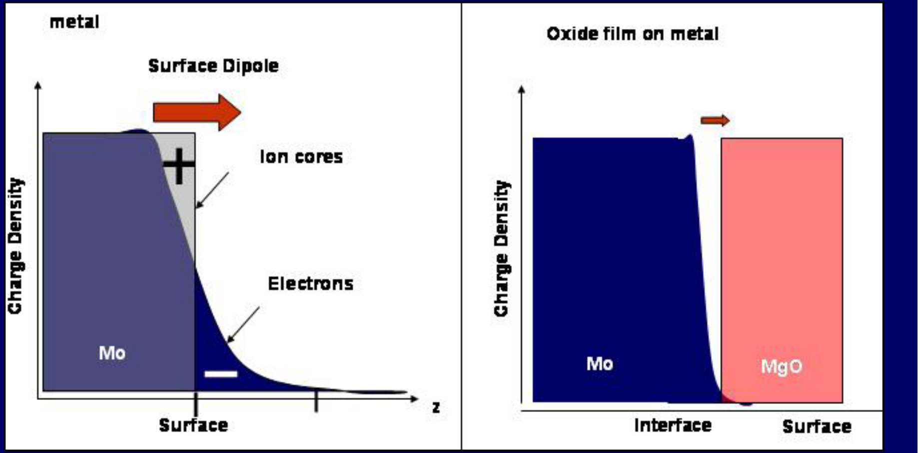
$\Delta\mu < 0$

raises Φ_{eff}

No CT at the interface

Pauli repulsion + polarization

MgO/Ag(100), MgO/Mo(100)



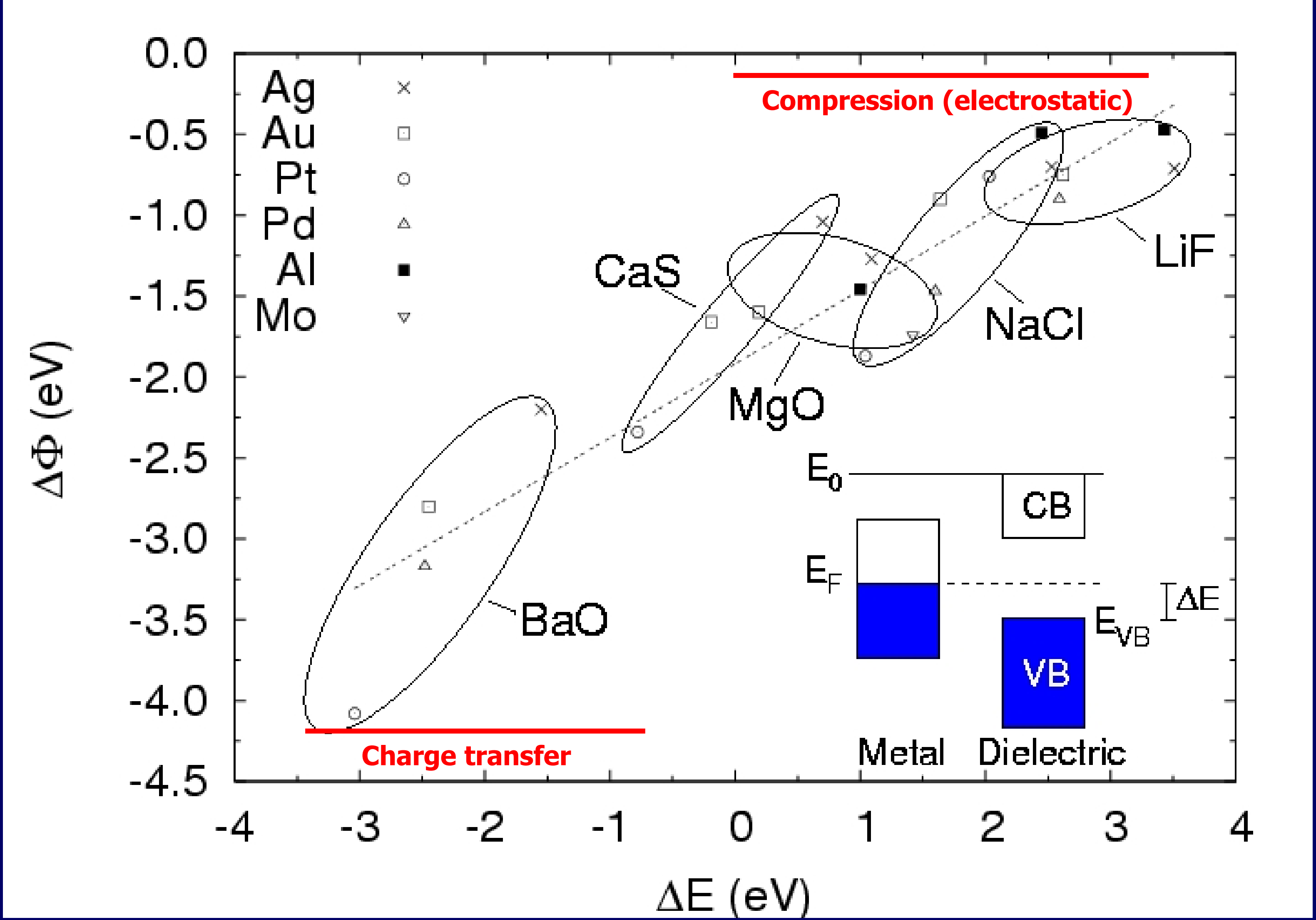
reduced charge spillover

$\Delta\mu > 0$

lowers Φ_{eff}

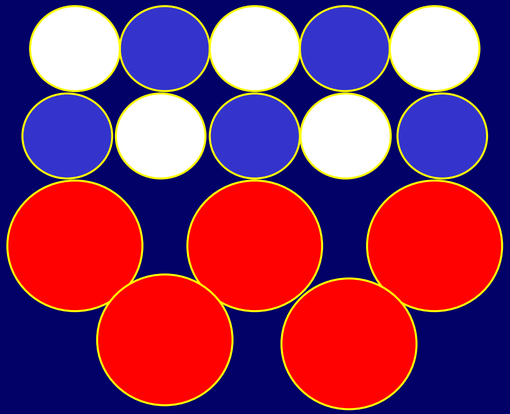
Goniakowski & Noguera, Interf. Sci. 12, 93 (2004)
Giordano, Cinquini, GP, Phys. Rev. B 73, 045414 (2005)

Factors affecting the work function change

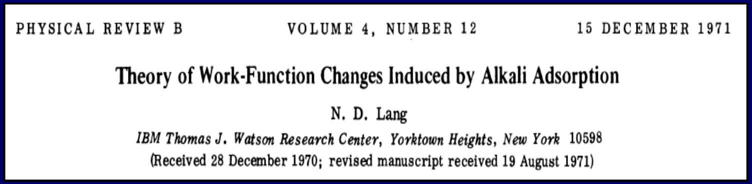


Prada, Martinez, GP, Phys. Rev. B 78, 235423 (2008)

CAN WE TURN AN INACTIVE SURFACE LIKE SiO_2/Mo(112) INTO AN ACTIVE ONE?



MODIFY PROPERTIES OF OXIDE ULTRATHIN FILMS: DOPING



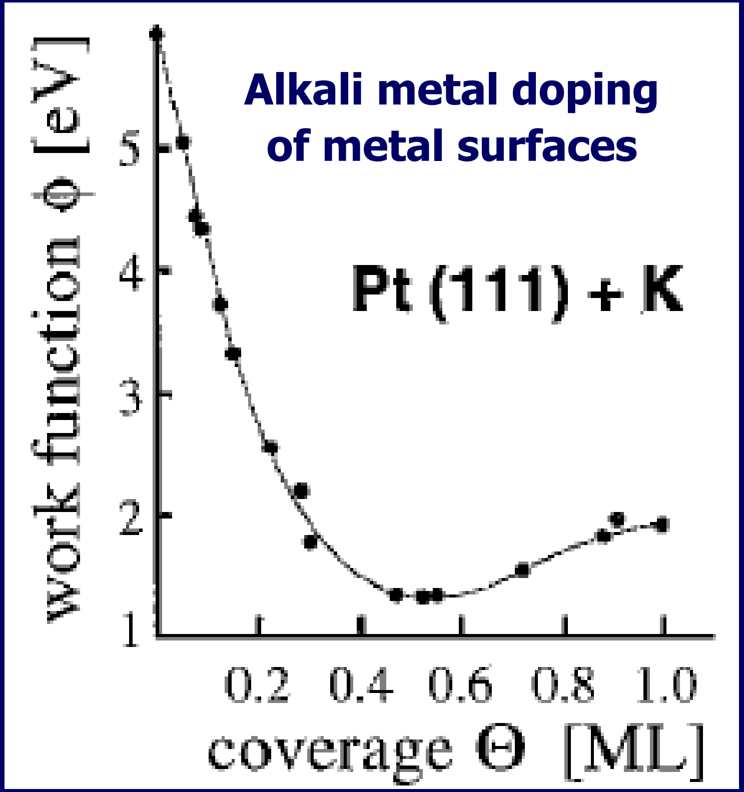
PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

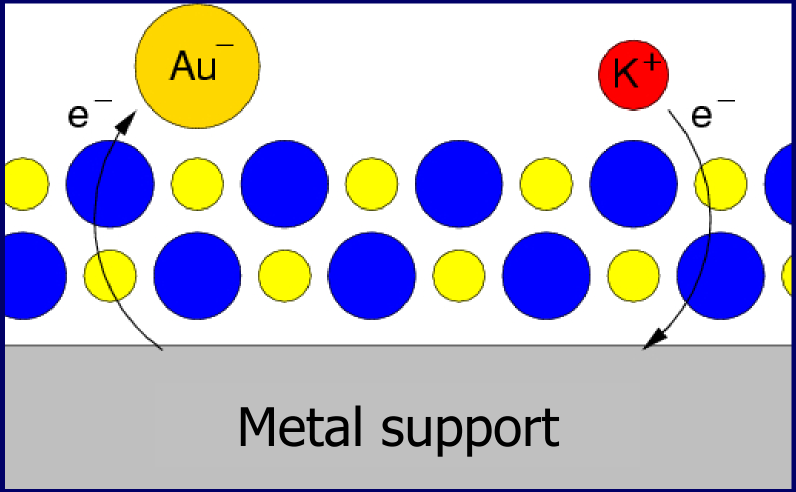
Theory of Work-Function Changes Induced by Alkali Adsorption

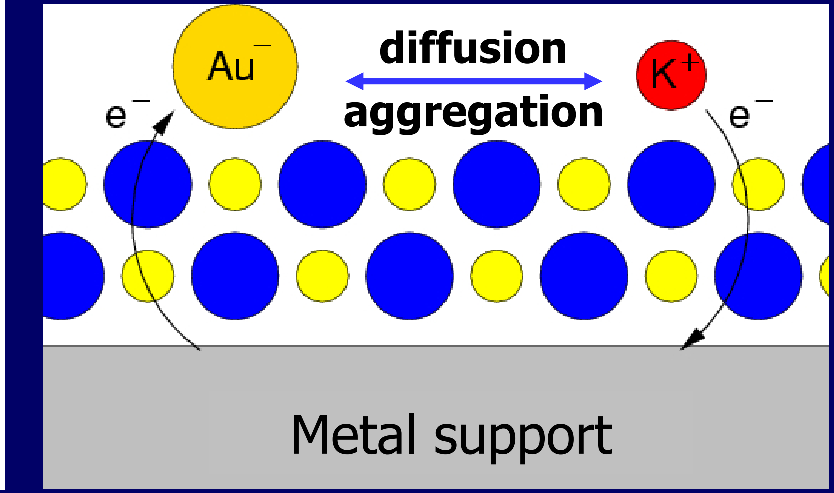
N. D. Lang

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 28 December 1970; revised manuscript received 19 August 1971)



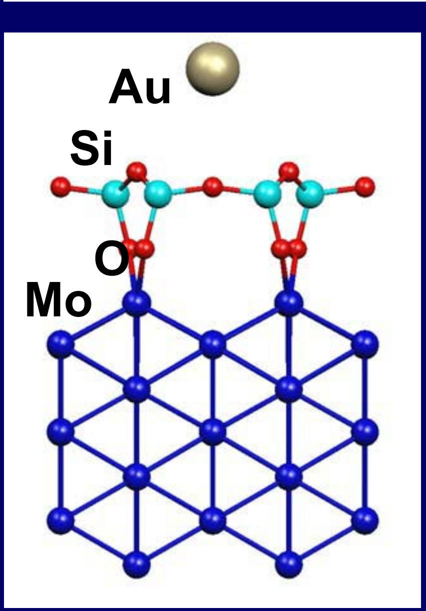


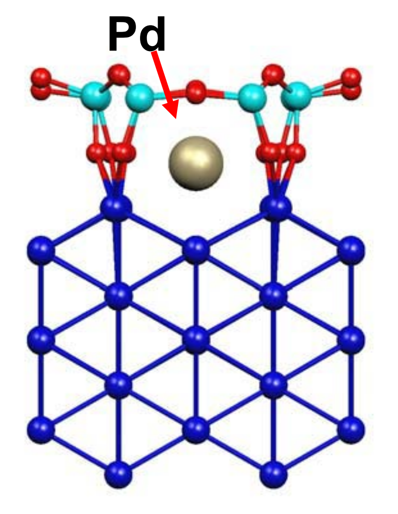


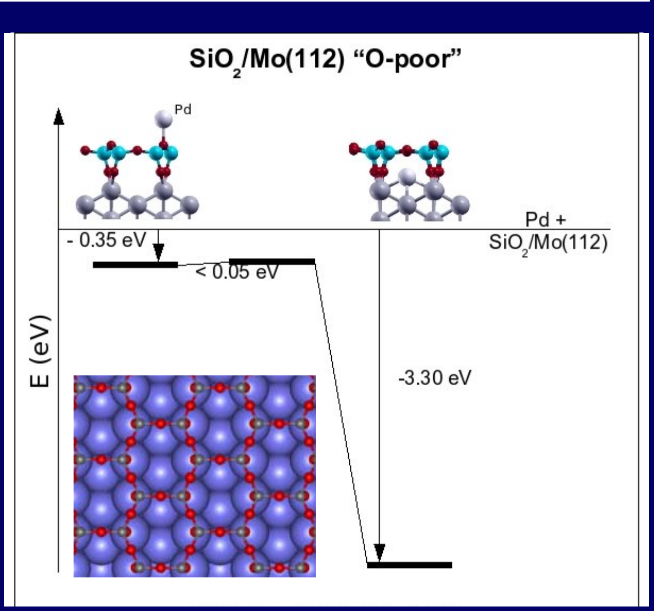
OXIDE ULTRA-THIN FILMS AS MOLECULAR SIEVES

Au and Pd adsorption: different behavior

- Au binds on the surface by 0.1 eV (easy diffusion and aggregation)
- Pd penetrates the rings & binds strongly at the interface (3.3 eV)

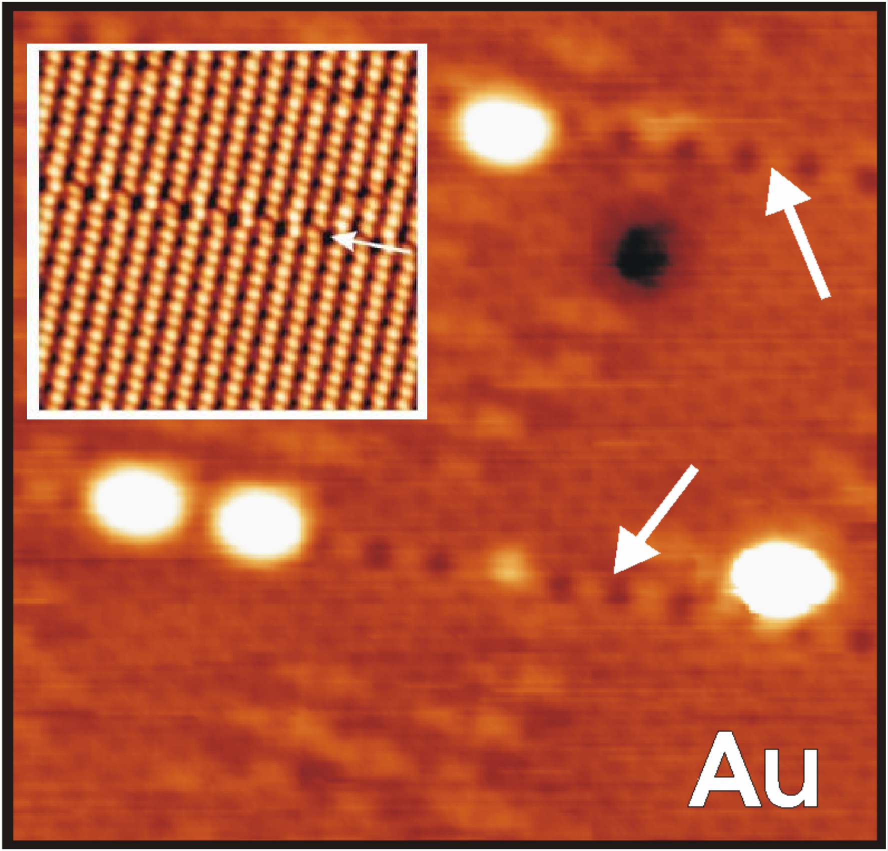




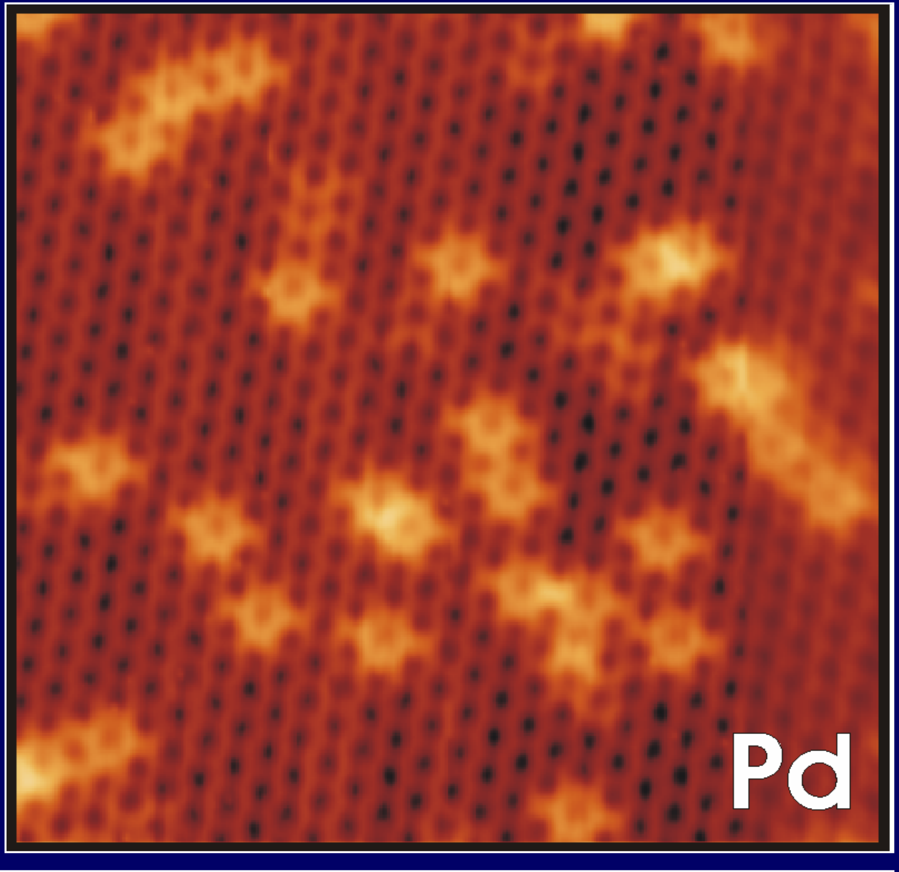


Giordano, Del Vitto, GP, J. Chem. Phys. 124, 034701 (2006)

Au and Pd on SiO_2/Mo(112): low temperature STM



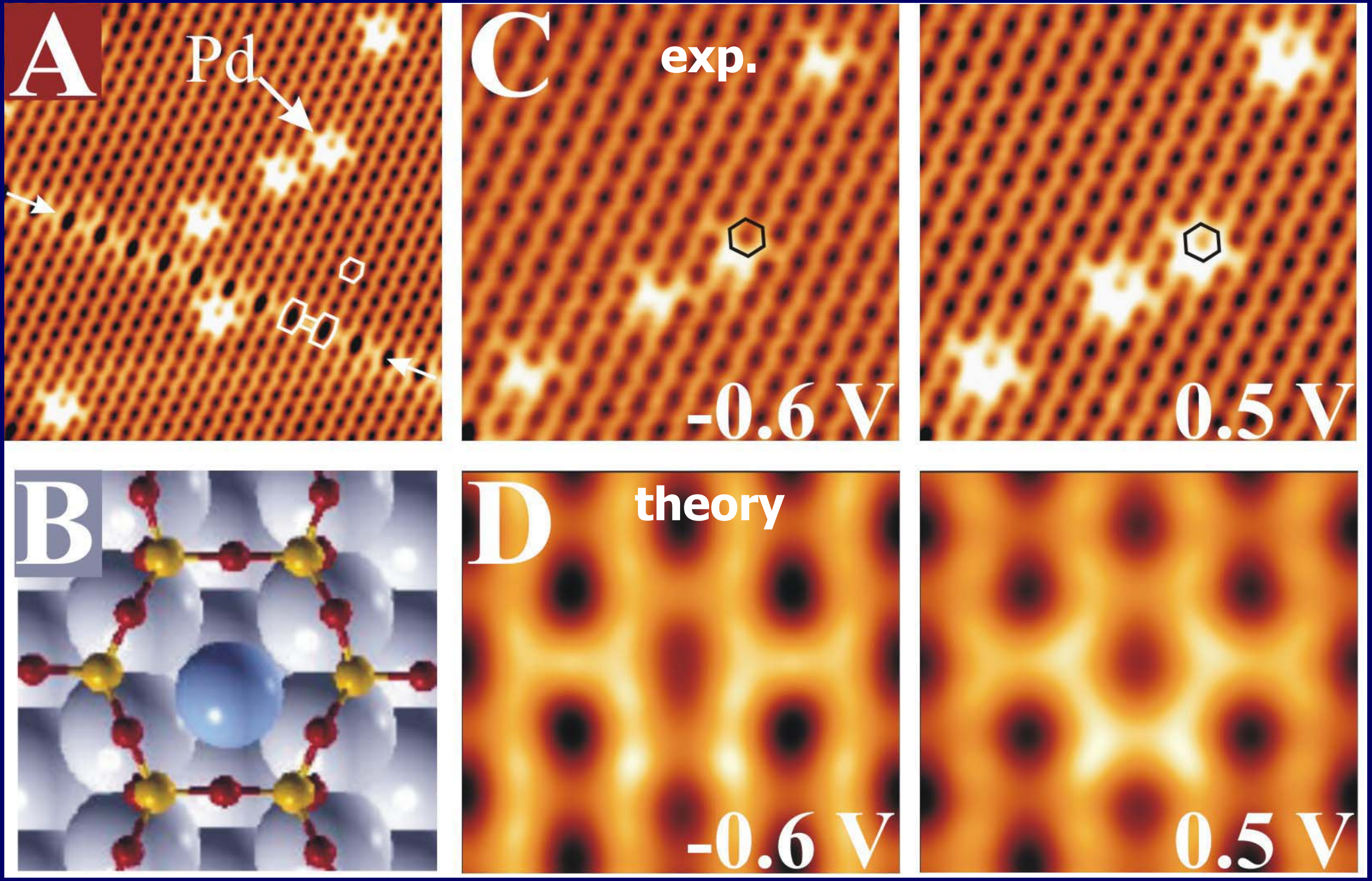
No atoms present on the surface; only clusters along line defects



No atoms or clusters on the surface; only brighter ring images

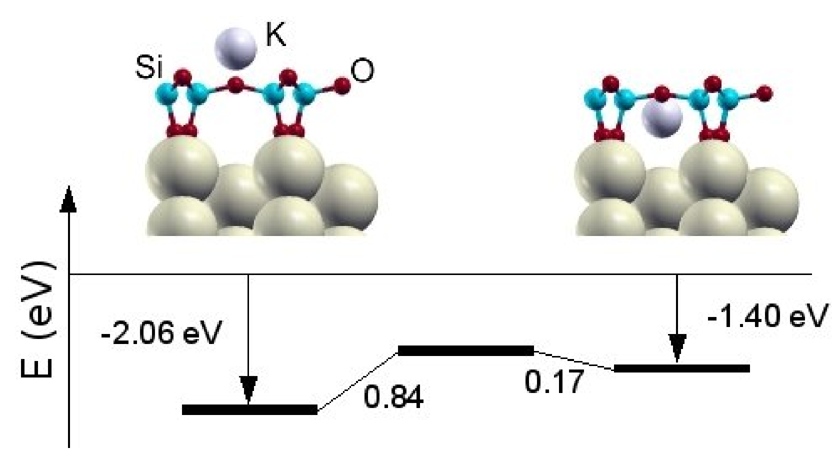
Ulrich, Nilius, Freund, Martinez, Giordano, GP, ChemPhysChem. 9, 1367 (2008)

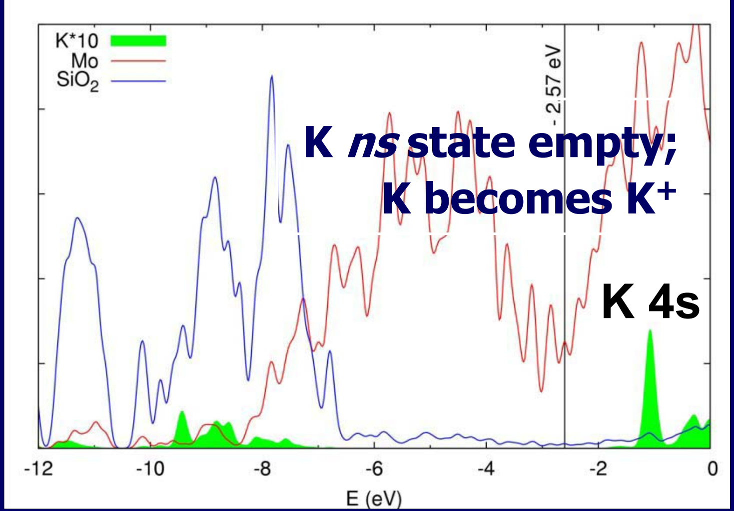
Pd on SiO_2/Mo(112): exp. and computed STM images



SiO_2/Mo(112): two-dimensional molecular sieve

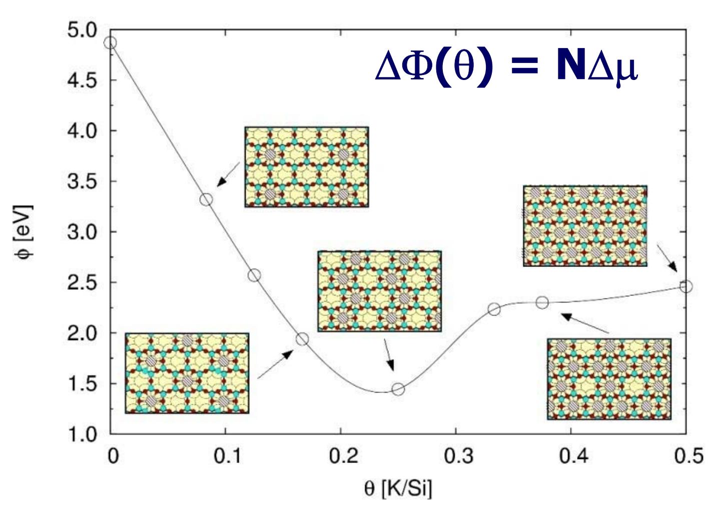
Alkali atoms adsorption on SiO_2/Mo(112): DFT





K *ns* state empty;
K becomes K^+

	Site	E_a, eV	ΔΦ, eV
K	**Surface**	**2.1**	**–2.3**
	Interface	**1.4**	**–0.6**
Na	**Surface**	**1.8**	**–1.7**
	Interface	**1.7**	**–0.5**
Li	**Surface**	**2.1**	**–1.5**
	Interface	**2.4**	**–0.4**

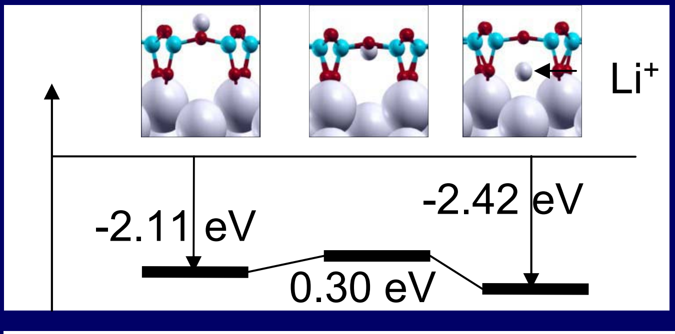


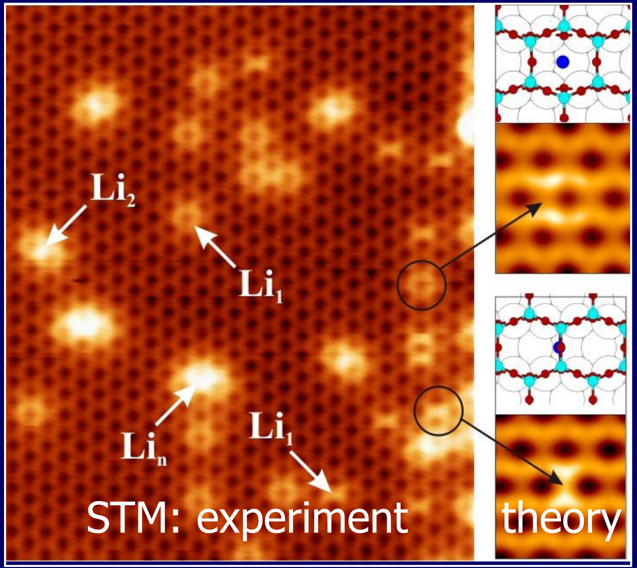
$$\Delta\Phi(\theta) = N\Delta\mu$$

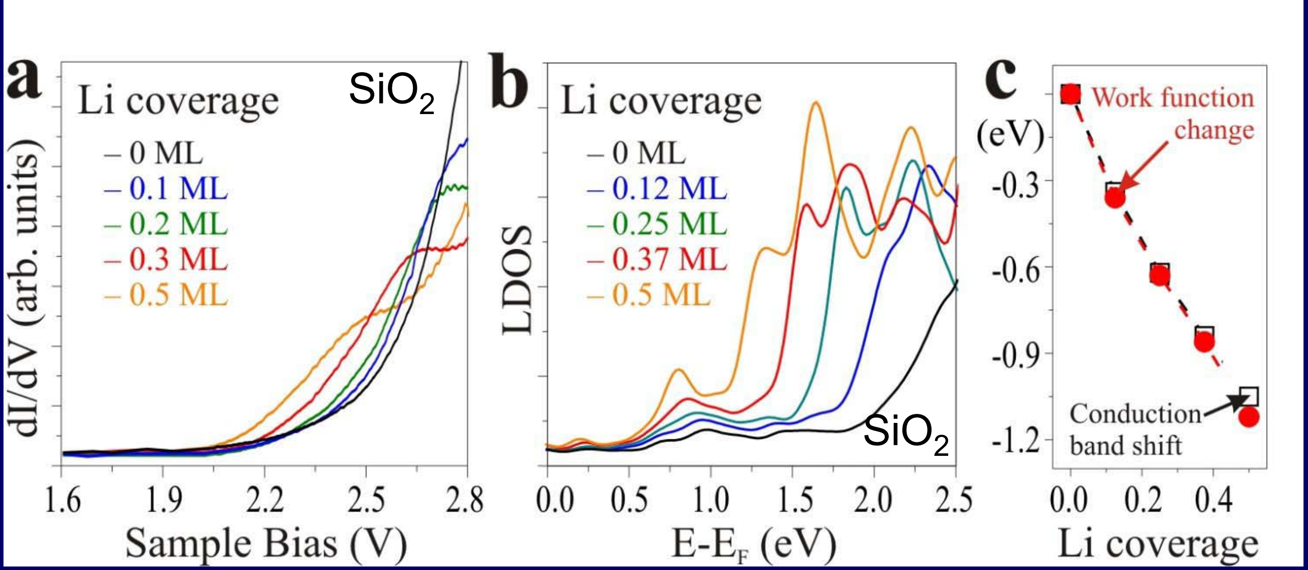
Martinez, Giordano, GP, J. Chem. Phys. 128, 164707 (2008)

Li-doped SiO_2/Mo(112): STM

Li at interface: thermally stable
Two adsorption sites at interface with same binding energy (2.4 eV) (confirmed by STM images)



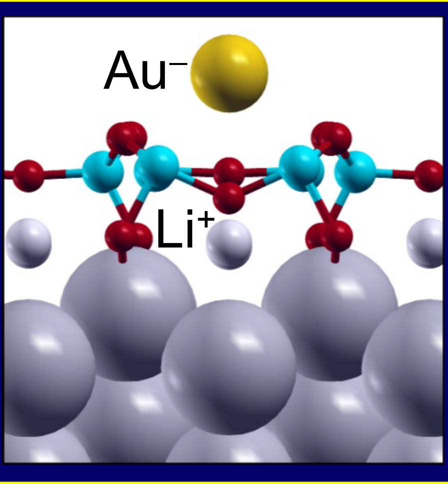


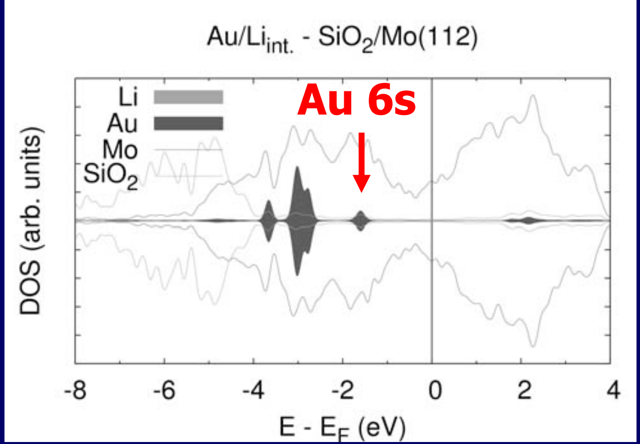


Jerratsch, Nilius, Freund, Martinez, Giordano, GP,
Phys. Rev. B 80. 245423 (2009)

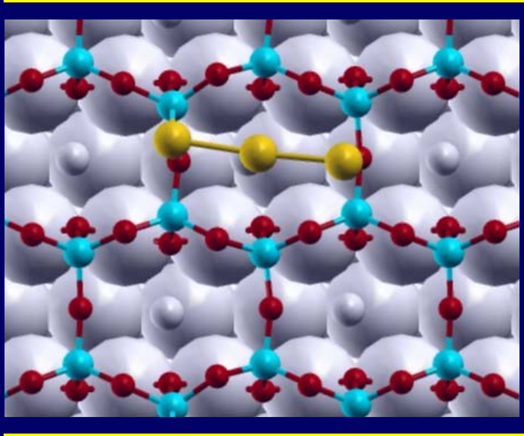
Au atoms (and clusters) on Li-doped SiO_2/Mo(112): DFT

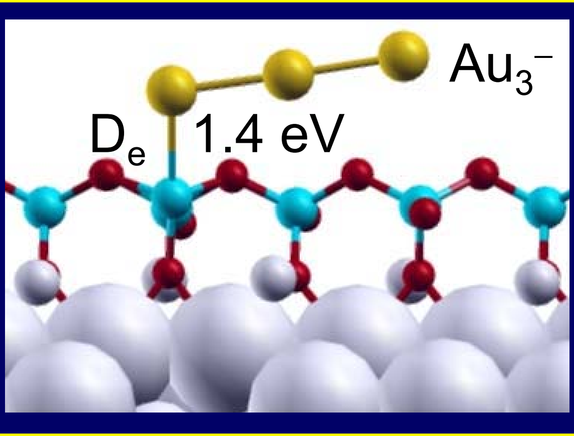
- On Li-doped silica films **Au atom becomes Au^-**
- The lattice undergoes a strong distortion (polaron)
- D_e is now 1.3 eV, Au stable on silica terraces

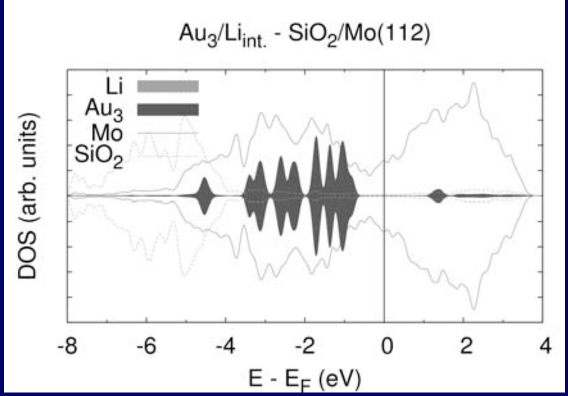




Au_3 on Li-doped silica: negatively charged







Charging induced by interface engineering!

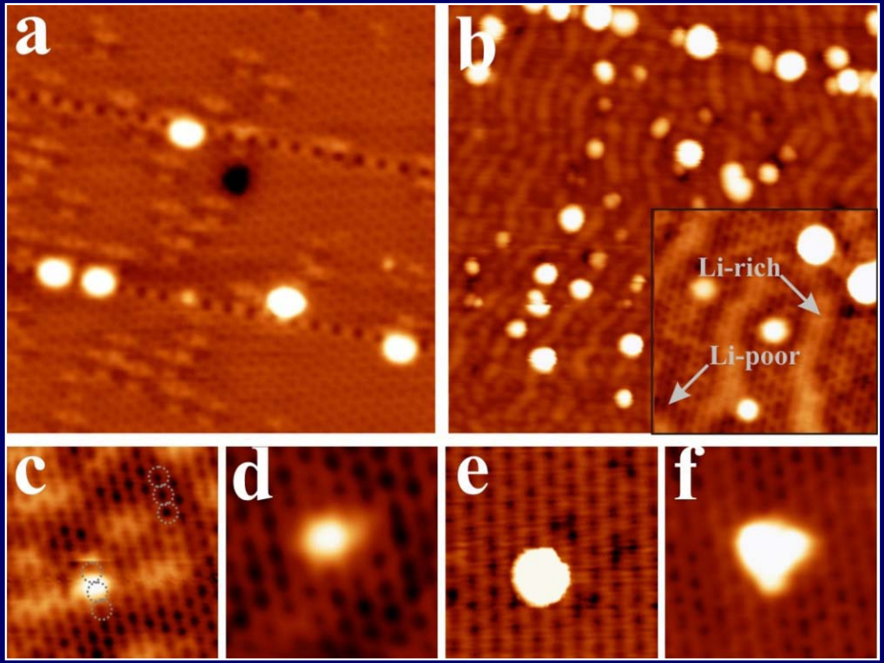
Au atoms and clusters on Li-doped SiO_2/Mo(112): STM

(a) SiO_2: Au particles only along line defects

(b) Li-doped SiO_2: Au clusters on defect free oxide patches

(c) Au monomer (on top of a bridging oxygen)

(d, e, f) 3D Au clusters



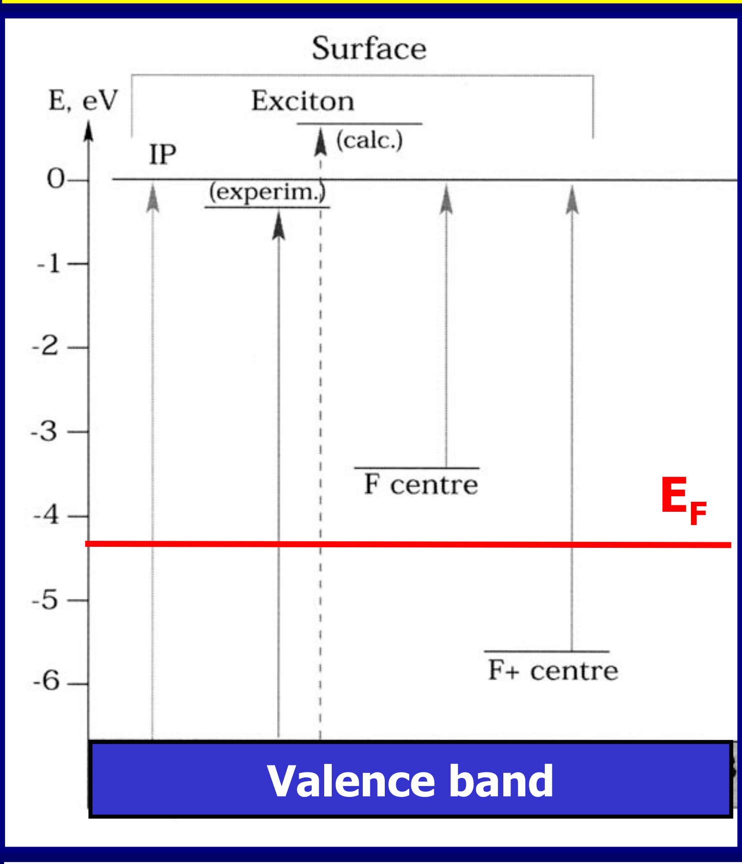
Surface adsorption properties modified by Li-doping

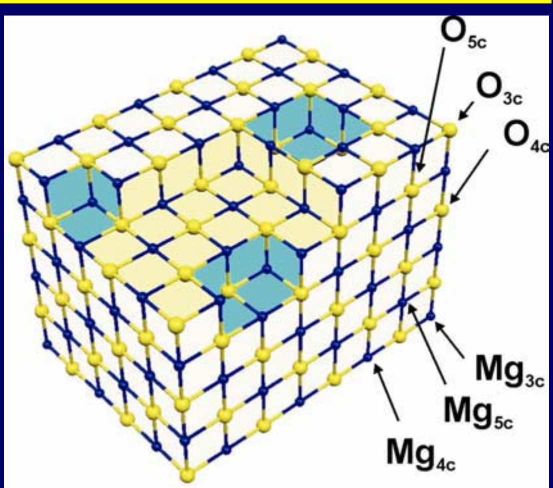
Martinez, Jerratsch, Nilius, Giordano, GP, Freund, PRL 103, 056801 (2009)

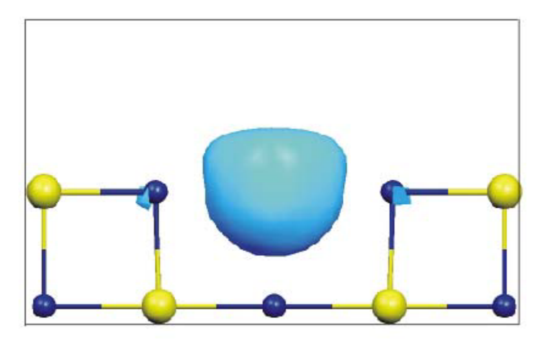
MODIFY PROPERTIES OF OXIDE ULTRA-THIN FILMS

1) DOPING
2) **DEFECTS**

O vacancies (F centers) on MgO





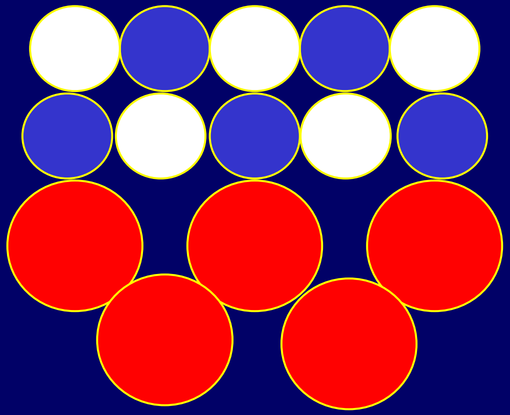


Relative position of F^0 and F^+ states in MgO gap
Sushko, Shluger, Catlow Surf. Sci. 450, 153 (2000)

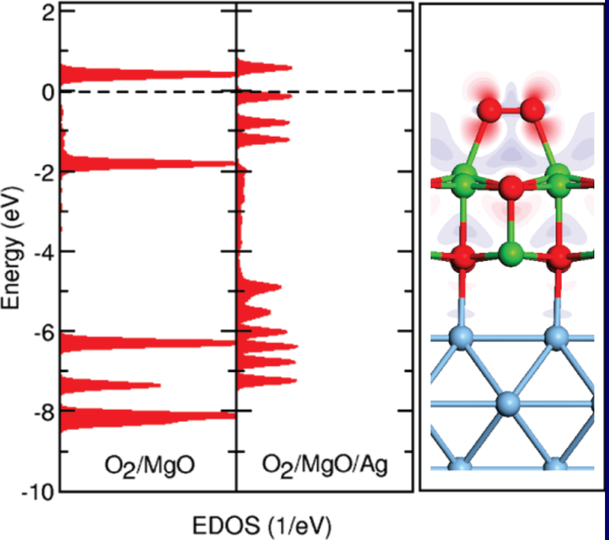
Work function of most metals between 4 and 5 eV

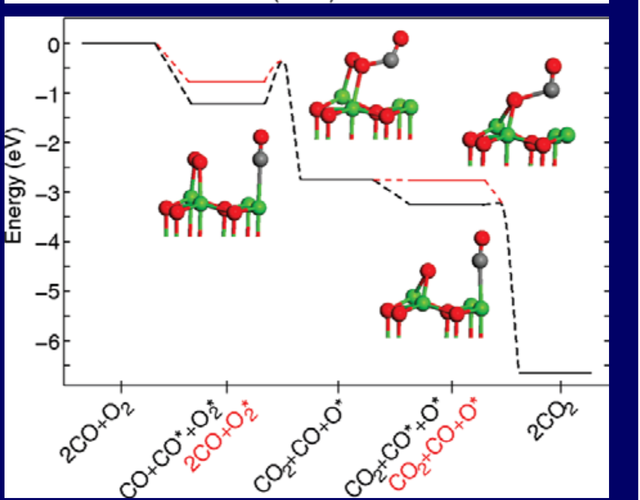
Giordano, Martinez, GP, Watkins, Shluger, J. Phys. Chem. C 112, 3857 (2008)

CHARGE TRANSFER THROUGH OXIDE ULTRATHIN FILMS: ONLY GOLD?



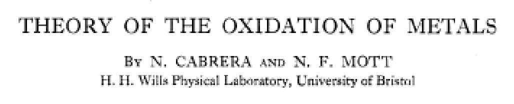
O_2 ON MgO/Ag(100): FORMATION OF O_2^- AND EASY CO OXIDATION



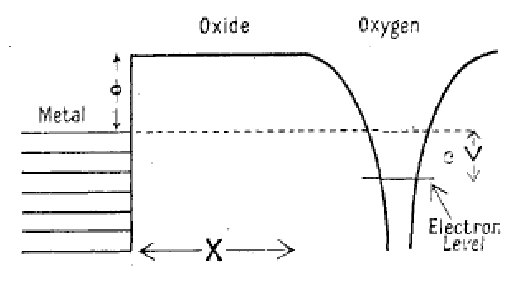


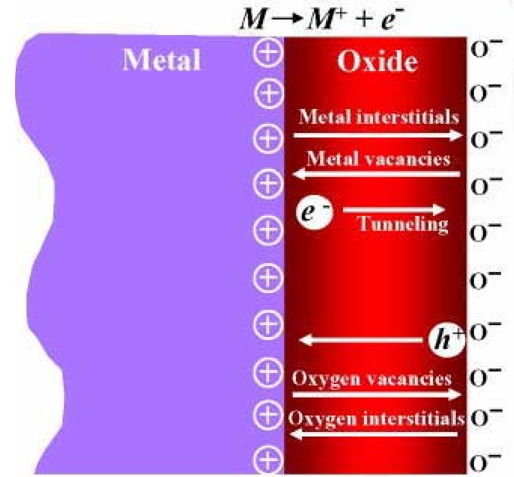
- DFT shows that O_2 on MgO/ Ag(100) results in formation of superoxide radical anion, O_2^-
- Subsequent reaction with CO leads to easy CO_2 formation
- General mechanism for CO oxidation on metals?

Hellman, Klakar, Grönbeck J. Am. Chem. Soc,131, 16636, 2009


THEORY OF THE OXIDATION OF METALS

BY N. CABRERA AND N. F. MOTT
H. H. Wills Physical Laboratory, University of Bristol

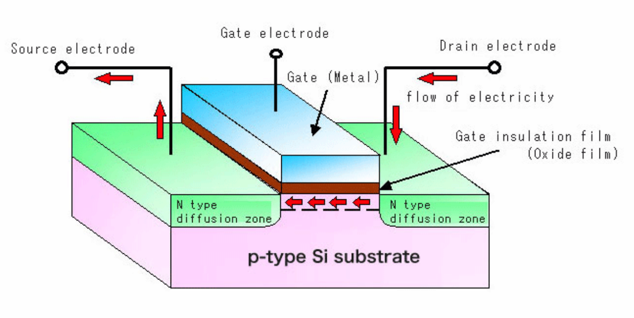




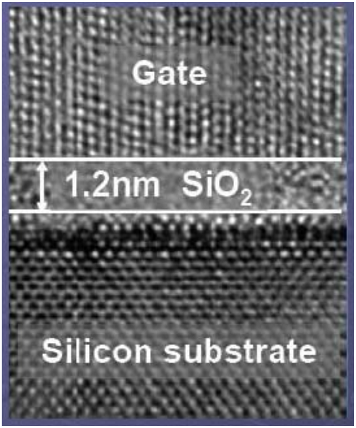
Cabrera & Mott, Rep. Progr. Phys. 2, 163,1949

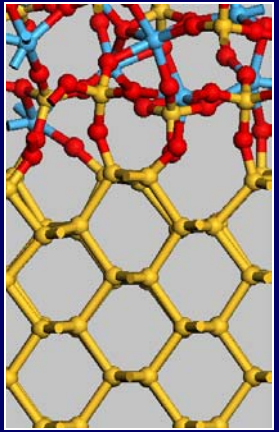
OXIDE AND INSULATING ULTRATHIN FILMS: ONLY IN MODEL SYSTEMS?

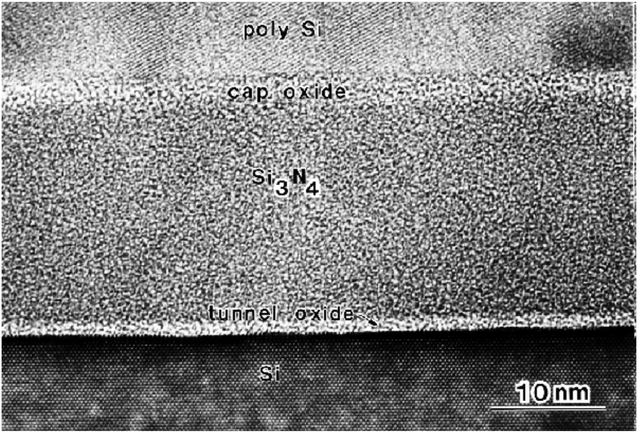
MICROELECTRONIC DEVICES



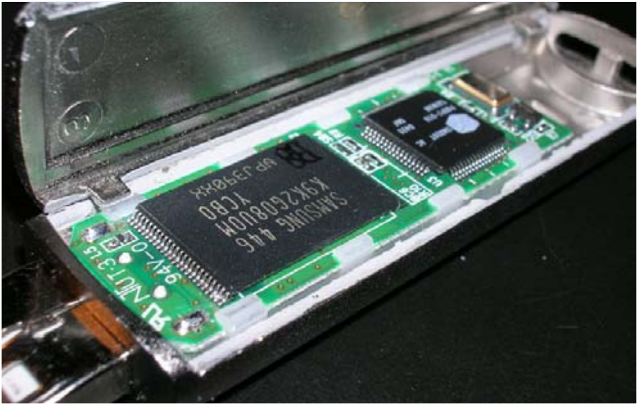
Last generation of MOSFET: an ultrathin SiO_2 layer separates gate from Si



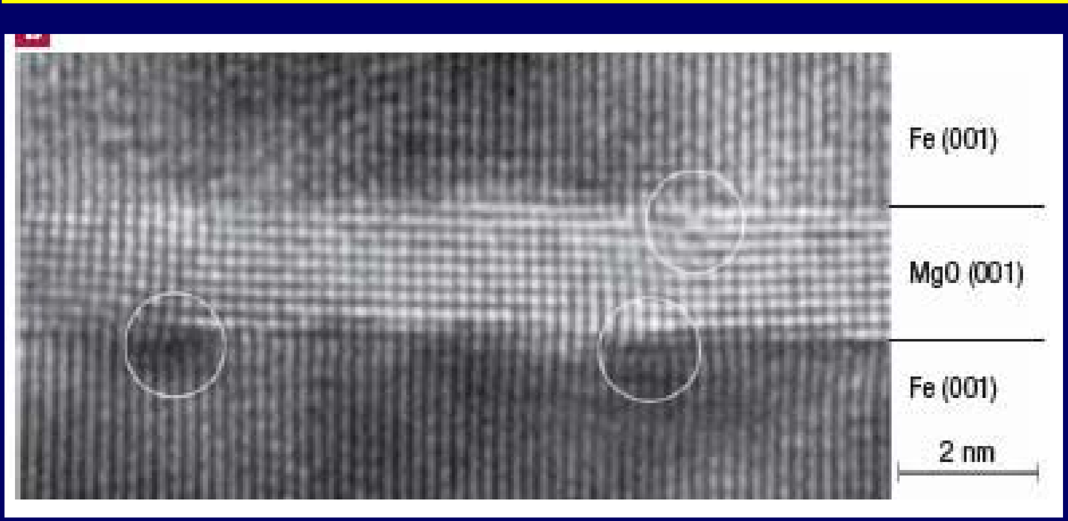


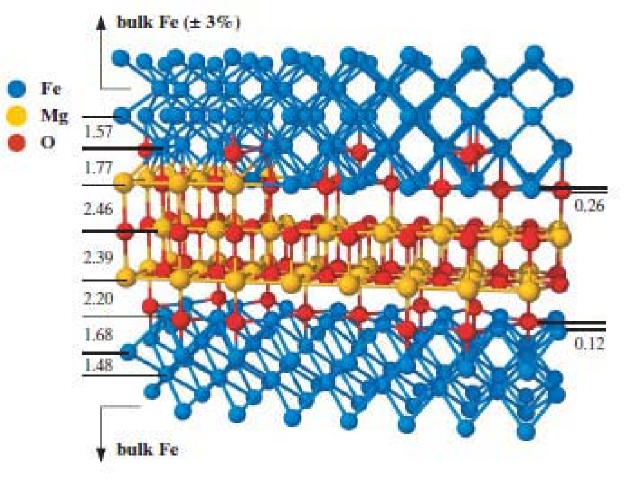


Flash memories make use of ultrathin oxide layers



TUNNEL MAGNETO RESISTANCE (SPINTRONICS)



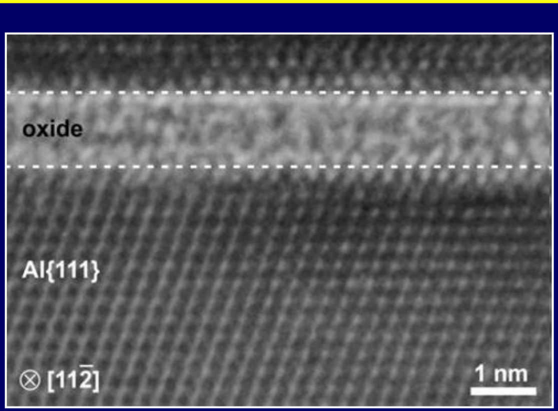


Tunnel magneto resistance (TMR): important phenomenon for the design of magnetic tunnel junctions and random-access memories

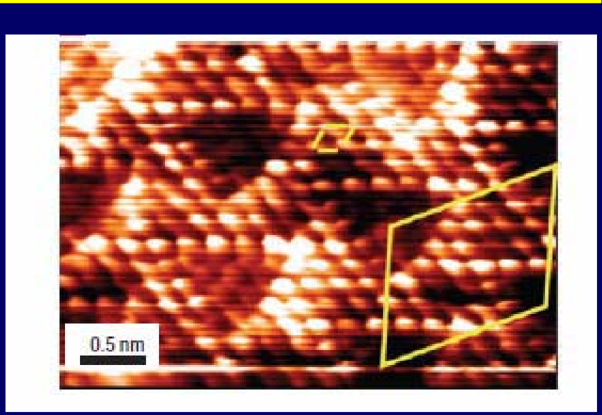
A few layers of insulating material (MgO) separate two ferro-magnetic electrodes (Fe). Tunnel current through the barrier depends on orientation of magnetic moments of the electrodes

PASSIVE FILMS ON METALS (CORROSION PROTECTION)

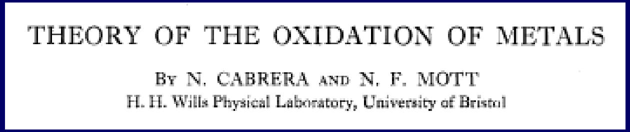
Outstanding corrosion resistance of stainless steel due to a thin oxide “passive” film typically 1-3 nm thick



HR-TEM micrograph of an amorphous Al_2O_3 oxide film grown on a bare Al(111)



STM of the TiAl(111) surface covered by a 0.6-nm-thick alumina layer [Maurice et al. Nat. Mater. 3, 687 (2004)]



THEORY OF THE OXIDATION OF METALS

BY N. CABRERA AND N. F. MOTT
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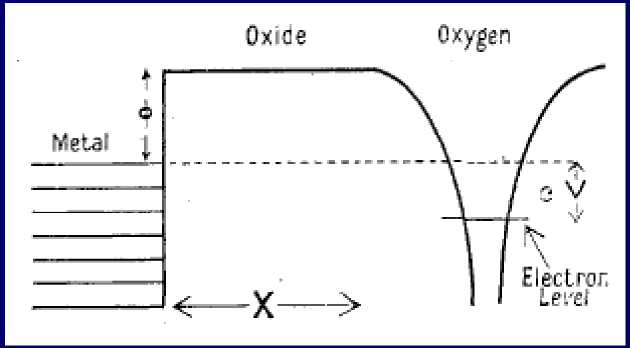
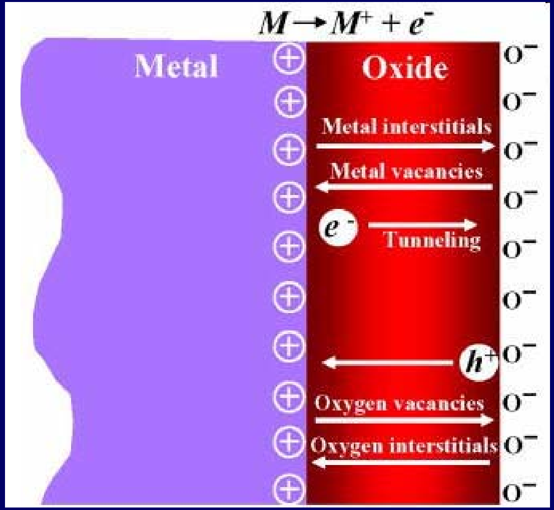


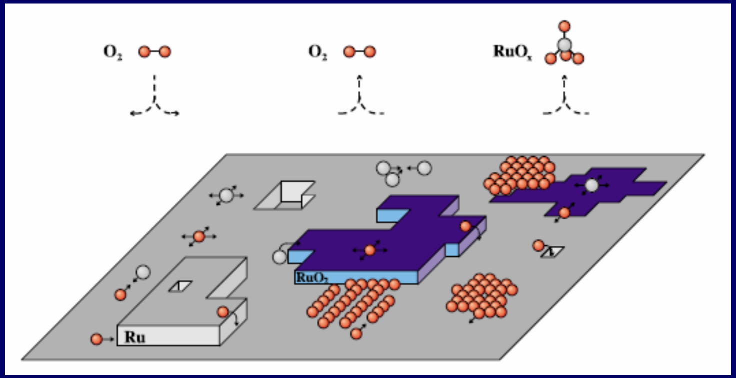


Cabrera, Mott, Rep. Progr. Physics (1949)

Olsson, Landolt, Electrochim. Acta 48, 1093 (2003)

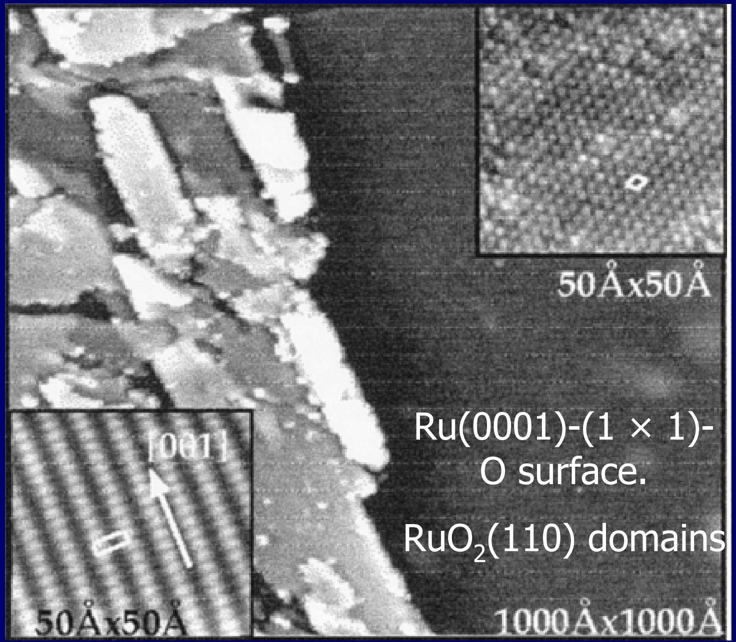
Schultze, Lohrengel, Electrochim. Acta 45, 2499 (2000)

OXIDE FILMS: RELEVANT FOR CATALYSIS BY METALS?



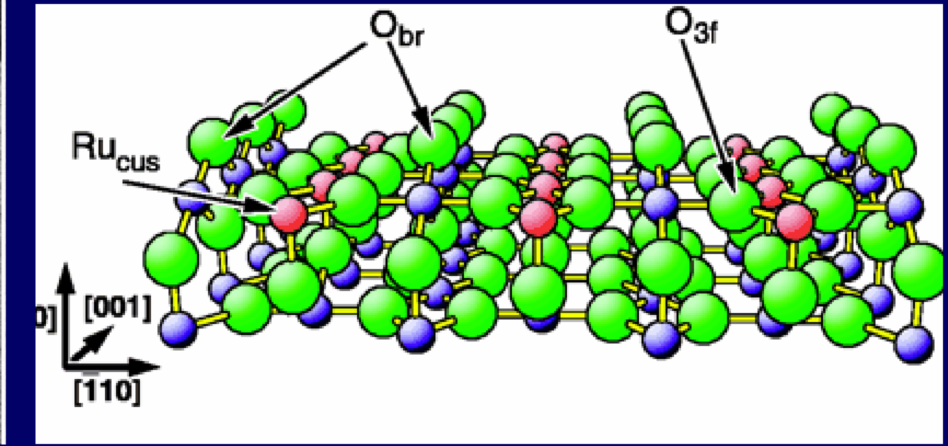
Ru metal in UHV is practically inactive in CO oxidation; it becomes very active at atmospheric pressure. Active phase under high O_2 exposures on Ru(0001) is a thin overlayer of $RuO_2(110)$

Over, Kim, Seitsonen, Wendt, Lundgren, Schmid, Varga, Morgante, Ertl, *Science* **2000**, *287*, 1474

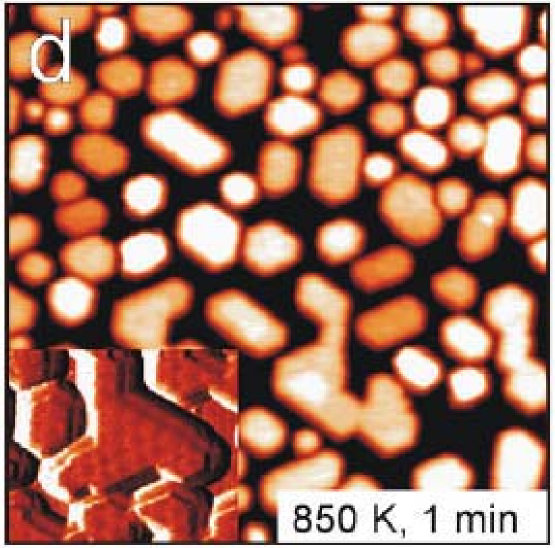


Ru(0001)-(1 × 1)-O surface.

$RuO_2(110)$ domains

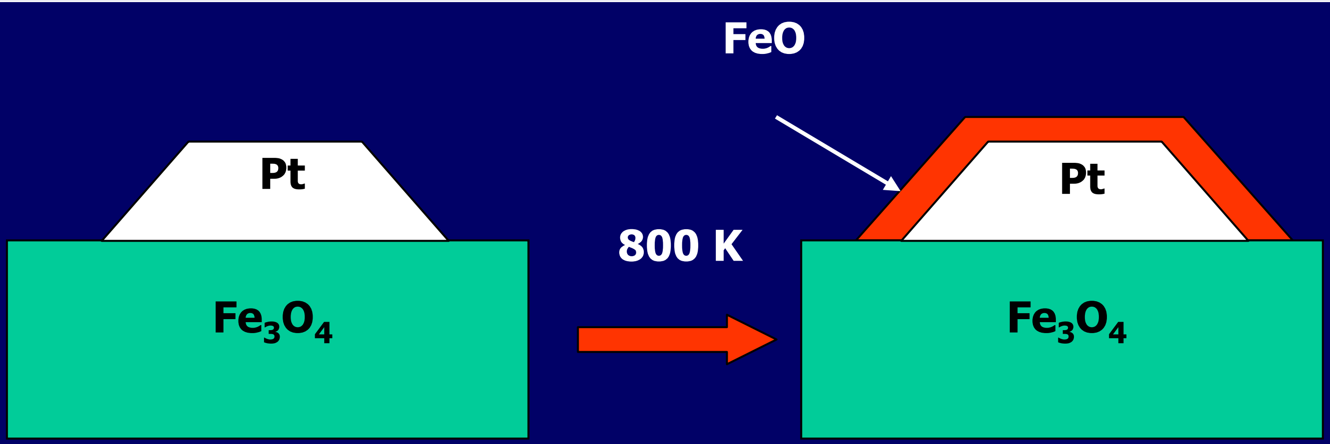


STRONG METAL SUPPORT INTERACTION (SMSI) IN CATALYSIS BY SUPORTED METAL PARTICLES

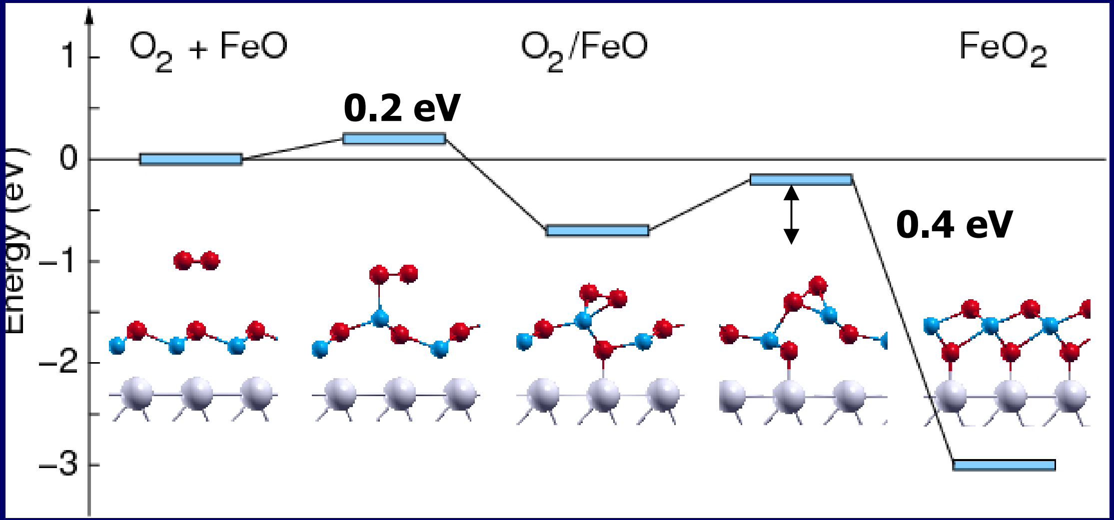


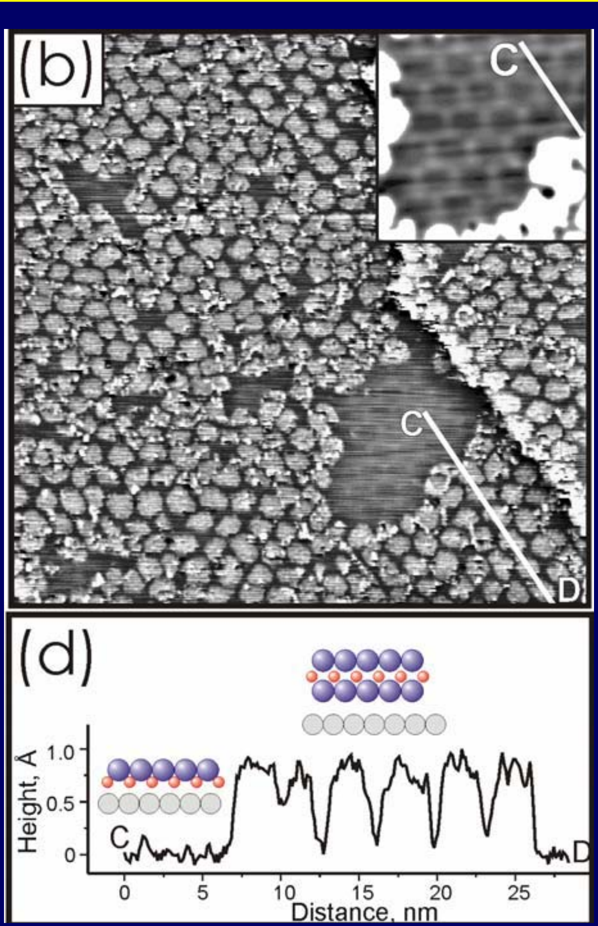
- SMSI: encapsulation of metal particles on oxides by a thin oxide film
- Usually results in reduced activity
- Recently examples have been reported of increased activity in CO oxidation
- Pt on Fe_3O_4: the encapsulating layer has the FeO/Pt(111) structure

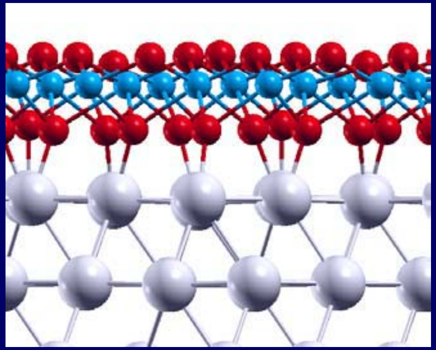
Shaikhutdinov, Freund, et al. J. Catal. **2009**, 266, 359



O_2 DISSOCIATION ON FeO/Pt(111)



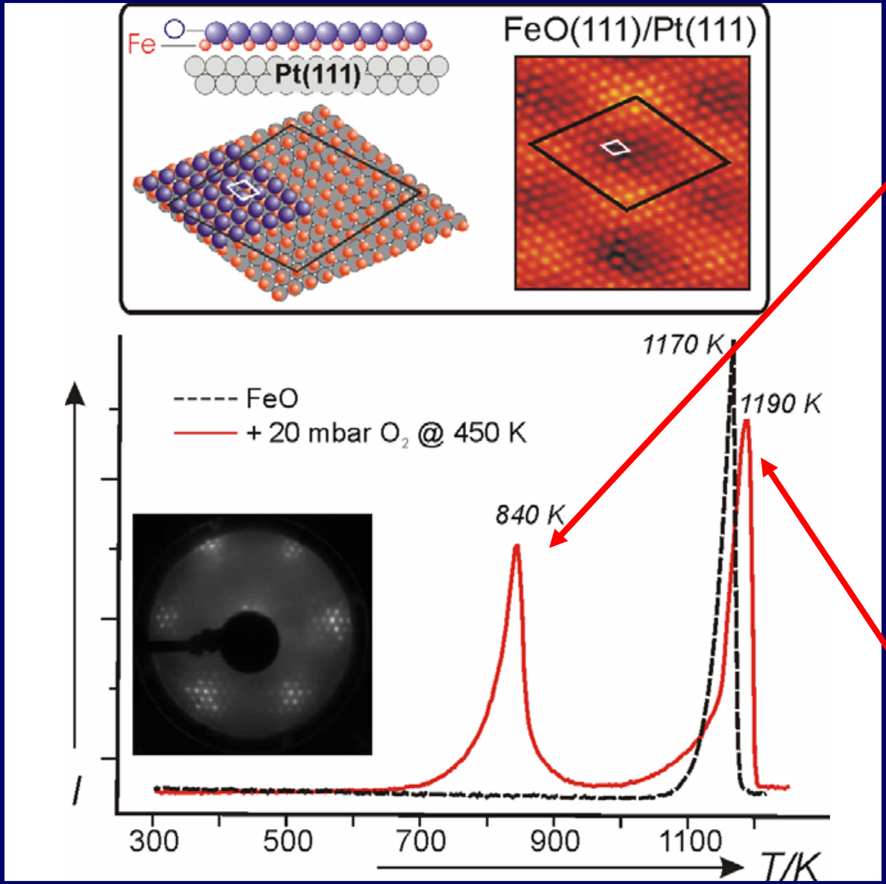




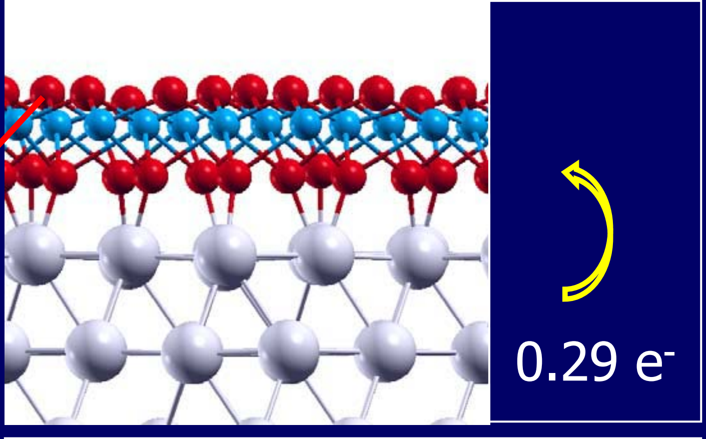
- O_2^{2-} peroxo species dissociates overcoming a barrier of ~ 0.4 eV
- A new FeO_2 phase forms (also from STM)

Exposure of FeO/Pt(111) films to O_2 pressure leads to a FeO_2 film with an O-Fe-O trilayer structure

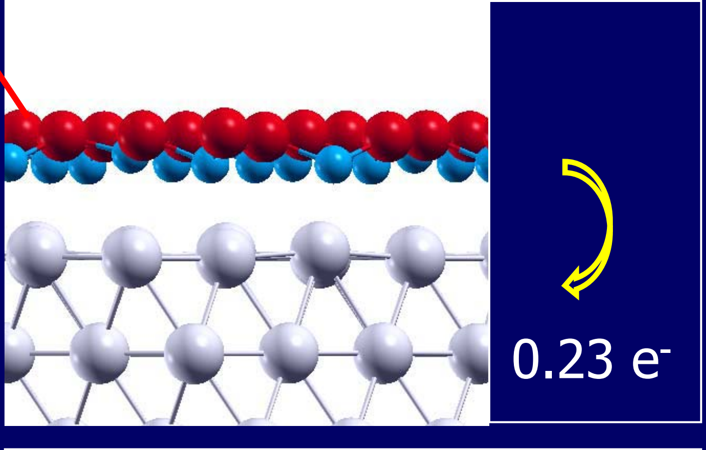
FeO/Pt(111) VERSUS FeO_2/Pt(111)



- FeO_2: two O_2 desorption peaks at 840 K and 1190 K
- Consistent with DFT calculations showing easier O desorption from FeO_2 than from FeO top layer

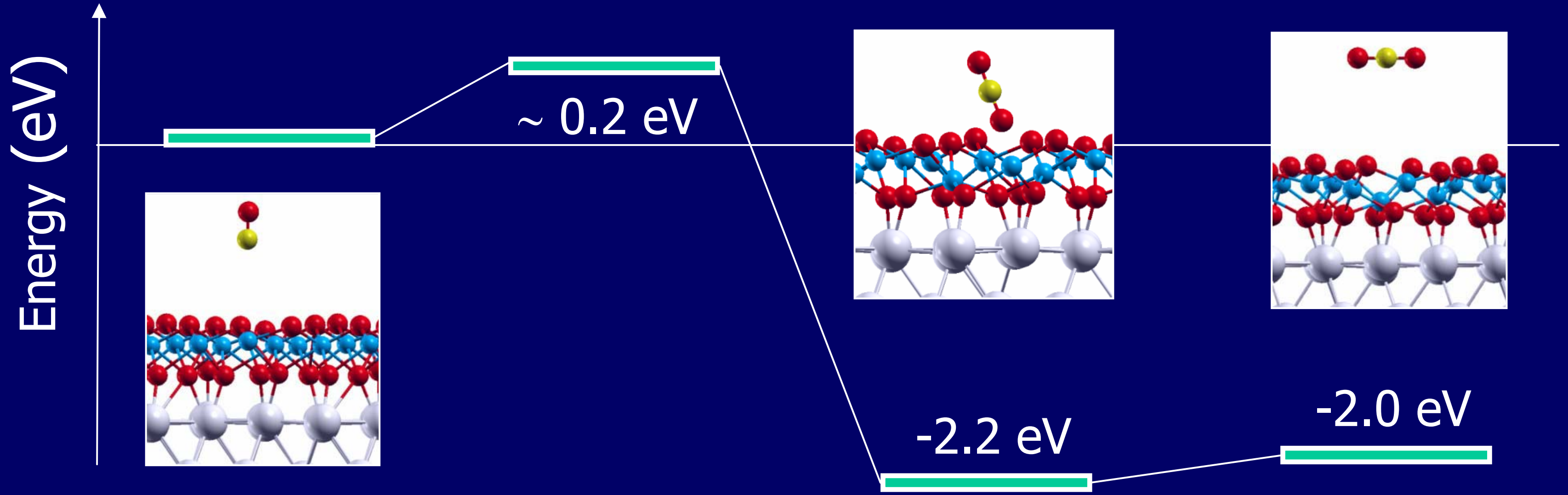


$$FeO_2 \rightarrow \tfrac{1}{2}\, O_2 + FeO_{2-x}$$
$$\Delta H = 1.3\ \text{eV}$$



$$FeO \rightarrow \tfrac{1}{2}\, O_2 + FeO_{1-x}$$
$$\Delta H = 2.8\ \text{eV}$$

CO ADSORPTION AND OXIDATION ON FeO_2/Pt(111)



$CO + FeO_2 \rightarrow CO_2 + FeO_{2-x}$ $\Delta H = -2.0$ eV

High energy gain related to low cost of vacancy formation (1.3 eV)

- **Small vacancy formation energy, FeO_2/Pt(111) film promotes CO oxidation**
- **Ambient O_2 restores the O content of the film. Reaction follows a classical Mars-Von Krevelen mechanism**

Giordano, Goniakowski, Shaikutdinov, GP, Freund et al. Angew. Chem. (2010)

SOME CONCLUSIONS

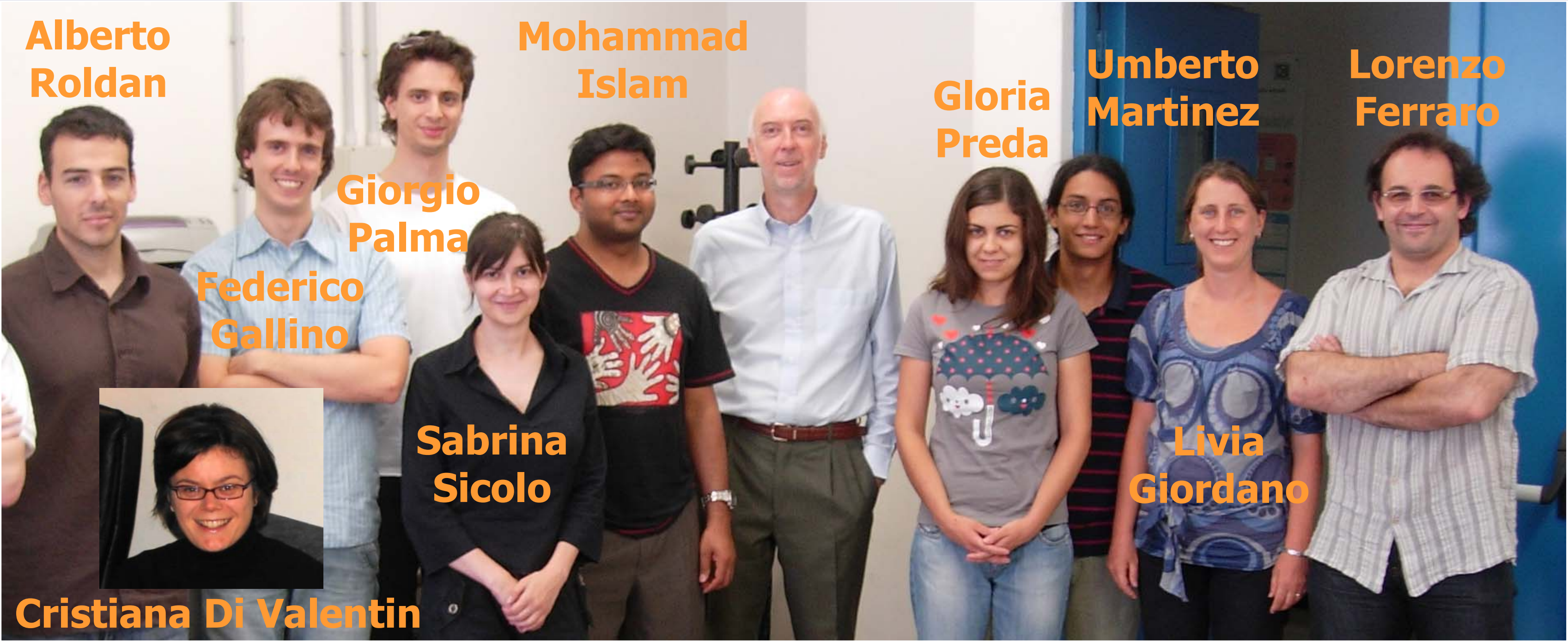
- Ultrathin oxide films **may** behave differently from bulk oxides (new phases, properties connected to the reduced dimensionality, structural flexibility and easy reconstruction)

- Charging of supported atoms & clusters (and molecules) occurs by tunneling through the thin dielectric layer

- Charge transfer depends on (a) electron affinity of adsorbates, (b) work function of oxide/metal interface, (c) possibiilty for the oxide film to undergo polaronic distortion, (d) film thickness

- Engineering of metal/oxide interfaces:
    - alkali metal adsorption
    - selected defects (not shown)
    - multilayer growth (not shown)

- Consequences:
    - enhanced cluster reactivity
    - enhanced surface reactivity



HJ Freund

M Heyde

N Nilius

T Risse

M Sterrer

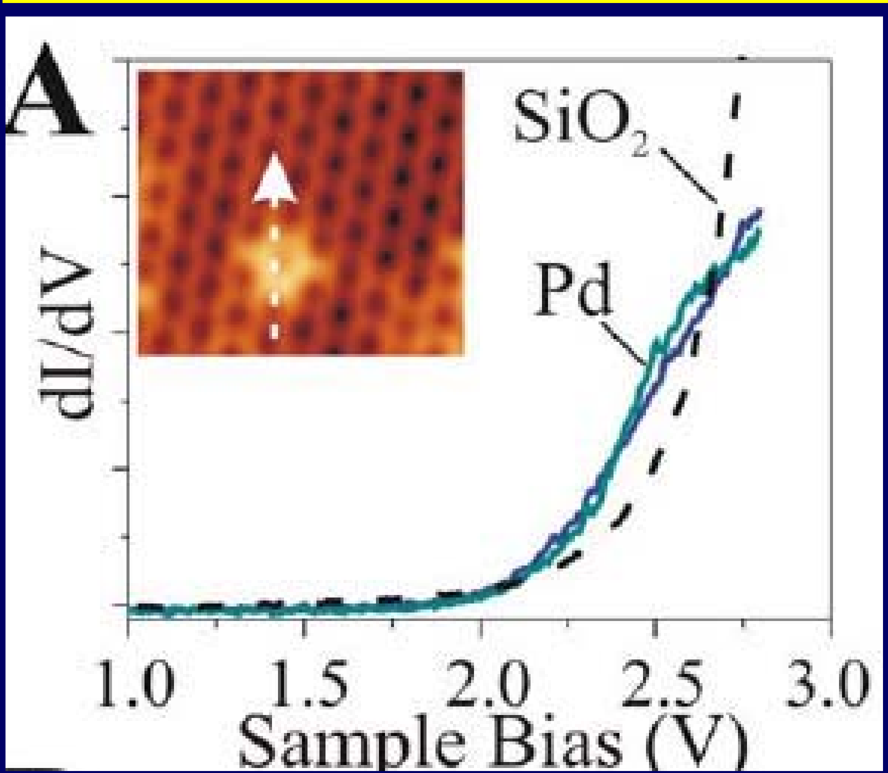
Shaikutdinov

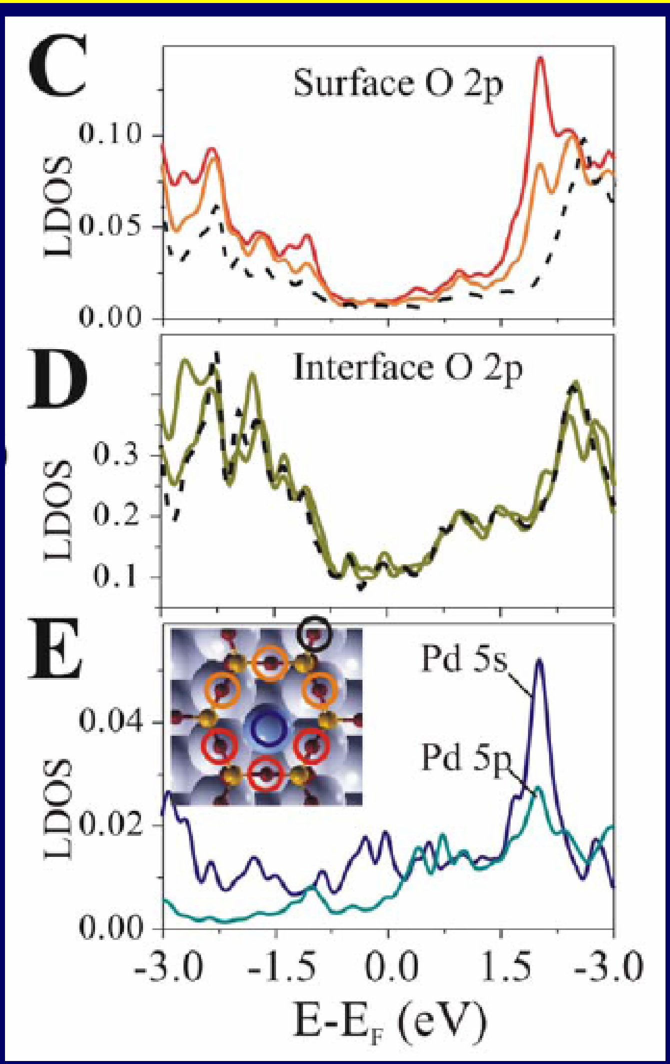
J Goniakowski

Universitè Paris VI

Support: Barcelona Supercomputing Center – CILEA Computing Center – Univ. Milano Bicocca – COST D41

Pd on SiO_2/Mo(112): measured and experimental images





- Enhanced brightness of silica ring due to hybridization of O *2p* states with Pd_1 *5s* empty state (see DOS)
- Consistent with dI/dV curves

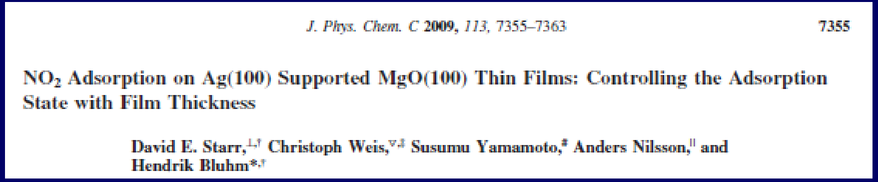
CHARGE TRANSFER THROUGH THIN FILMS: NO_2/MgO/Ag(100)

J. Phys. Chem. B **2006,** *110,* 11977–11981 **11977**

Mechanism for NO_2 Charging on Metal Supported MgO

Henrik Grönbeck*

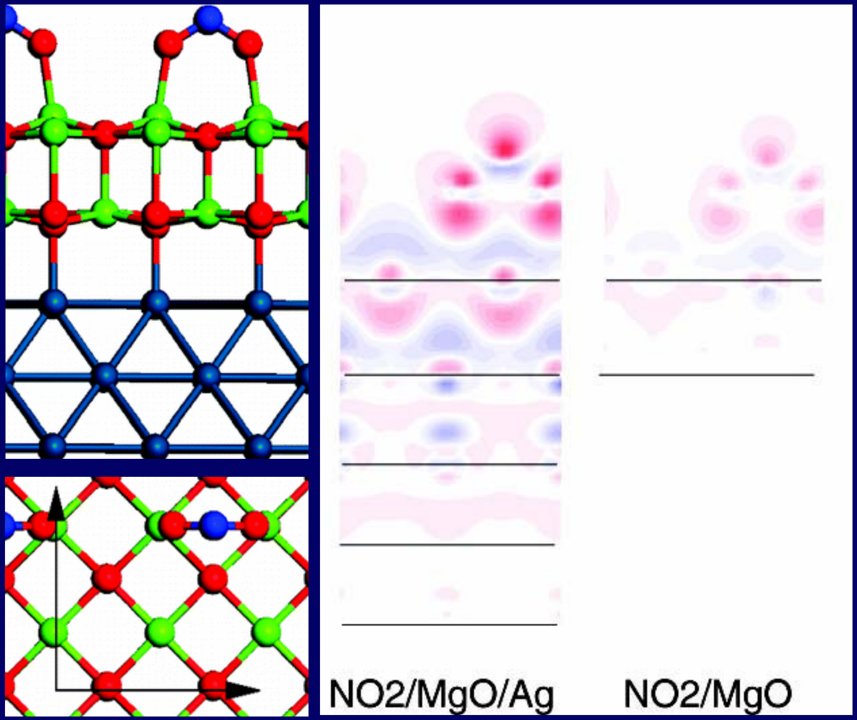
Competence Centre for Catalysis and Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden



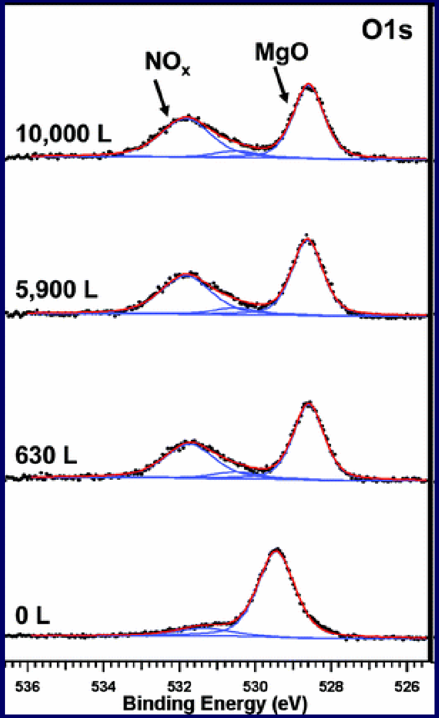
J. Phys. Chem. C **2009,** *113,* 7355–7363 **7355**

NO_2 Adsorption on Ag(100) Supported MgO(100) Thin Films: Controlling the Adsorption State with Film Thickness

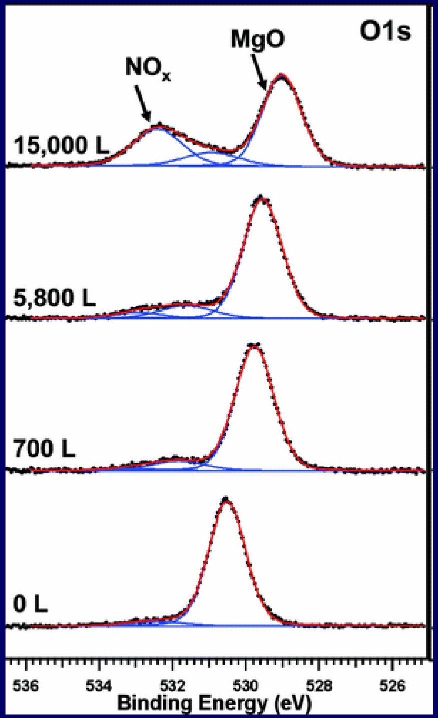
David E. Starr,[⊥,†] Christoph Weis,[∇,‡] Susumu Yamamoto,[#] Anders Nilsson,[||] and Hendrik Bluhm*[,†]



Charge density difference for NO_2 adsorbed on a 2 ML thick MgO/Ag(100) and on bare MgO. The plot shows accumulation of charge on the thin film



O 1s spectra for increasing NO_2 exposure to a 2 ML thick MgO/Ag(100) film

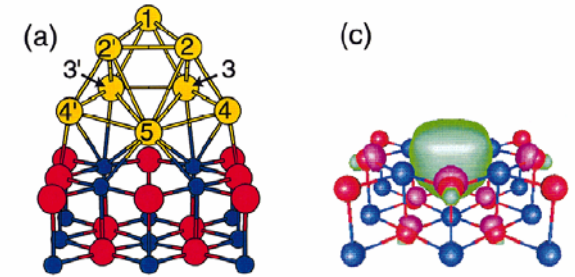


O 1s spectra for increasing NO_2 exposure to a 8 ML thick MgO/Ag(100) film

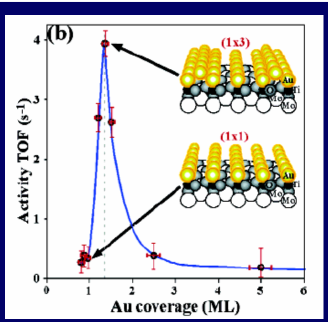
Possible effects on catalysis

- Au$_n$ on a thin film: 2D
- larger periphery
- extra charge, more active

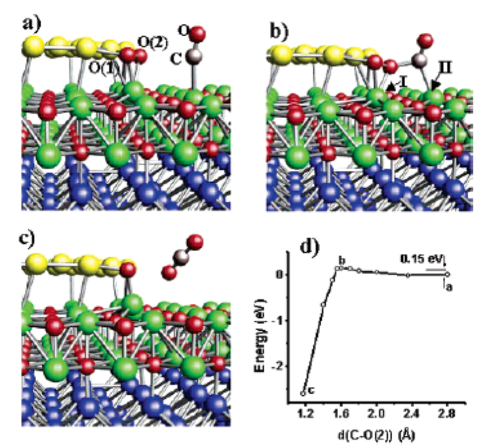
- Au$_n$ on a thick film: 3D
- smaller periphery
- neutrals, less active



Charged Au$_8$/MgO cluster on F center more active than same cluster on non-defective MgO
(Sanchez, Heiz, Landman et al. JPC A 103, 9573, 1999)

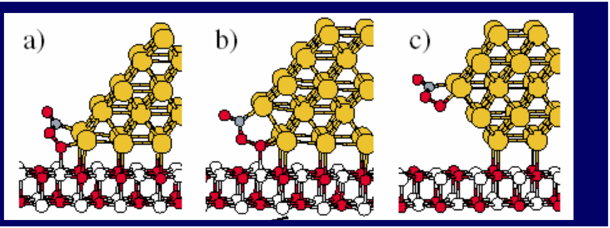


Au/TiOx/Mo: Au 2L much more active than 3L-5L of Au
(Chen, Goodman, Acc. Chem. Res. 39, 739, 2006)

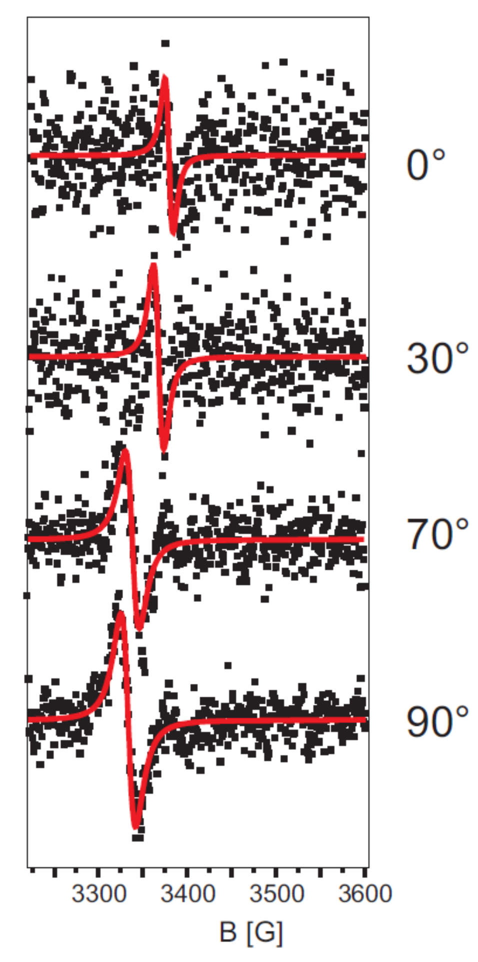


Au$_{20}$/MgO/Mo: Au$_{20}$ 2D more active than Au$_{20}$ 3D in CO oxidation
(Zhang, Yoon, Landman J. Am. Chem. Soc. 129, 2228, 2007)

Au cluster on MgO: periphery more active
(Molina, Hammer, PRL 90, 206102, 2006)



FORMATION OF O_2^- ON MgO/Ag(100): PROOFS FROM EPR

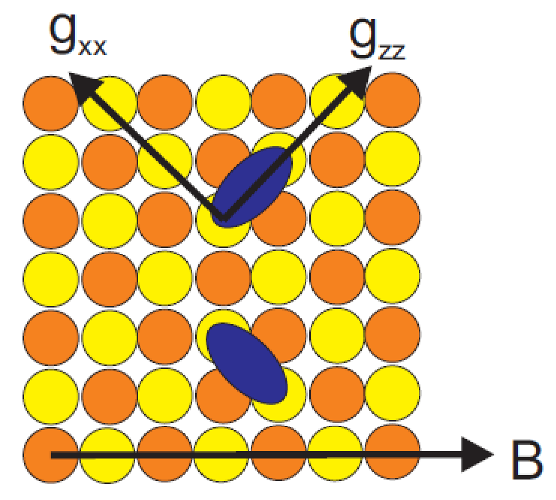


Fit-Parameter

$g_{xx} = 2.004(5)$

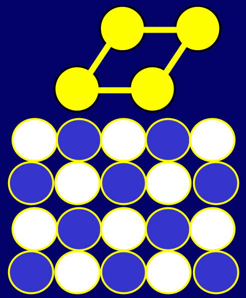
$g_{yy} = 2.015$

$g_{zz} = 2.072$

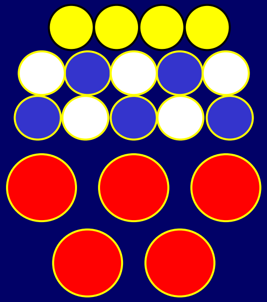


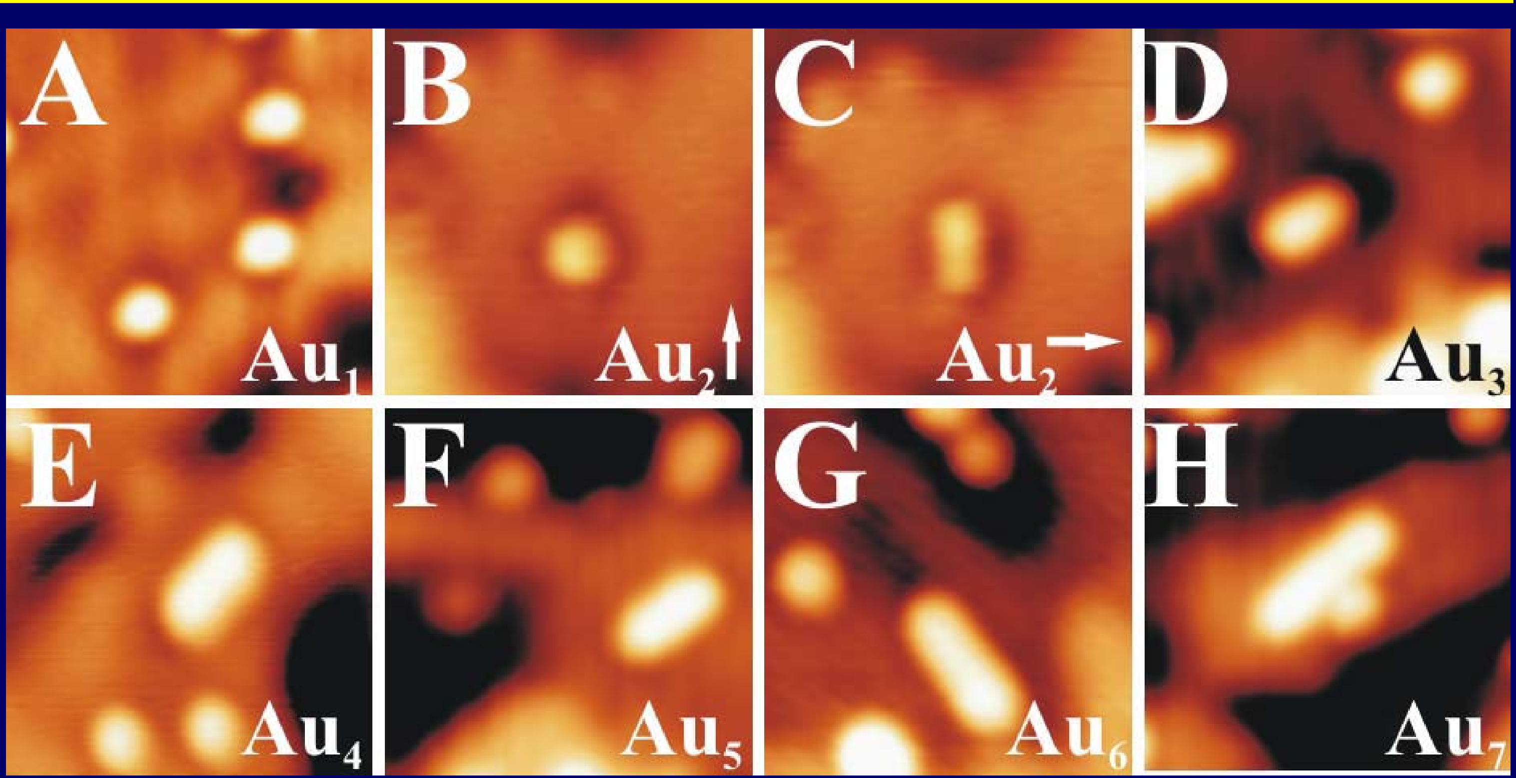
Small Au clusters on MgO/Ag(100)

MgO(100)



MgO/Ag





Structure of small gold clusters different on MgO(100) and MgO/Ag(100)

Simic-Milosevic, Heyde, Lin, König, Rust, Sterrer, Risse,
Nilius, Freund, Giordano, GP, Phys. Rev. B, 78, 235429 (2008)
Frondelius, Hakkinen, Honkala, Phys. Rev. B 76, 073406 (2007)