Morphology, structure and interface properties in metal/oxide systems

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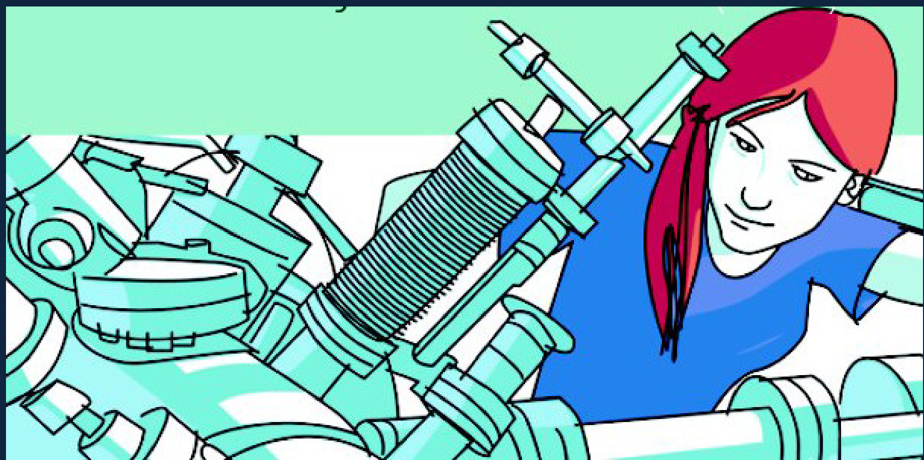
Modena
Italy



overview

1. cerium oxide ultrathin films on Pt(111) + growth of Ag nanoparticles

- introduction
- morphology, composition and structure
- the CeO_2/Pt interface

2. the Fe/NiO interface

- introduction
- depth-resolved magnetic characterization by NRS

cerium oxide

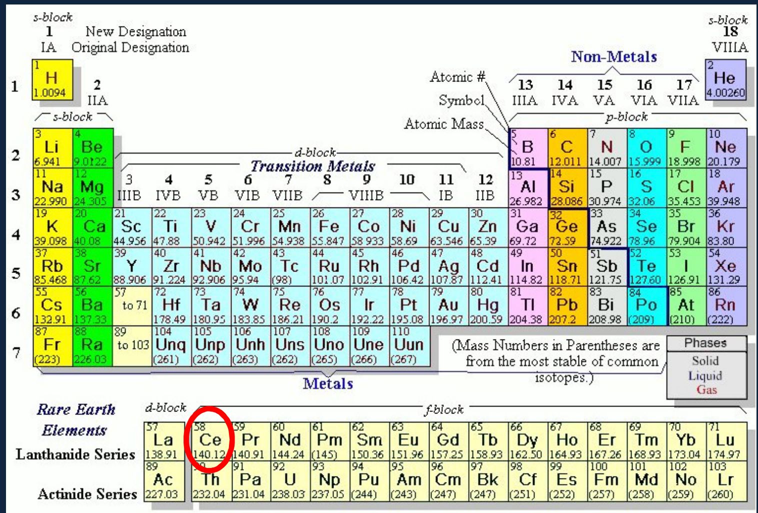
store, transport and release oxygen

oxydizing conditions

$CeO_2 \Leftrightarrow Ce_2O_3$

Ce^{4+} Ce^{3+}

reducing conditions

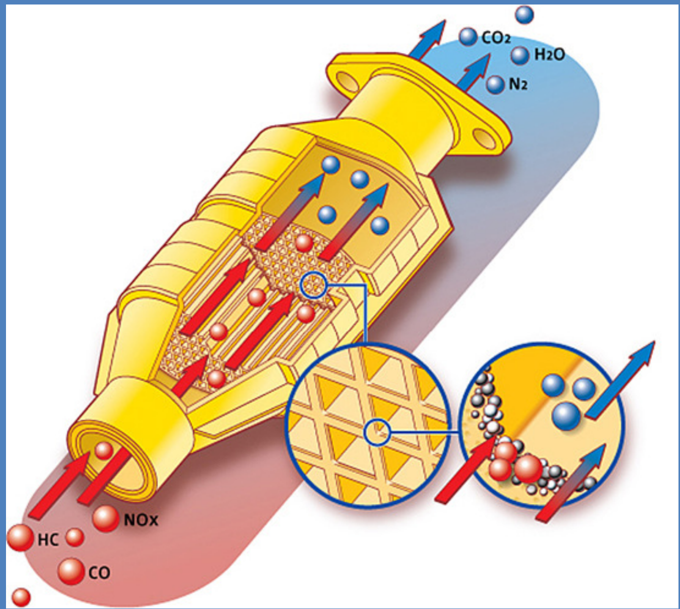


Ce: [Xe] $4f^1$ $5d^1$ $6s^2$

+ metals
- supported nanoparticles (Pt, Ag, Au, Rh,...)
- dopants (Sm, Gd, La,...)

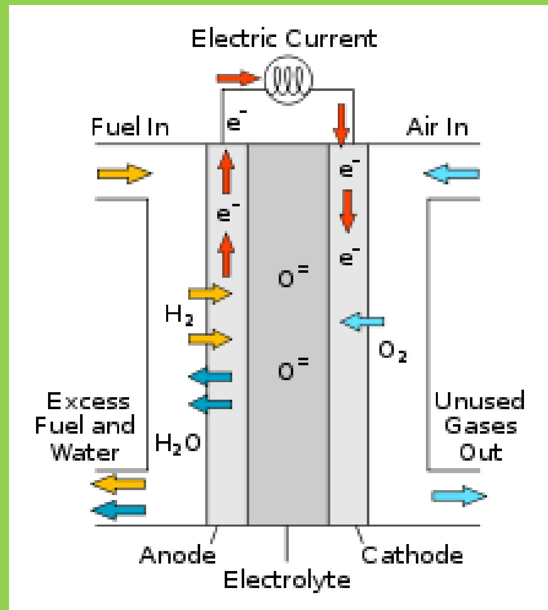
cerium oxide

catalytic converters



- oxidize CO to CO_2
- reduce NO_x to N_2
- self clean from C deposits

solid-oxide fuel cells



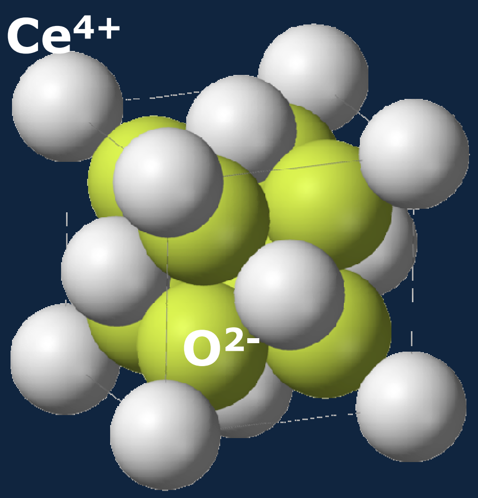
- solid electrolyte
  high conductivity for O ions
- production of hydrogen
  water gas shift
  theromochem. water splitting

cerium oxide

model systems ⇒ understand and optimize the properties

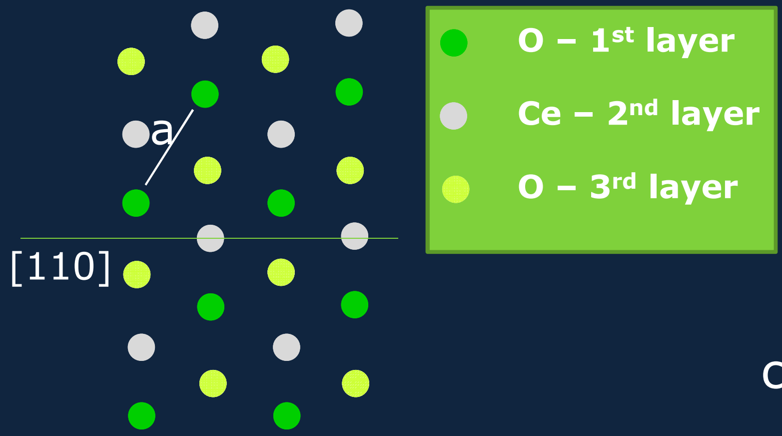
CeO_2

CaF_2 - structure



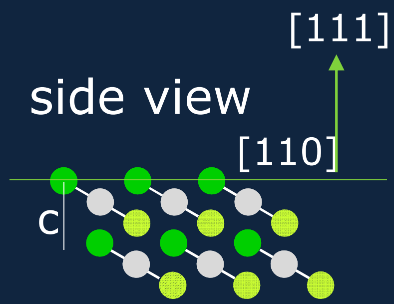
(111) surface

top view



a_{CeO2}=3.826 Å

side view

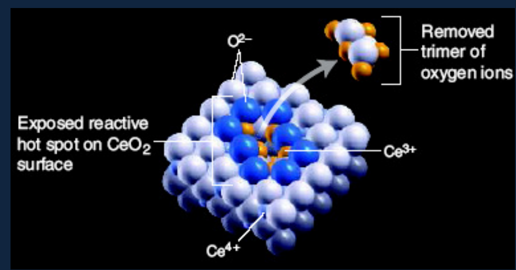


c_{CeO2}=3.124 Å

previous studies

open points

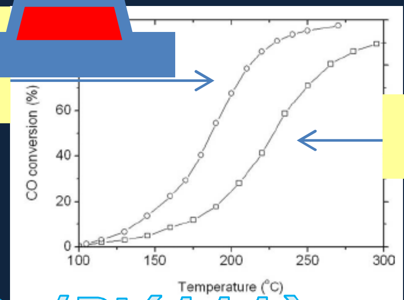
1. oxygen vacancy formation mechanism



F. Esch et al., Science 309 (2005) 752

2. metal/oxide interaction

and {100}



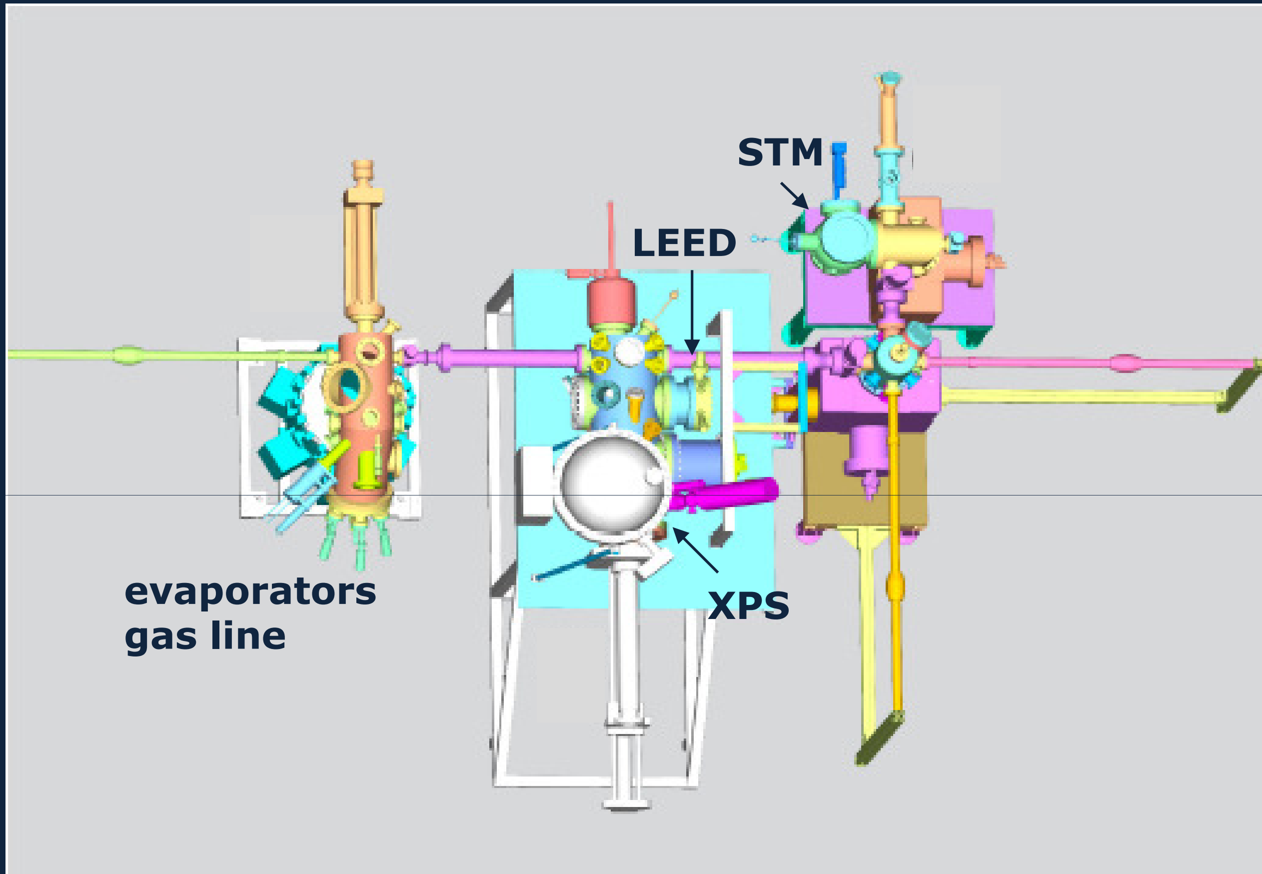
np exposing mainly {111}

3. stabilization of surfaces different from (111)

⇒ **XPS, STM, LEED study of CeO_2/Pt(111)**

Z. Zhou et al., J. Cat. 299 (2005) 206

experimental



substrate

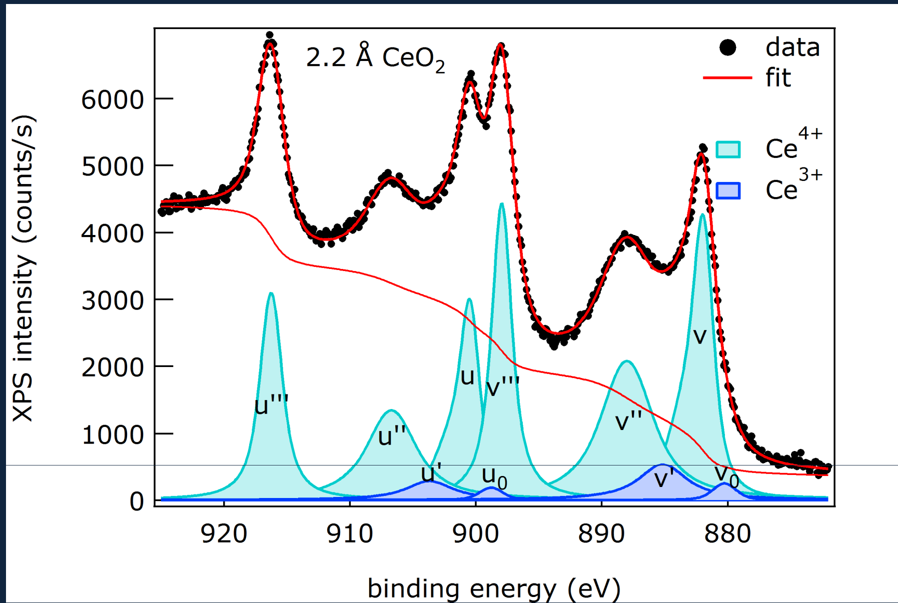
Pt(111) → a_{Pt}=2.775 Å
a_{CeO2}=3.826 Å

m=38%

CeO_2 growth conditions

R_{Ce} = 3×10^{-3} Å/sec @ RT
P_{O2}=1×10^{-7} Torr

Ce 3d XPS

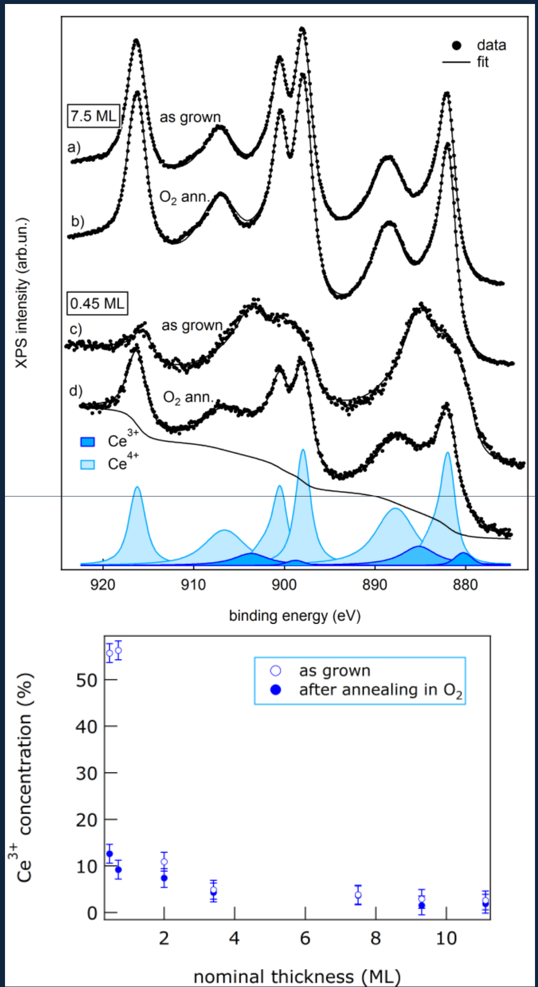


ION	Initial state	Final state	peak
Ce^{3+}	$3d^{10}4f^1$	$3d^9 4f^2 V^{n-1}$	v^0, u^0
	$3d^{10}4f^1$	$3d^9 4f^1 V^n$	v’, u’
Ce^{4+}	$3d^{10}4f^0$	$3d^9 4f^2 V^{n-2}$	v, u
	$3d^{10}4f^0$	$3d^9 4f^1 V^{n-1}$	v”, u”
	$3d^{10}4f^0$	$3d^9 4f^0 V^n$	v’’’, u’’’

M. Romeo, et al. Surf. Interface Anal. 20 (1993) 508.
Skala et al. J. Electron Spectrosc. Rel. Phen. 169 (2009) 20

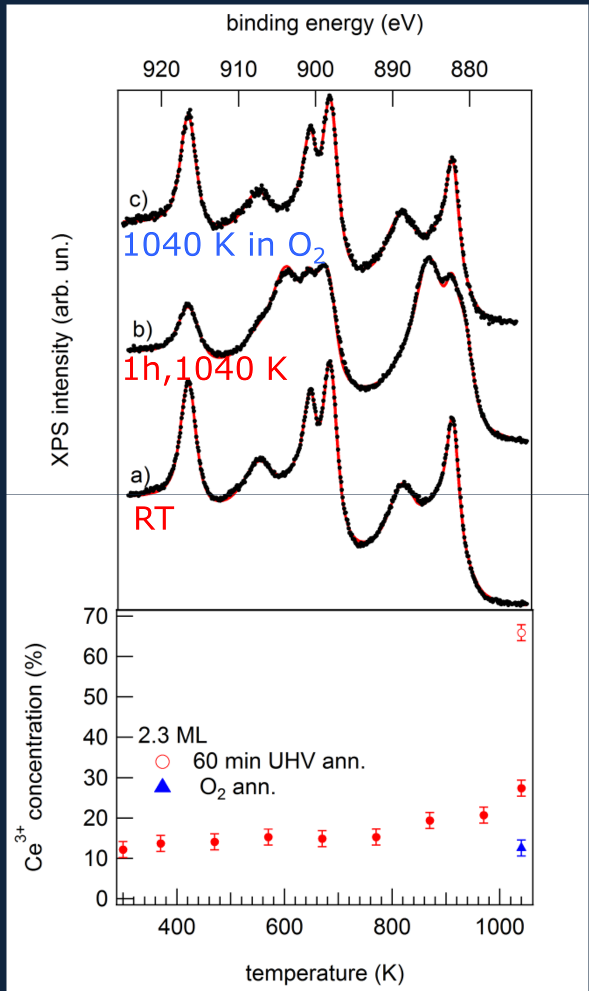
stoichiometry

Ce 3d XPS



annealing @1040 K in O_2 oxidizes the films

Ce 3d XPS



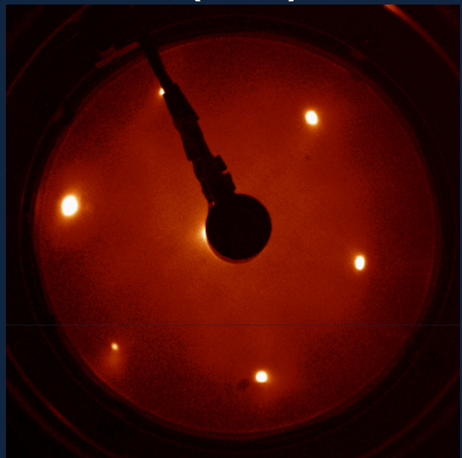
annealing in UHV reduces the films

structure

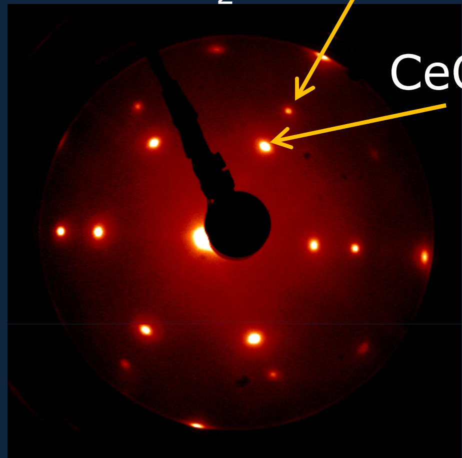
LEED

E=80 eV

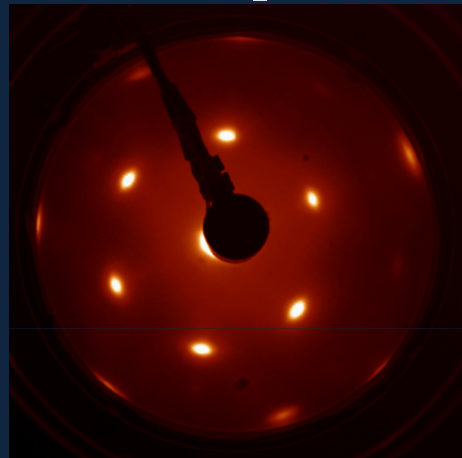
clean Pt(111)



2 ML CeO_2



11 ML CeO_2



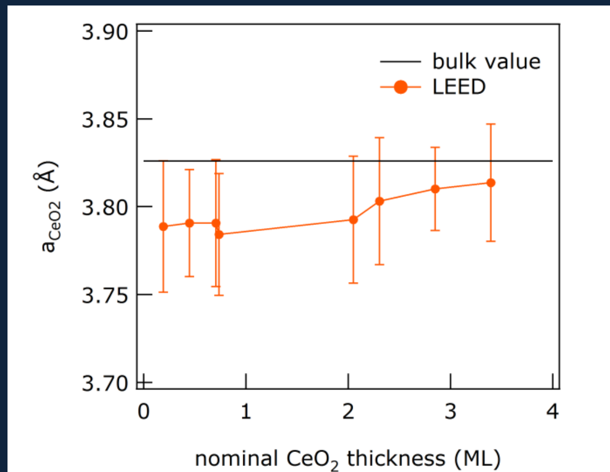
a_{CeO2}=3.826 Å

a_{Pt}=2.775 Å

m=38%

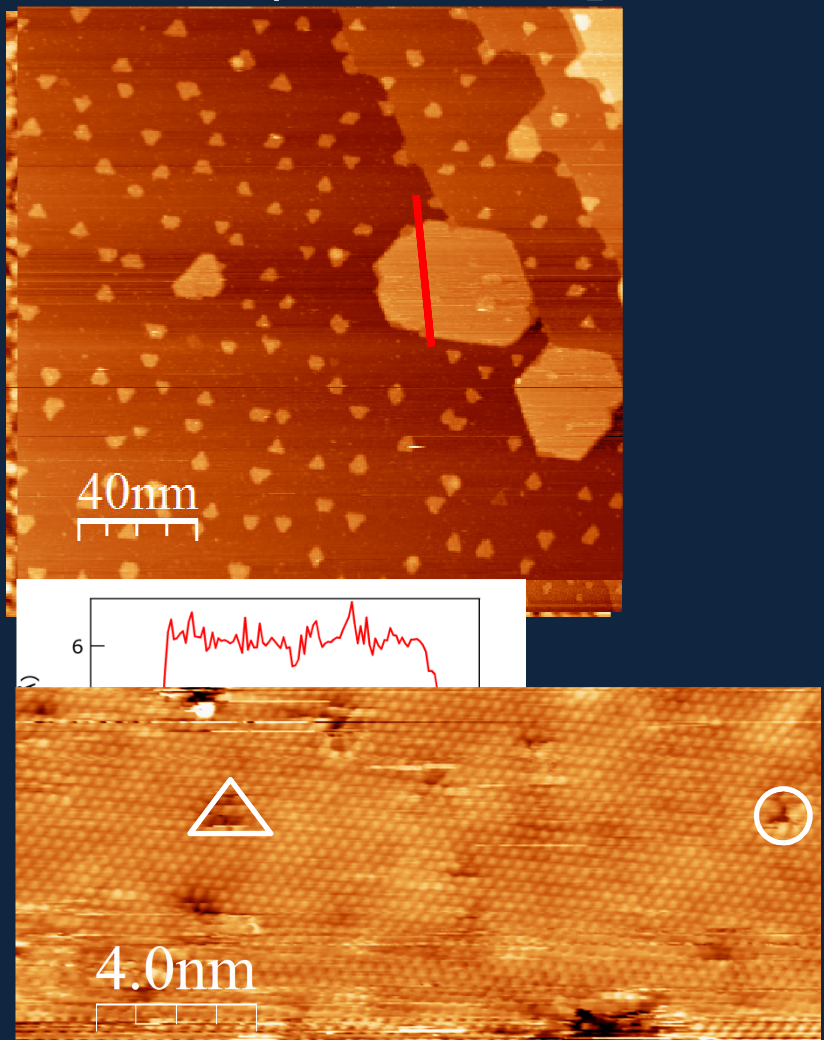
epitaxial films

(111) CeO_2
<110>$_{CeO2}$//<110>$_{Pt}$



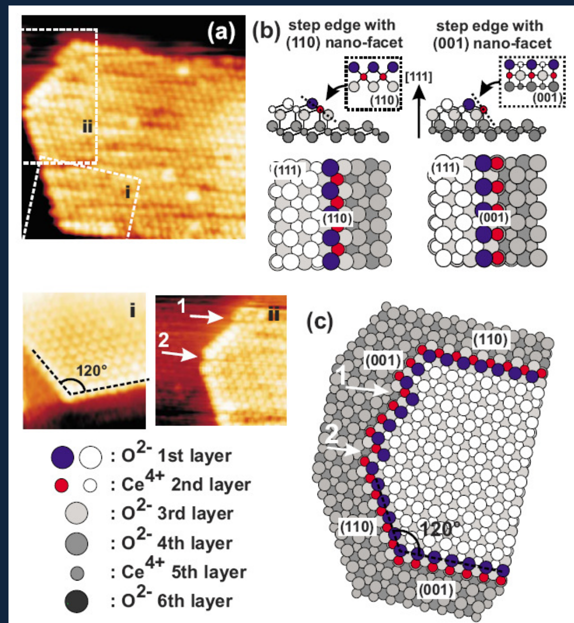
morphology

20ML as deposited / 2 ML dep. 1040 K O_2



1. Large islands → CeO_2

- 30-50 nm wide
  6 Å (2 O-Ce-O ML) high
- atomically flat
- preferentially at Pt step edges
- straight edges, kinks at 120°

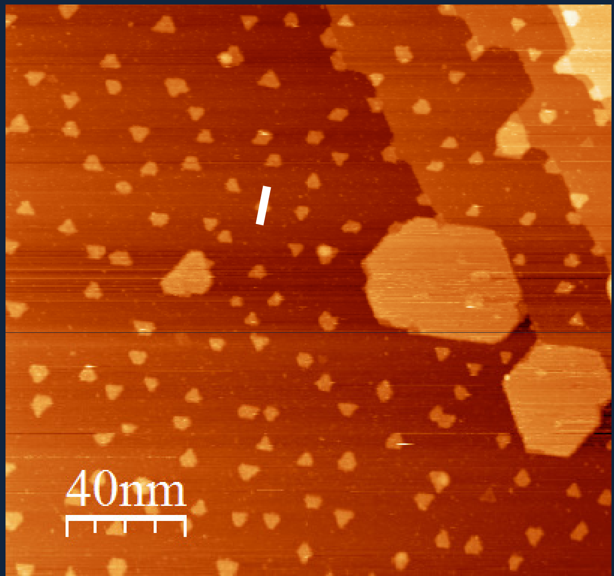


309(05)752

S. Torbrügge et al. APL 93 (08) 073112

morphology

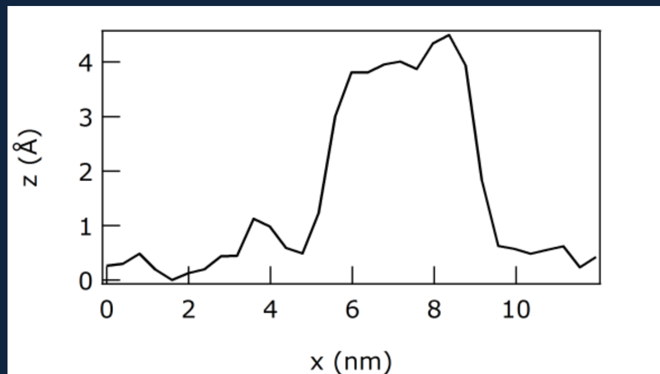
0.2 ML ann. 1040 K O_2



0.5 V 0.2 nA

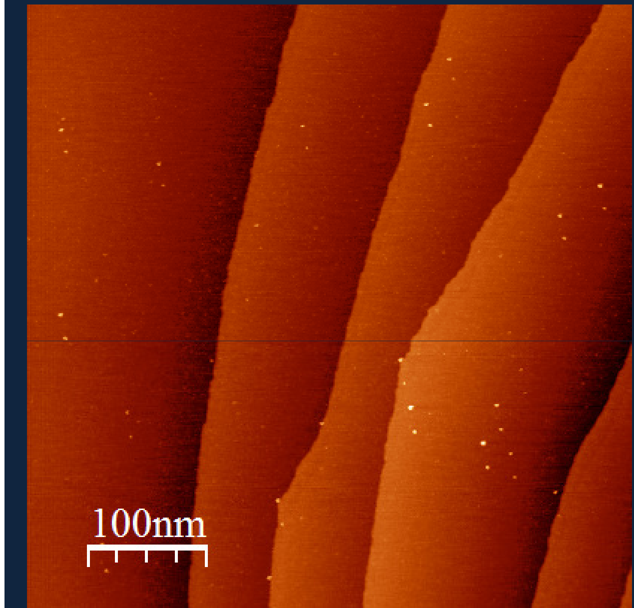
1. Small islands

- ~ 5 nm wide
  ~ 3 Å high
- atomically flat
- uniformly distriubuted
- triangular shape (kinks at 60°)

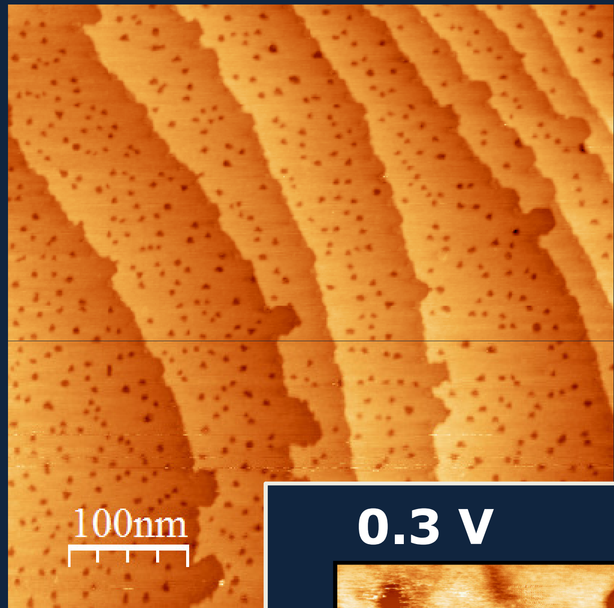


morphology

clean Pt(111)

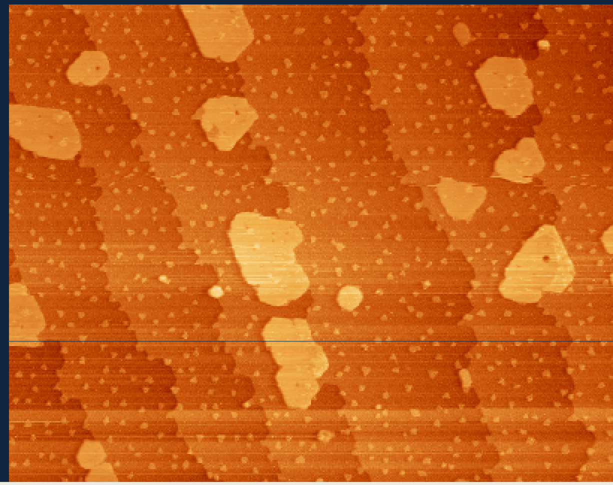


Pt (111)
ann. @ 1040 K O_2

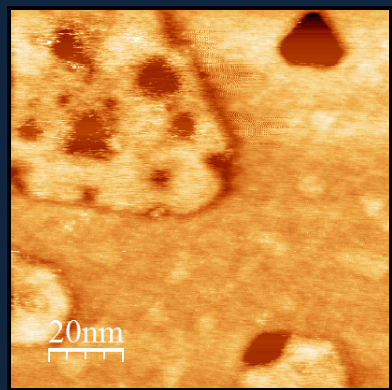


0.5 V 0.1 nA

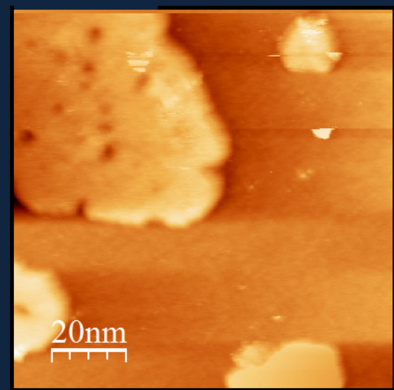
0.2 ML CeO_2
ann. @ 1040 K O_2



0.3 V



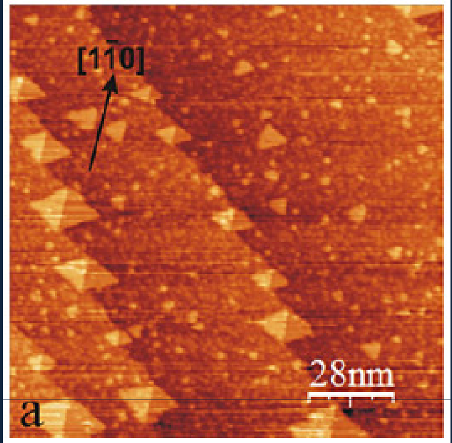
1 V



0.7 ML CeO_2 0.1nA

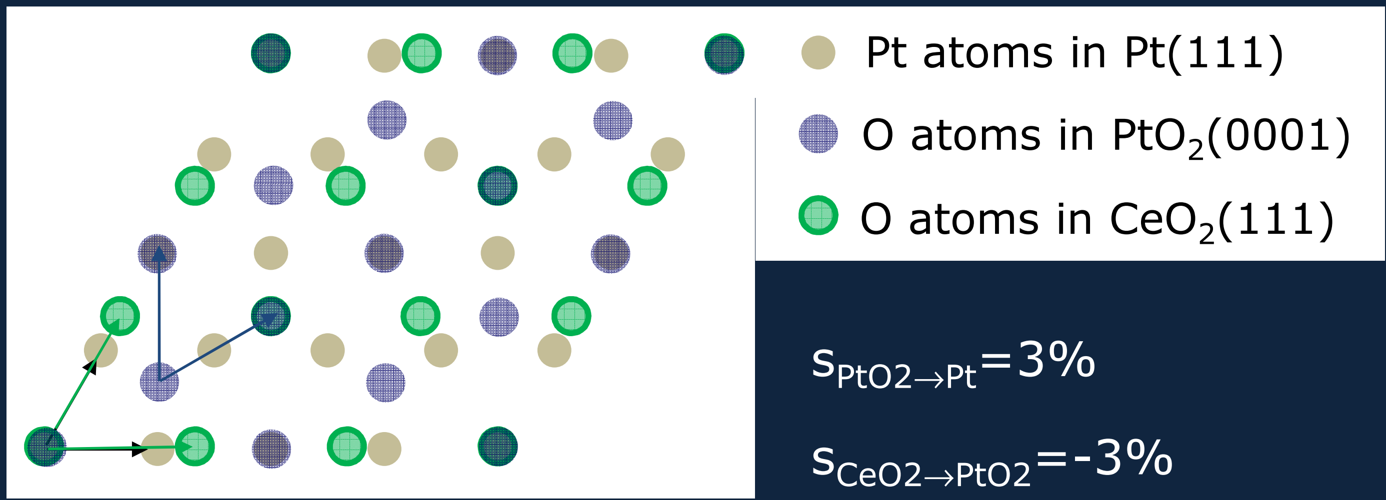
morphology

α-$PtO_2(0001)$ nanoislands



S.A. Karsnikov et al.
Nanotech. 21 (10) 335301

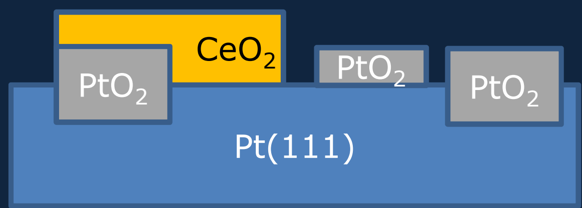
$a_{Pt}=2.78$ Å
$a_{PtO2}=3.12$ Å
$a_{CeO2}=3.83$ Å



$s_{PtO2\rightarrow Pt}=3\%$

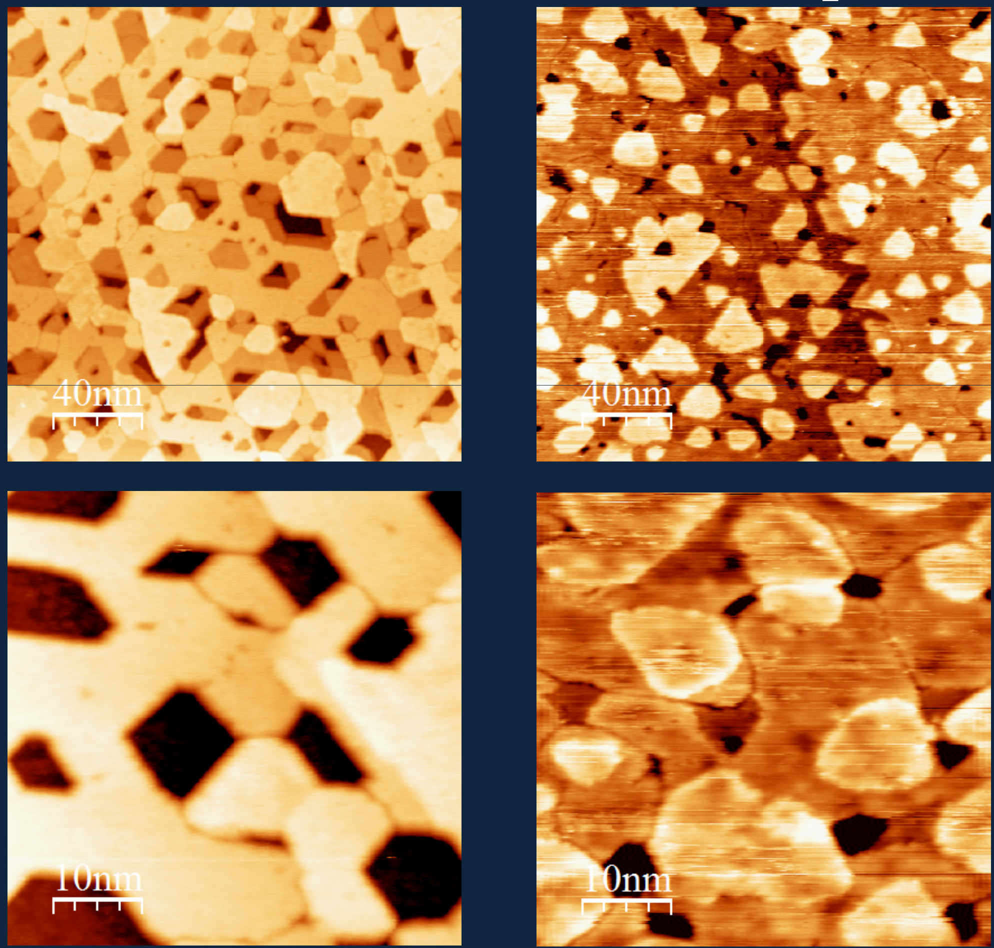
$s_{CeO2\rightarrow PtO2}=-3\%$

PtO_2 islands may act as a template for the stabilization of CeO_2 in the observed epitaxial orientation



morphology

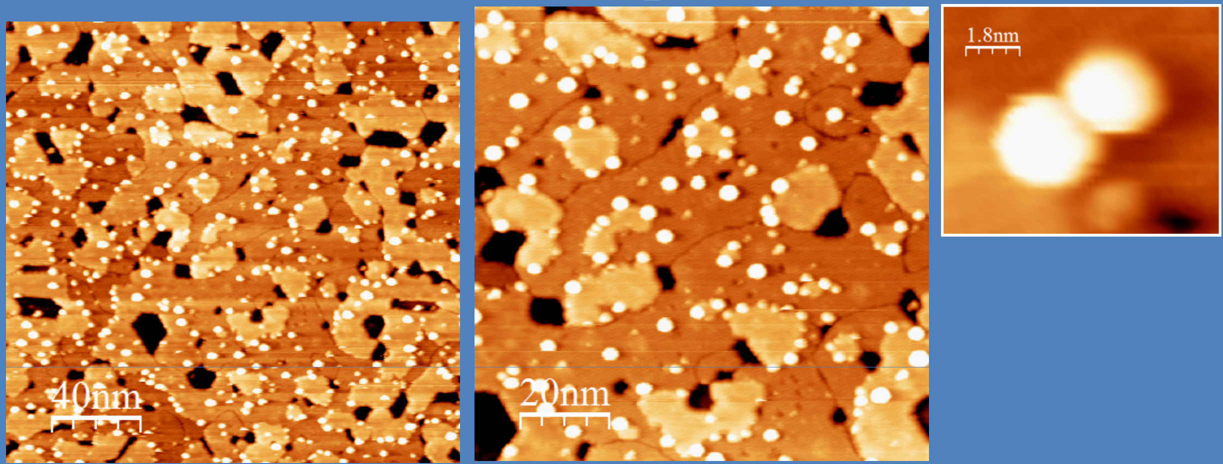
3.4 ML CeO_2 9.3 ML CeO_2



- flat CeO_2 terraces
- straight edges 120°
- linear defects

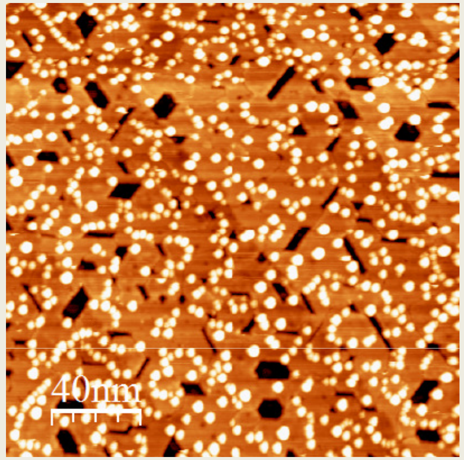
Ag/CeO_2

0.07 Å Ag / 3 ML CeO_2



d=0.5-3nm
h=0.5-1 nm

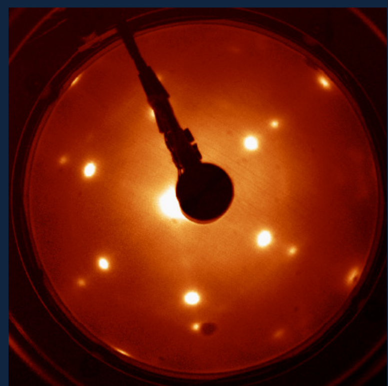
0.2 Å Ag / 3 ML CeO_2



d= 2-5 nm
h=0.5-2 nm

- decoration of CeO_2-CeO_2 steps
- hexagonal shape → (111) orientation

epitaxy

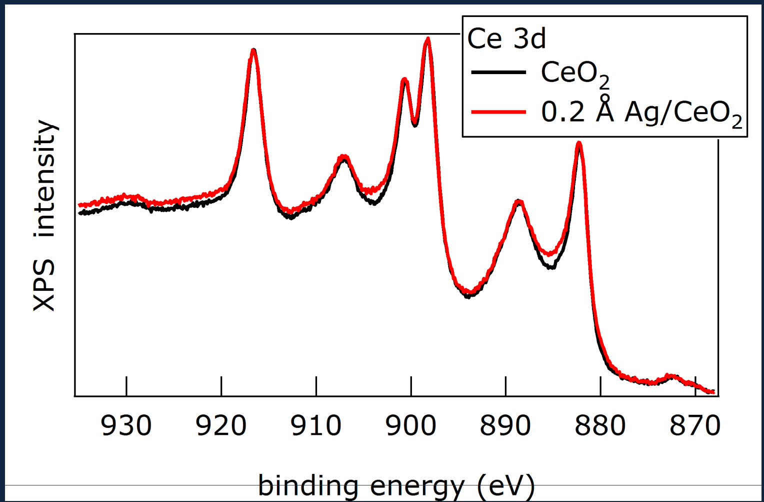


Ag film on CeO_2

a_{CeO2}=3.826 Å
a_{Ag}=2.892 Å

m=32%

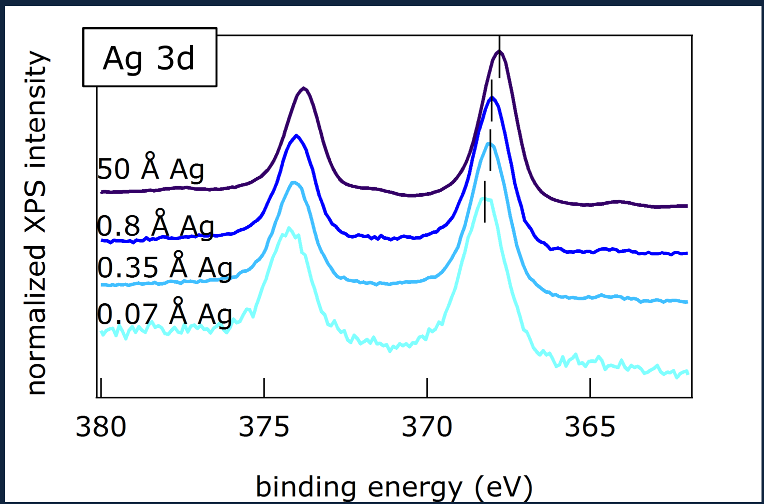
Ag/CeO_2

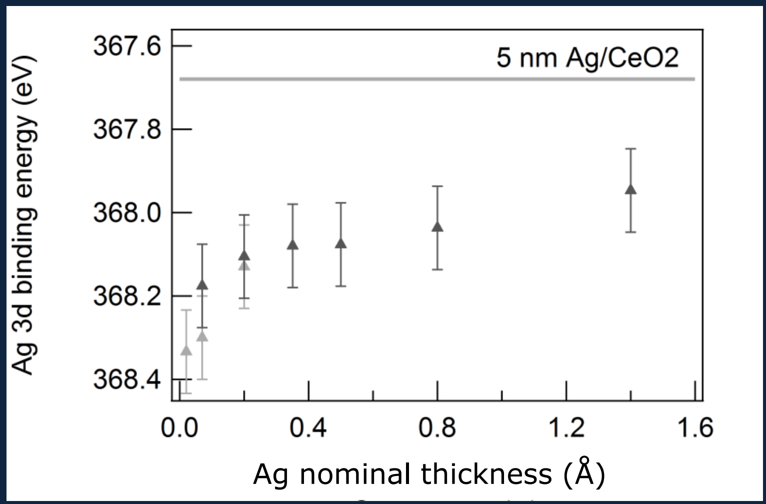


ceria reduction

higher Ag 3d BE

oxidation, dimensionality, charge transfer

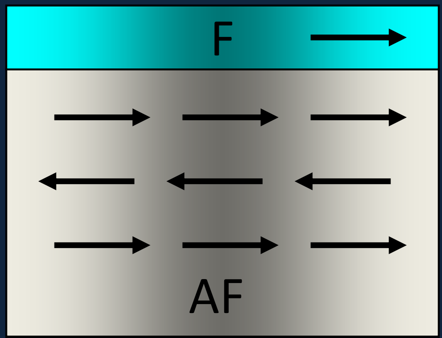




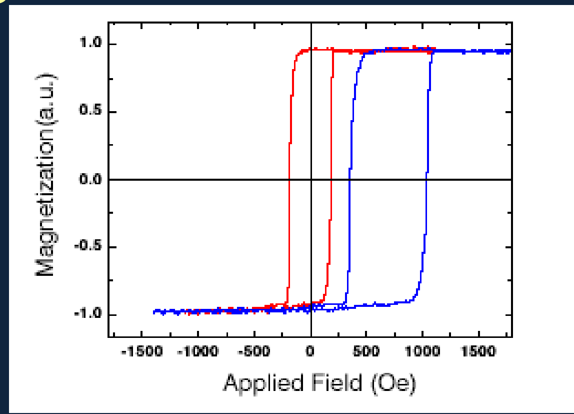
Fe/NiO

motivation

F/AF interface – exchange bias

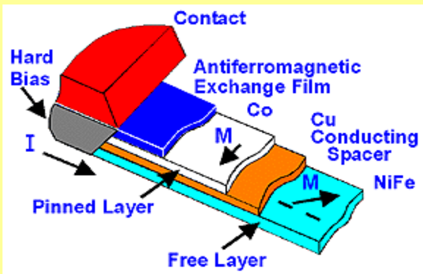


heating up to T_N
+
cooling in H



exchange bias

pinning of the magnetization of one of the FM layers in magnetoresistive devices



extra source of anisotropy to shift the SPM limit in ultrahigh density magnetic memories

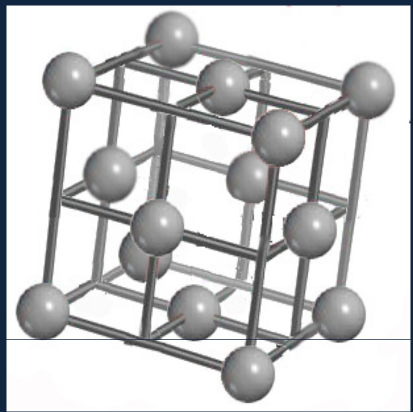
V. Skumryev et al., Nature 423 (2003) 850.

- no complete and quantitative physical model of exchange bias
- strong dependence on the structure of the interfaces

study of atomic-scale characterized systems

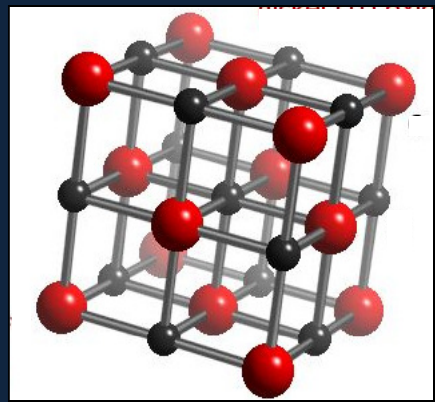
structure

Ag



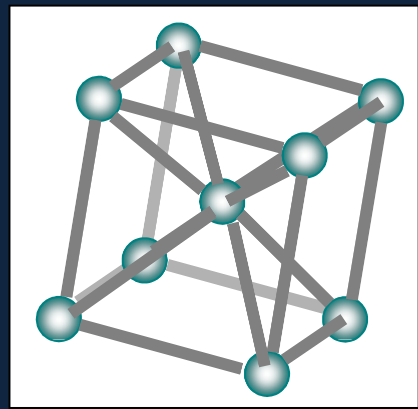
a_{Ag}= 4.086 Å

NiO



a_{NiO}= 4.176 Å

Fe



a_{Fe}= 2.866 Å

d_{Fe} = 4.053 Å

$m_{NiO\text{-}Ag}$ ~ 2%

$m_{Fe\text{-}NiO}$ ~ 3%

Fe

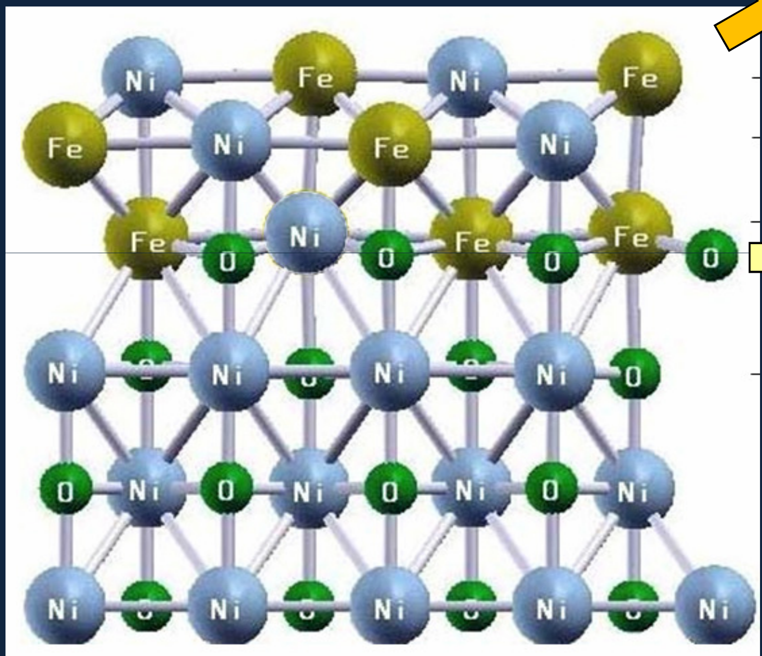
NiO

Ag(001)

epitaxial system

NiO T_N=520 K >> RT

previous studies



bct Fe-Ni alloy formation (3 ML)

P. Luches et al., Surf. Sci. 532 (2003) 409.
S. Benedetti et al., Surf. Sci. 572 (2005) L348.

planar FeO-like phase

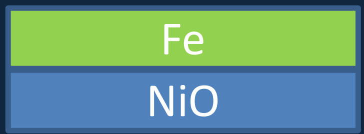
P. Luches et al. , Phys. Rev. Lett. 96 (2006) 106106.

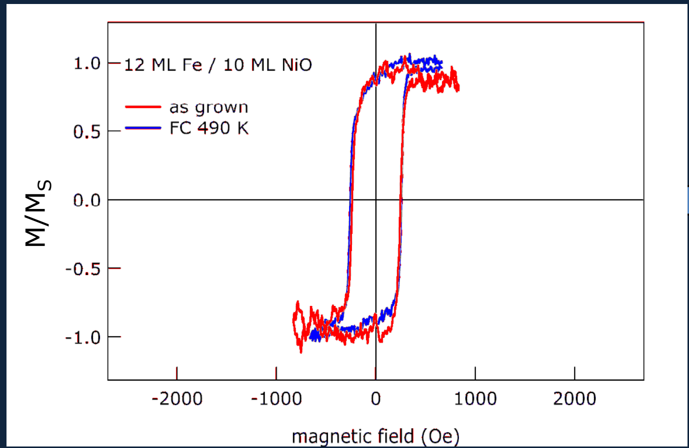
NiO reduction+ Fe oxidation

T.J. Regan et al., Phys. Rev. B 64 (2001) 214422.
R. De Masi et al. Surf. Sci. 513 (2002) 523.

magnetic properties

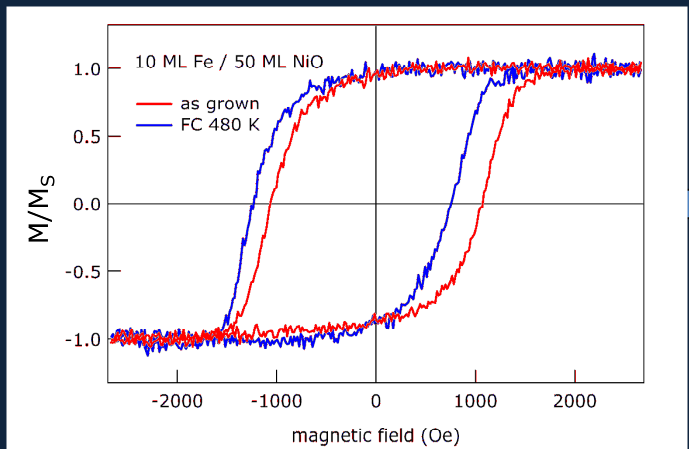
MOKE





H_{EB}= 0 Oe

no EB for $t_{NiO} \leq$ 25 ML

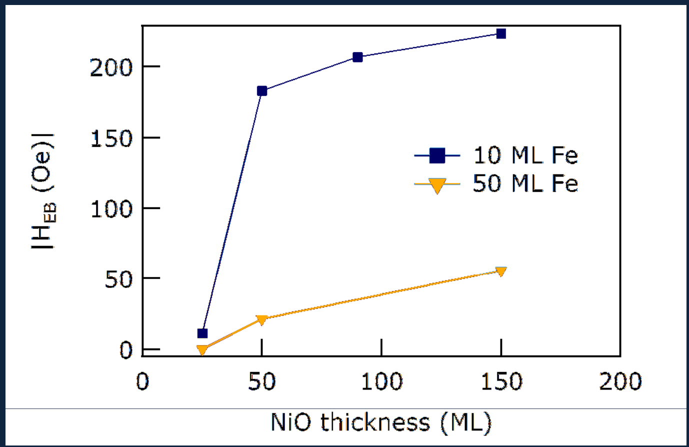


H_{EB}= -220 Oe

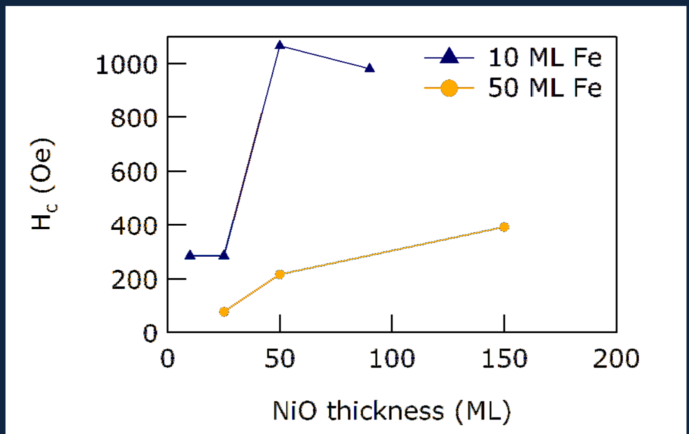
P. Luches et al., PRB 81 (2010) 054431

magnetic properties

exchange bias



coercive field



P. Luches et al., PRB 81 (2010) 054431

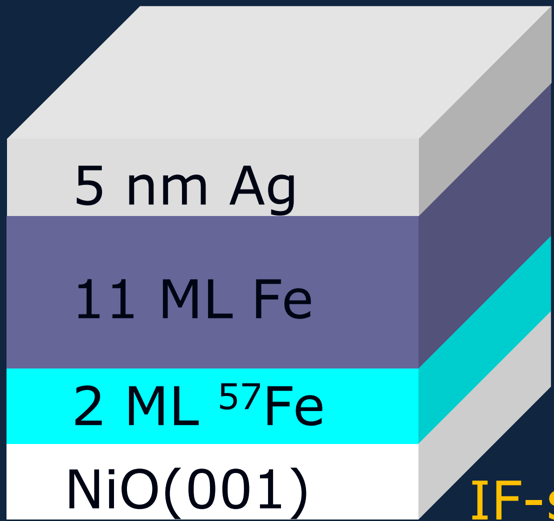
? **role of the interface**

oxidized Fe phase
uncompensated moments in NiO

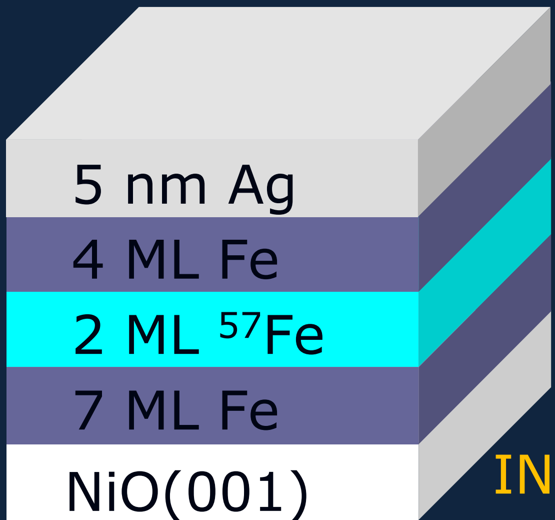
→ **depth resolved magnetic characterization by NRS**

P. Luches et al., NIMB 268 (2010) 361.

experimental



IF-sample



IN-sample

growth conditions

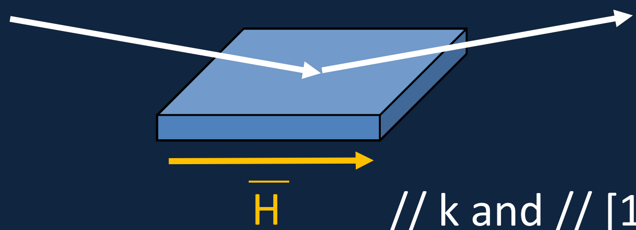
Substrate: Ag(001)

NiO: R_{Ni}~1 Å/min P_{O2}~1X10^{-7} torr
T_{Ag}=460K

Fe: R_{Fe}~1 Å/min RT

+ NRS measurements
@ ESRF ID18

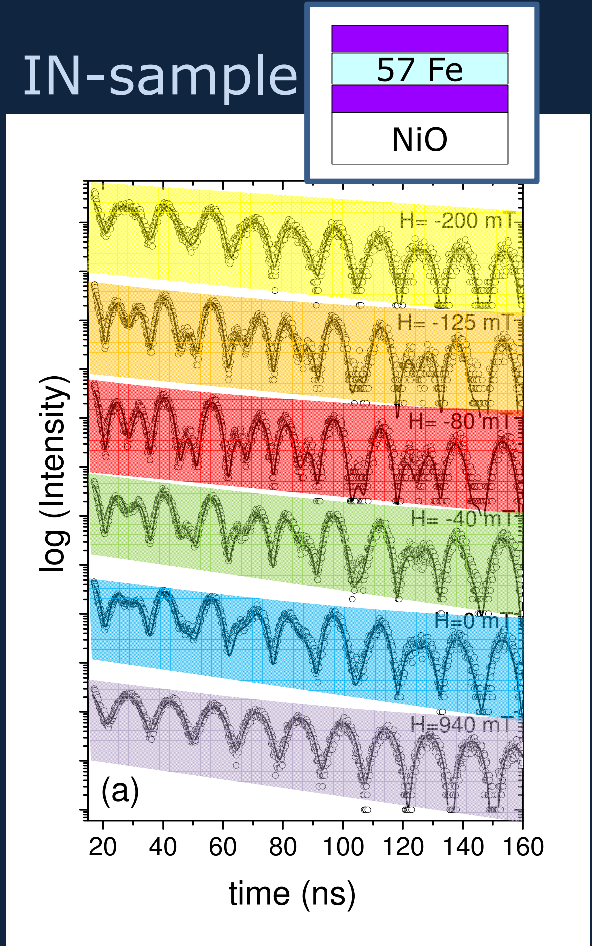
hν=14.4 keV Δt=176 ns



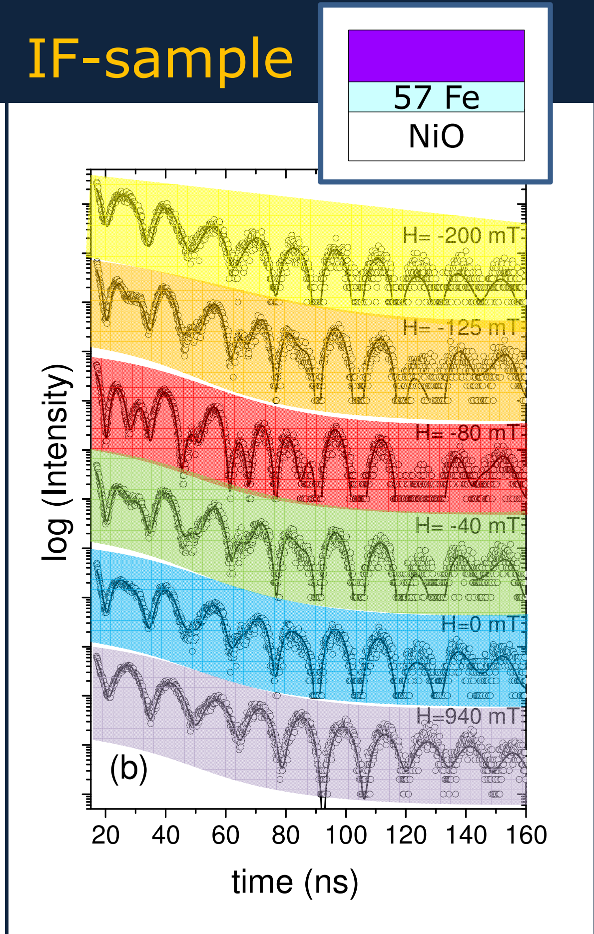
// k and // [100] Fe

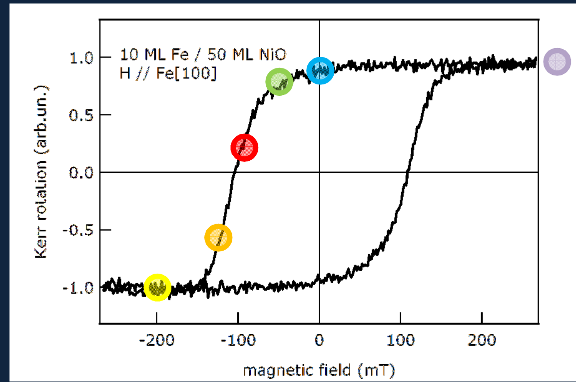
NRS data

IN-sample



IF-sample





fit by NRS package
by C. L'abbe
W. Sturhan, HH 125 (200) 149

Sample	Component #	IS (mm/s)	B_{HF} (T)	ΔB_{HF} / B_{HF} (%)	RW (%)
IN	1	0 fixed	-33.2 (2)	2	100
IF	1	0 fixed	-33.5 (2)	6 (1)	60 (6)
	2	0.42 (5)	-37.2 (3)	11 (2)	20 (2)
	3	0.42 (5)	+25.3 (5)	90 (5)	20 (2)

metallic

metallic

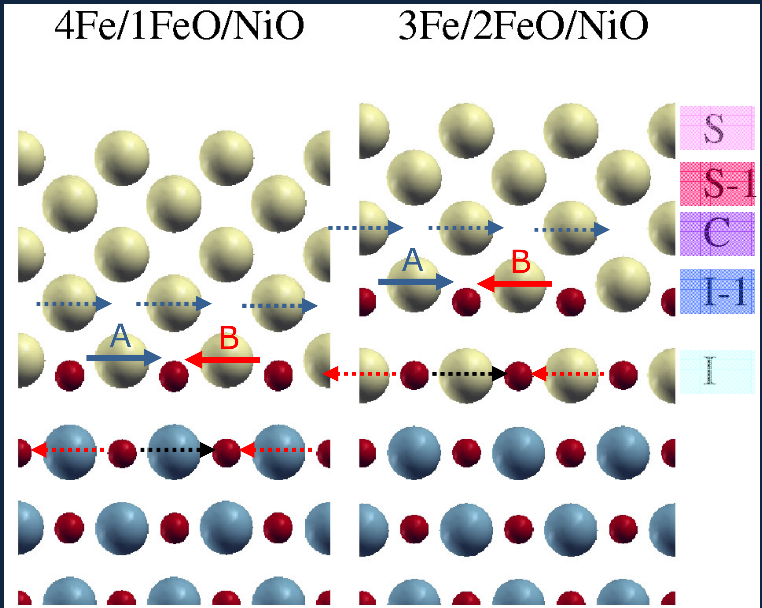
oxidized

large $|B_{HF}|$

P. Luches et al., PRB 83 (2011) 094413

comparison with theory

DFT APW+lo GGA



$$B_{hf}=B_C+\cancel{B_{dip}}+\cancel{B_{orb}}$$

$$B_C=B_{core}+B_{val}$$

$$B_{val}=B_{LOC}+B_{NON\text{-}LOC}$$

$$|B_A| = | B_{core}+B_{LOC}+4B_{NN}|$$

$$|B_B| = |B_{core}+B_{LOC}-4B_{NN}|$$

System	4Fe/1FeO/NiO		3Fe/2FeO/NiO	
	B_{HF}(T)	m (μ_B)	B_{HF}(T)	m (μ_B)
S	-24,-25	2.9	-22,-22	3.0
S-1	-37,-37	2.4	-37,-33	2.5
C	-32,-28	2.5	-25,-25	2.7
I-1	-31,-30	2.4	**-37,+14**	**3.1**
I	**-37,+17**	**3.1**	**-35,+37**	**3.5**

AFM config. for Fe atoms in FeO

asymmetry in positive and negative B_{hf}

NRS

Sample	Component #	IS (mm/s)	B_{HF} (T)	$\Delta B_{HF}/B_{HF}$ (%)	RW (%)
IF	1	0 fixed	-33.5 (2)	6 (1)	60 (6)
	2	0.42 (5)	-37.2 (3)	11 (2)	20 (2)
	3	0.42 (5)	+25.3 (5)	90 (5)	20 (2)

$\Rightarrow$ **antiferromagnetic FeO phase**

P. Luches et al., PRB 83 (2011) 094413

S. Blügel et al., PRB 35 (87) 3271

summary

CeO_2

- CeO_2(111) films with wide flat terraces can be obtained on Pt(111)
- the Ce^{3+} concentration in the films can be reversibly modified by thermal treatments in UHV or O_2
- Ag nanoparticles reduce ceria and have a higher 3d BE than the bulk

Fe/NiO

- an antiferromagnetic Fe oxide layer is present at the interface
- DFT calculations can be of great help to interpret the NRS data

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