Self-assembly and **Guided self-organization** of oxide nanostructures from chemical solutions

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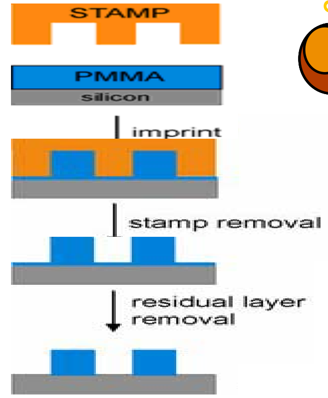
MOTIVATION AND AIM OF THE WORK

• **Nanotechnology** aims the low-cost and mass fabrication of increasingly small devices required for present and future applications

APPROACHES

Top-down

-e-beam lithography
-X-ray/UV lithography
-μC-printing
-Focused Ion Beam
-Nanoimprint Lithography (NIL)
-SPM...

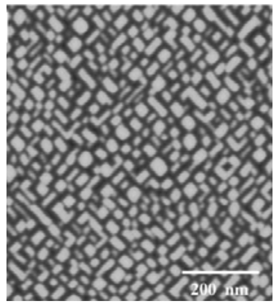


NIL process

Bottom-Up

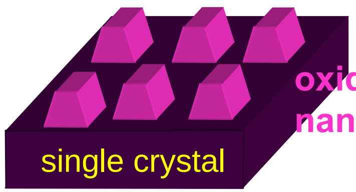
Self-assembly and Self-organized growth at surfaces

-supramolecular engineering
-metallic, semiconductor and oxide nanostructures...



Si_xGe_{1-x} grown over Si (111) substrate

• Oxide nanostructured templates



oxide nanostructures

exhibit interesting properties for

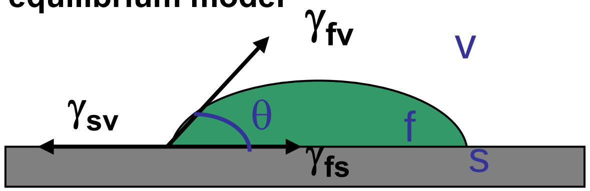
Our interest: self-assembling of oxide nanostructures with substrate modification through **NANOINDENTATION,** Focused Ion beam, …

superconductivity...

SELF-ASSEMBLY OF NANOISLANDS

Working Framework: THERMODYNAMICS

Liquid nucleus in equilibrium model

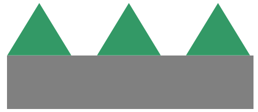


Young`s equation $\gamma_{sv}=\gamma_{fs}+\gamma_{fv}\cos\theta$

3 Growth Modes

•3D growth (Volmer-Weber)

$\gamma_{sv} < \gamma_{fs} + \gamma_{fv}$



•2D (Frank van der Merwe) growth

$\gamma_{sv} > \gamma_{fs} + \gamma_{fv}$

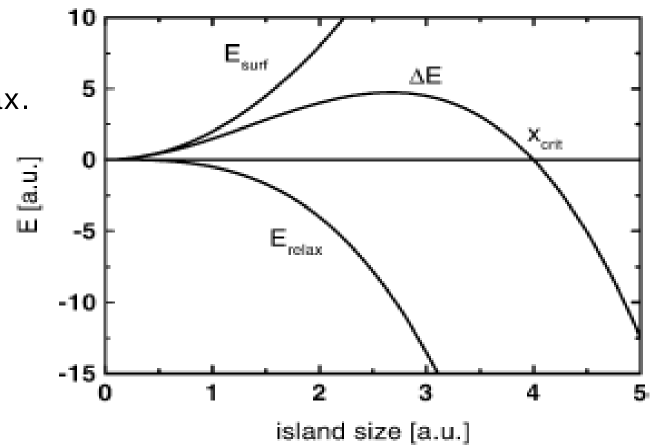
•Layer + Island growth (Stranski-Krastanov)

(ex; when strain energy due to lattice mismatch is present)

Heteroepitaxy

- Surface Free Energy ($\sim\gamma$)
- Elastic Relaxation Energy ($\sim\varepsilon^2$; $\varepsilon = (a_s - a_f)/a_f$)

$$\Delta E \sim \Delta E_{surf.} + \Delta E_{elast.\ relax.}$$

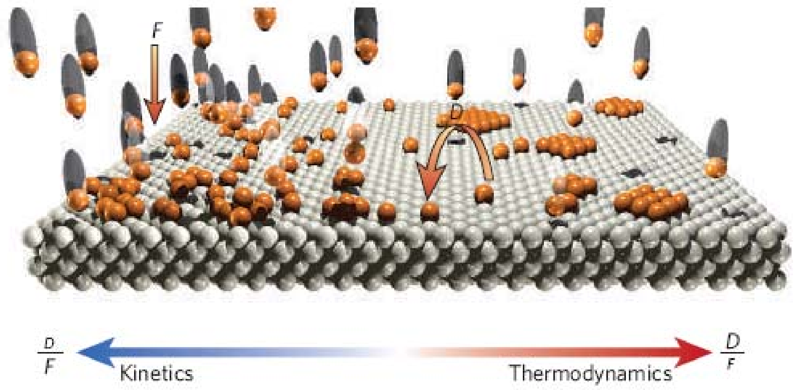


B. Voigtländer/Surface Science Reports 43 (2001)

BUT...

Working Framework: KINETICS

Real growth phenomena are **non-equilibrium**



Barth et al. NATURE 2005 Vol 437 I 29

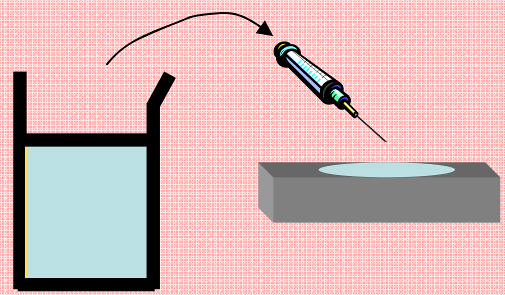
D ⇨ Diffusivity

F ⇨ Deposition rate

Chemical Solution Deposition (CSD)

CSD Vs Vacuum Techniques:

✓**Low Cost**
✓**Scalable**
✓**Rapid**



Different initial conditions!

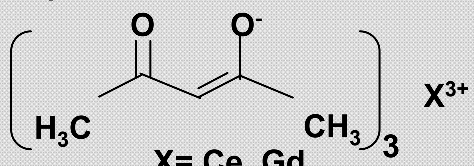
CHEMICAL SOLUTION DEPOSITION (CSD)

1 Precursor **solution synthesis**

(of a given concentration)

e.g. $Ce_{1-x}Gd_xO_{2-y}$ metallorganic precursor solution preparation (MOD-CSD)

•**X (III) 2,4-pentanedionate**

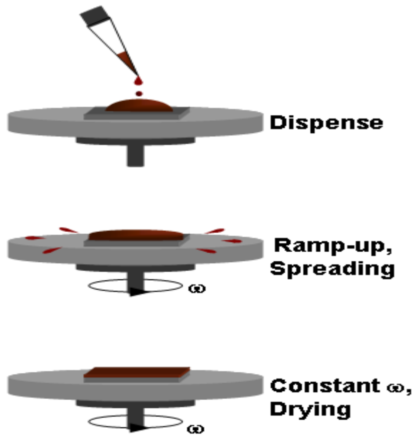


X= Ce, Gd

+

•**Isopropanol**
•**Propionic acid**

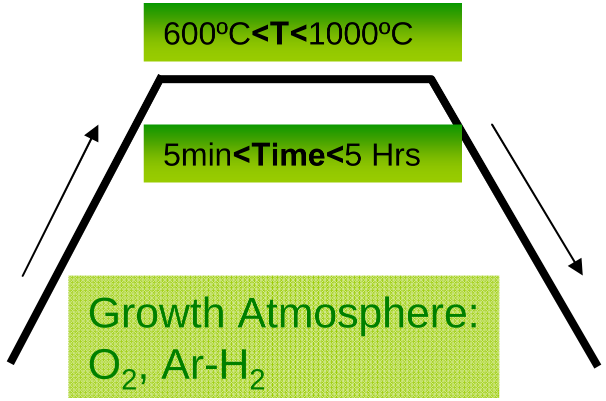
2 **Solution Deposition** by Spin Coating onto the substrate



3 **Heat treatment**

PYROLISIS of the organic species (~300ºC/400ºC)

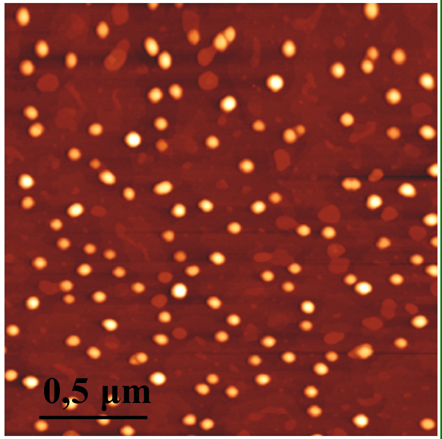
High temperature treatment for the amorphous layer crystallization



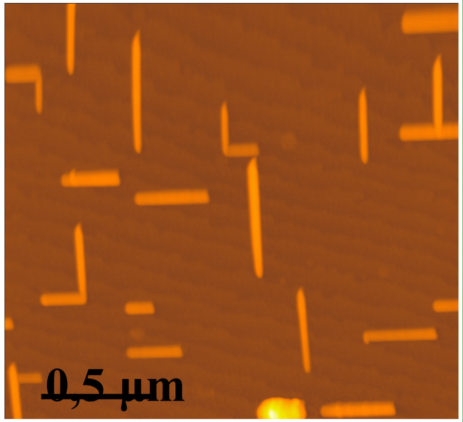
Islands' characteristics (size, morphology,…) can be tuned through the **kinetic** parameters (temperature, atmosphere, dwell time,….)

CSD: A general tool for nanostructured template fabrication

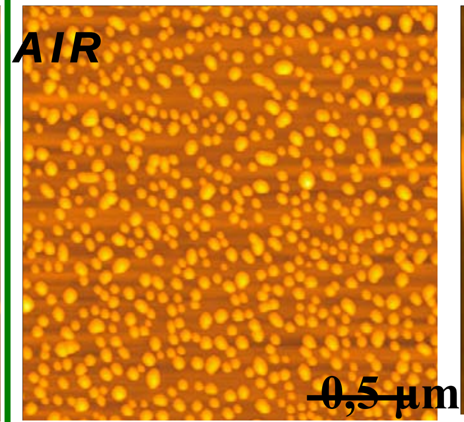
Fluorite: $Ce_{1-x}Gd_xO_{2-Y}$



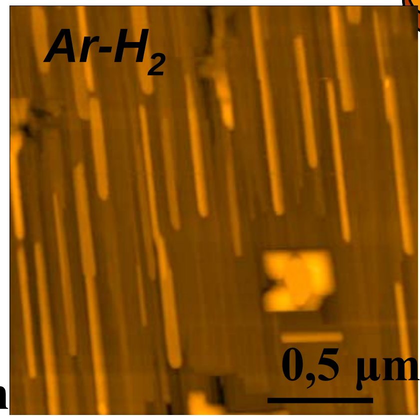
$YSZ_{fluorite}$



$LaAlO_{3\ perovskite}$



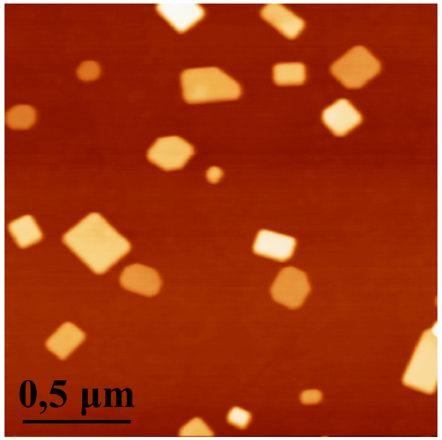
$NdGaO_{3\ perovskite}$



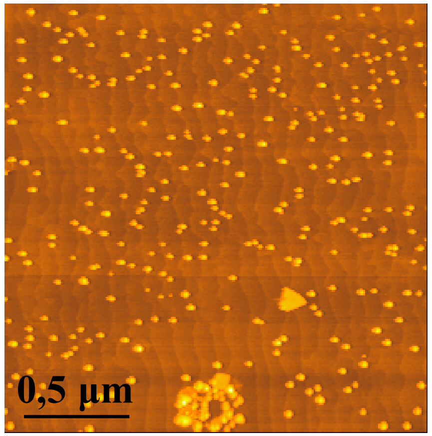
$NdGaO_{3\ perovskite}$

Cubic: Re_2O_3

Perovskite: $BaZrO_3$



$LaAlO_{3\ perovskite}$



$SrTiO_{3\ perovskite}$

Strain induced interfacial self-assembled nanostructures

M. Gibert et al.;Surf. Science (2007) 2680
M. Gibert et al.; Adv.Mat. (2007) 3937

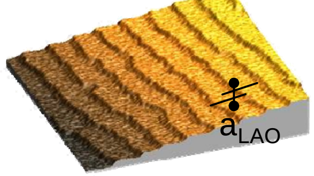
$Ce_{1-x}Gd_xO_{2-y}$(CGO)/$LaAlO_3$: a system of interest

• **Wide range of applications**:

catalysis, optical properties, ionic conductivity, dielectric properties, buffer layer, nanostructured templates for high T_c superconductors…

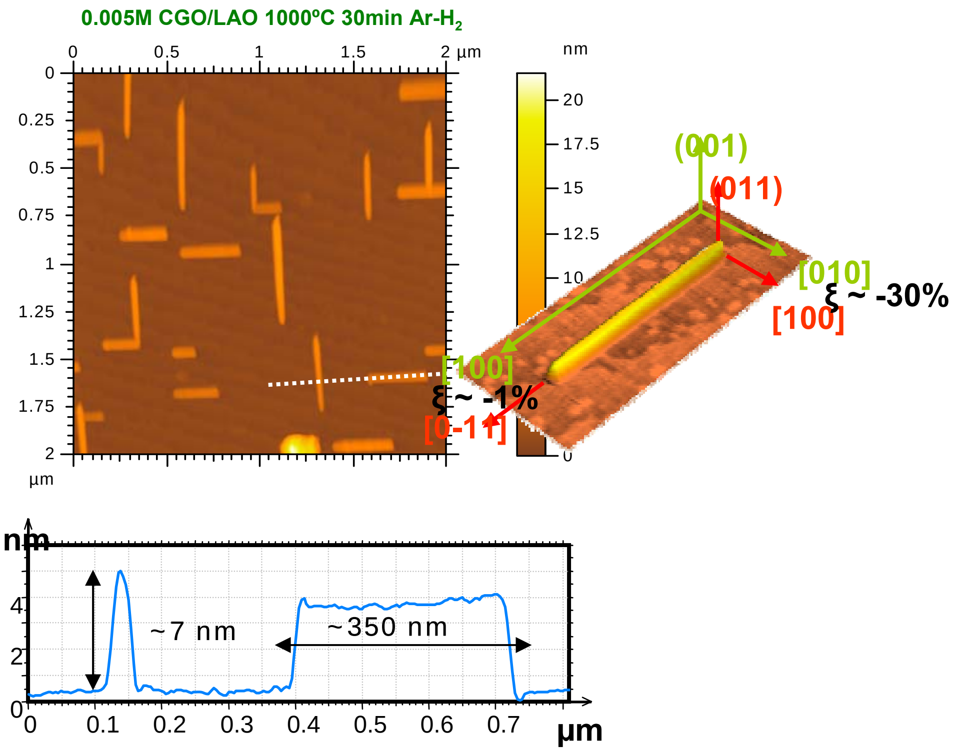
• **Oxide Heteroepitaxy:** fluorite ($Ce_{0.9}Gd_{0.1}O_{2-Y}$) over perovskite ($LaAlO_3$) structure

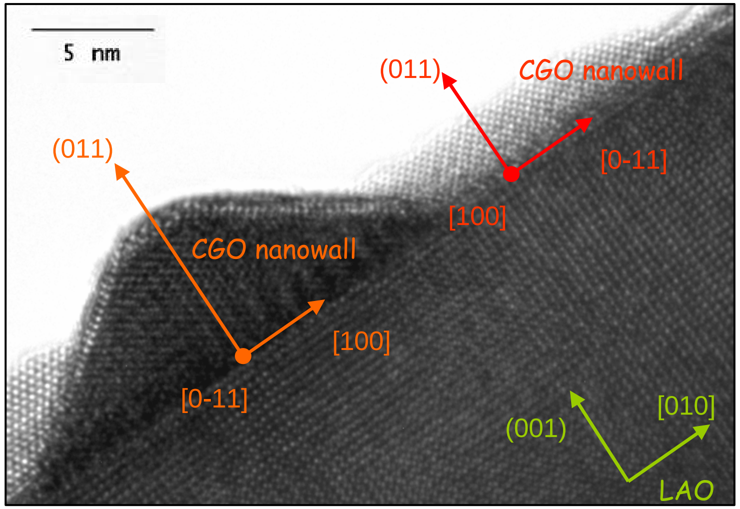
$Ce_{0.9}Gd_{0.1}O_{2-Y}$(CGO)
a_{CGO} ~ 5,41 Å



$LaAlO_3$ (LAO)
a_{LAO} = 3,79 Å

Thermally treated perovskite single crystal substrates show atomically flat terraces



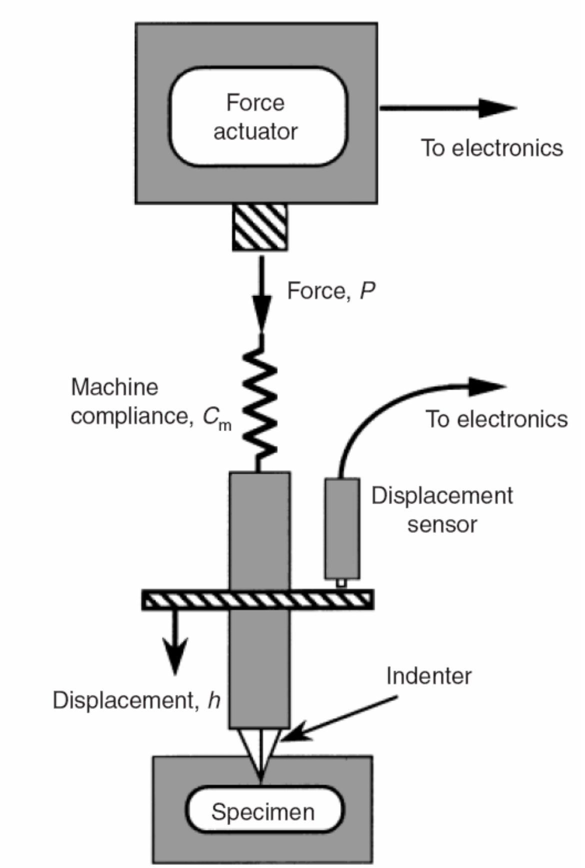


A.Benedetti, F.Sandiumenge
ICMAB-CSIC

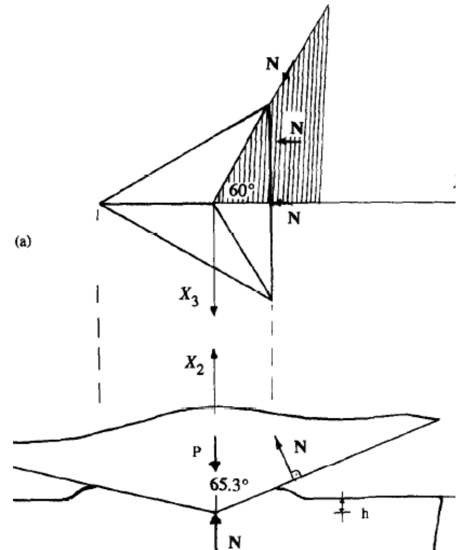
NANOINDENTATION: A tool for nanopatterning

- A sharp diamond tip is driven into and withdrawn from the material
- Ultra low loads are used (< **10mN**) and small deformations induced (<**100nm**)

The equipment

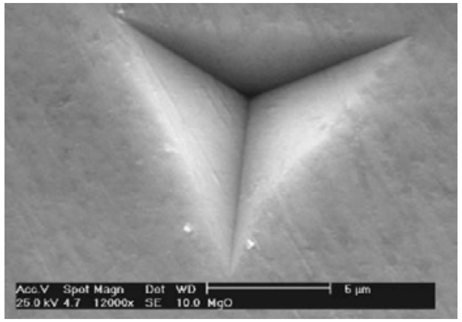


The tip

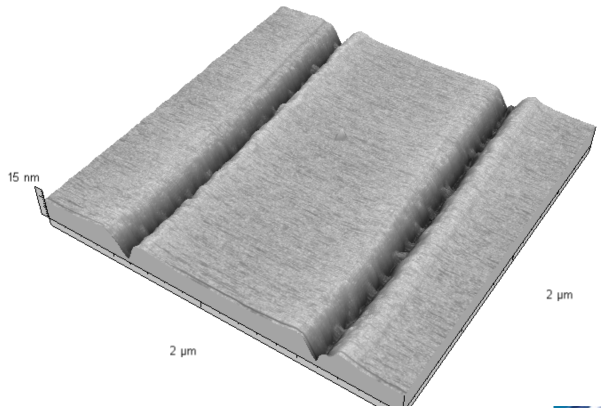


Top-down and lateral views of a Berkovich tip

The Indentation

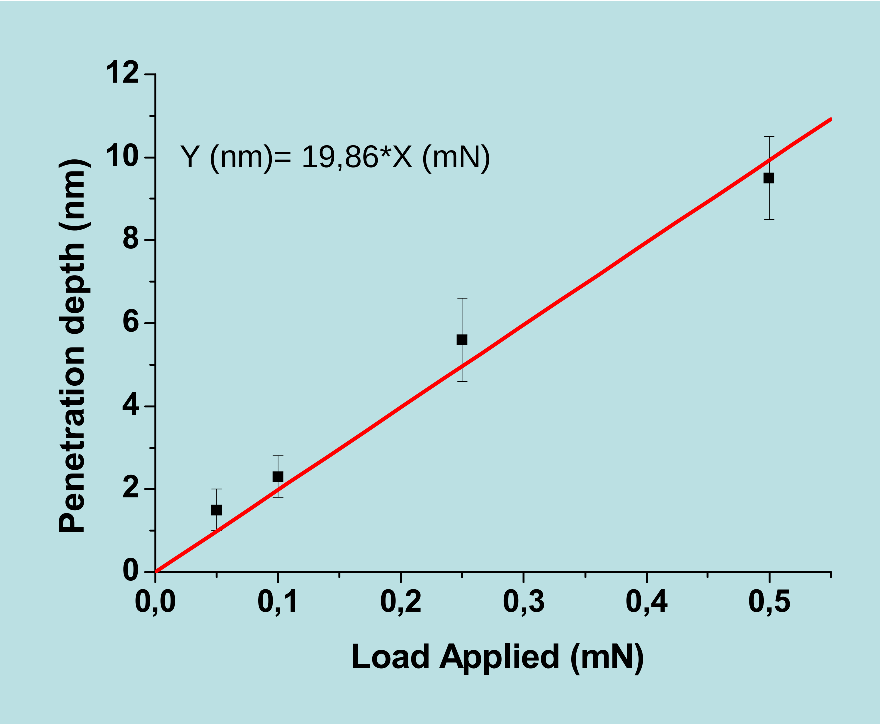


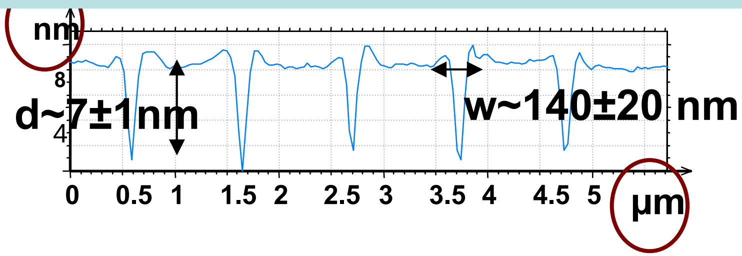
The Scratch



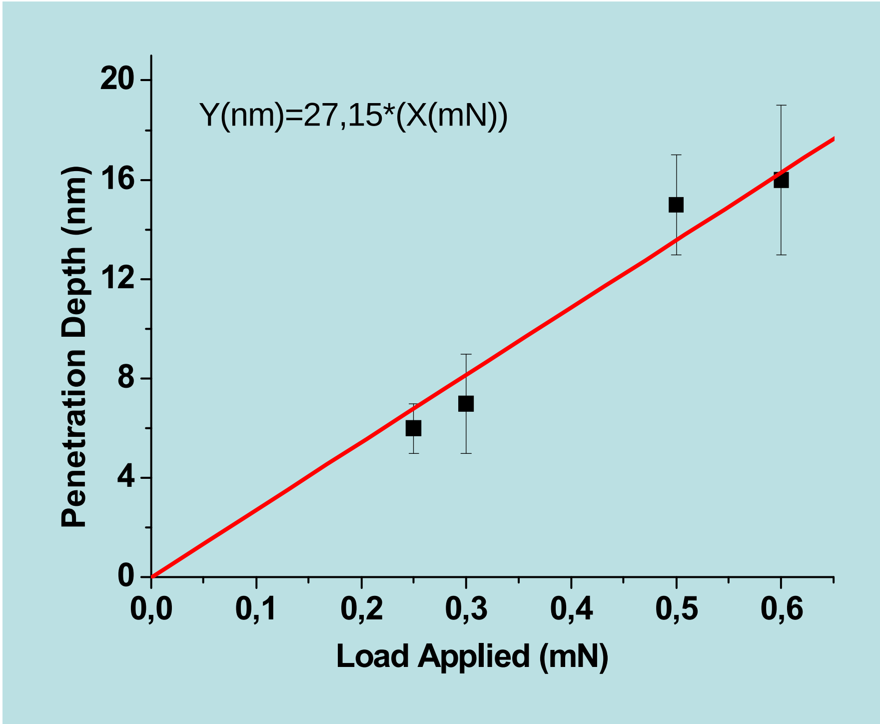
Nanoindentation on perovskite type substrates: tuning of the parameters

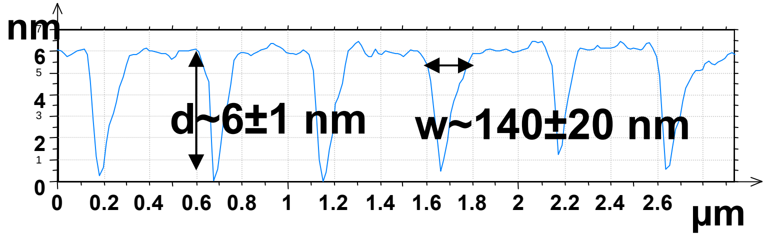
SCRATCH





INDENTATION



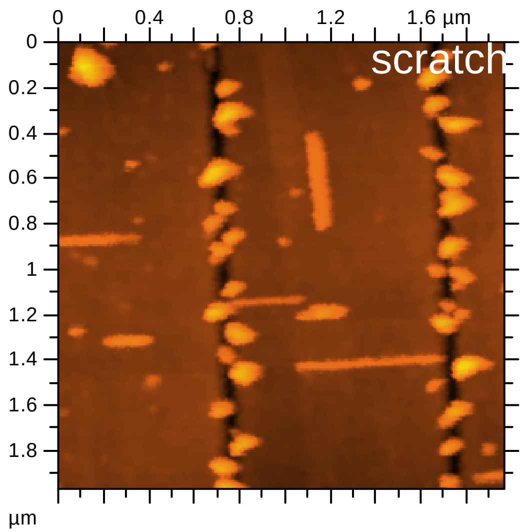


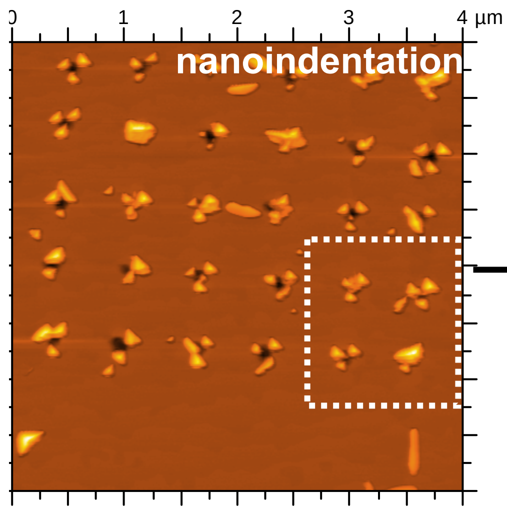
Extremely low-loads in the 0.05mN-0.6mN range are of interest

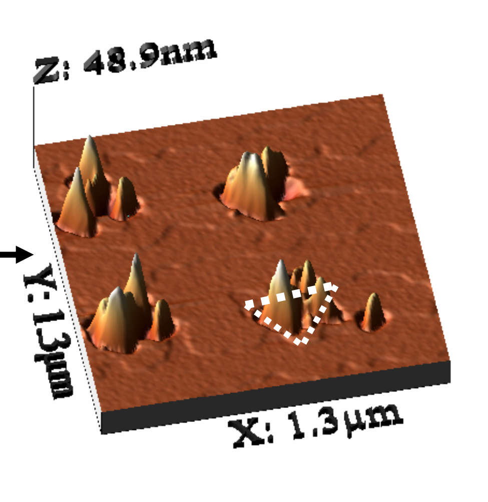
[2]*J.O.Ossó, MATGAS A.I.E*

Towards guided self-organization through Nanoindentation

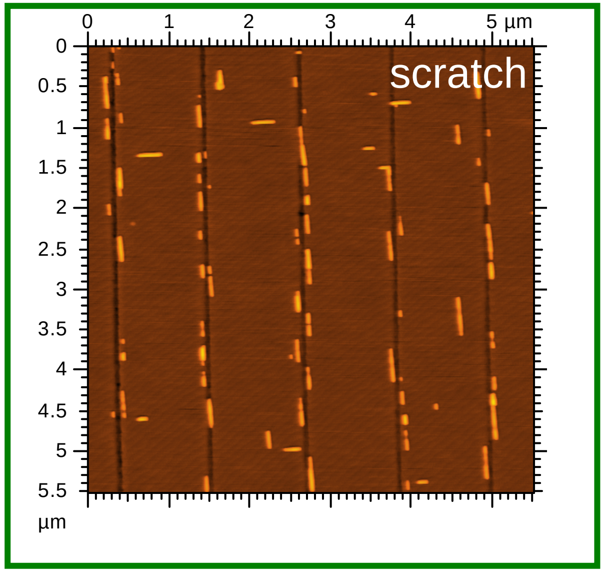
CGO on $SrTiO_3$ (STO)

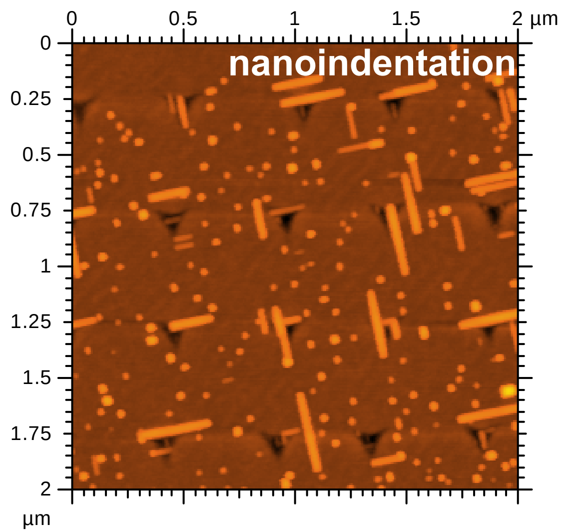




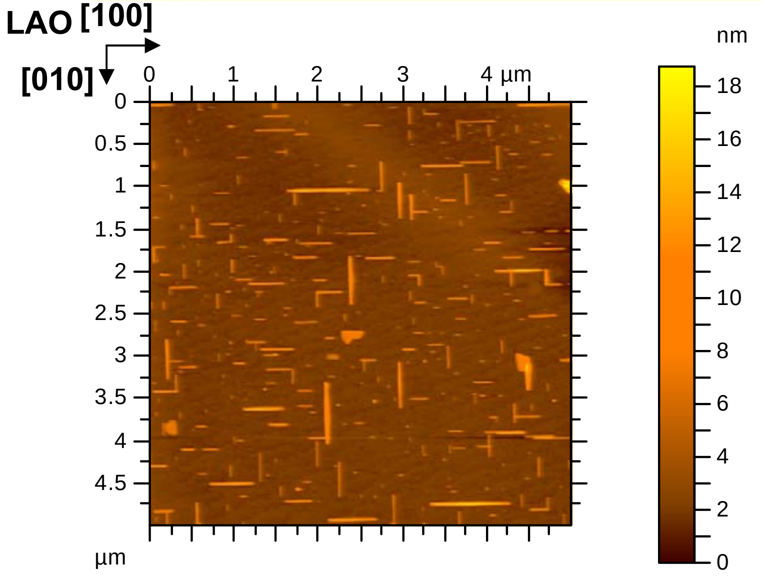


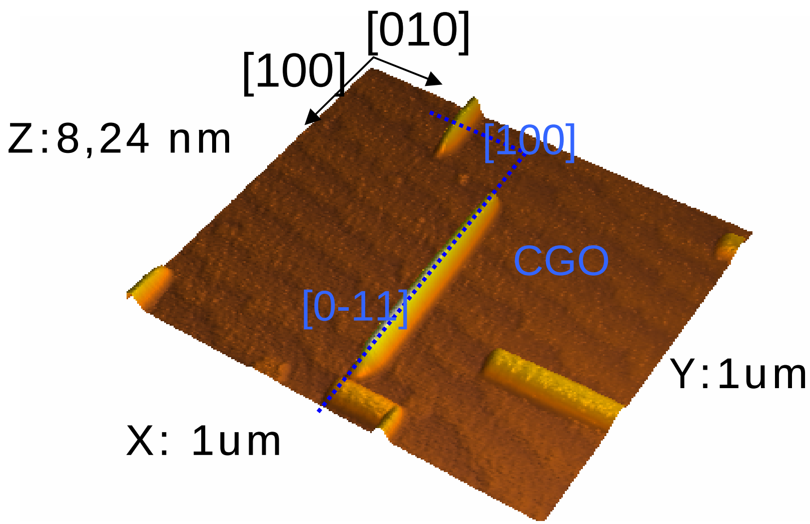
CGO on $LaAlO_3$ (LAO)

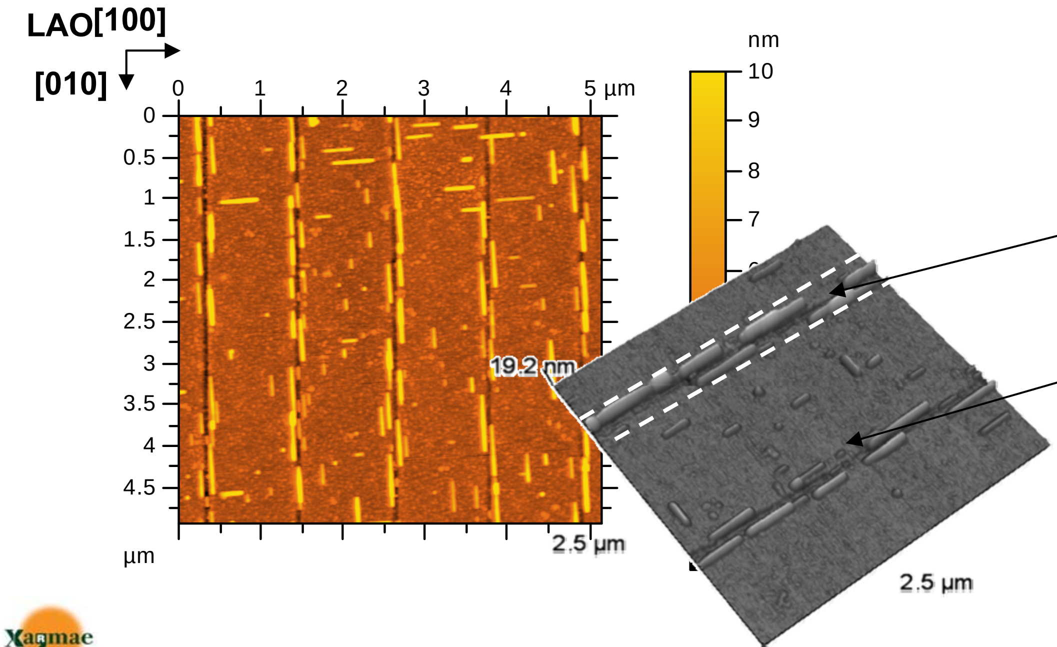




CGO nanowalls on LAO: the influence of scratches







0,1 mN Scratches	POPULATION DISTRIBUTION	ISLAND-OCCUPIED AREA
At Indentations	CGO [0-11] //LAO [010] ~ 99%	~40%
In between indentation lines	CGO [0-11] //LAO [010] ~ 60%	~ 5%

DISCUSSION


VOLUME 92, NUMBER 2 PHYSICAL REVIEW LETTERS week ending 16 JANUARY 2004

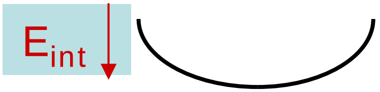
Local Strain-Mediated Chemical Potential Control of Quantum Dot Self-Organization in Heteroepitaxy

Bin Yang,[1] Feng Liu,[2] and M.G. Lagally[1]

Curvature (κ) dependent energy balance

$$E_{island} \sim E_{surface} + \underset{\sim f(\kappa)}{E_{interface}} + \underset{\sim f(\kappa^2, \varepsilon^2)}{E_{elastic\ relax}} + \ldots$$

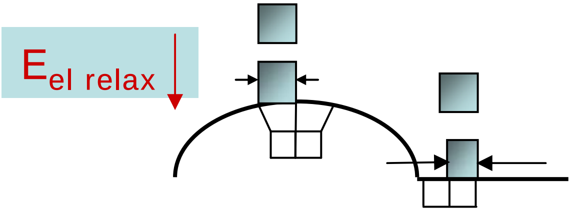
E_{int}: related to chemical bonding among the interface atoms



$\kappa<0$ concave

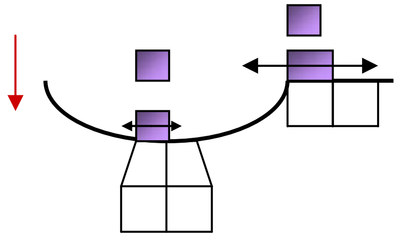
$E_{elast\ relax}$: related to the lattice mismatch between the solid crystalline materials

compressive ($a_f > a_s$)



$\kappa>0$ convex

tensile ($a_f < a_s$)

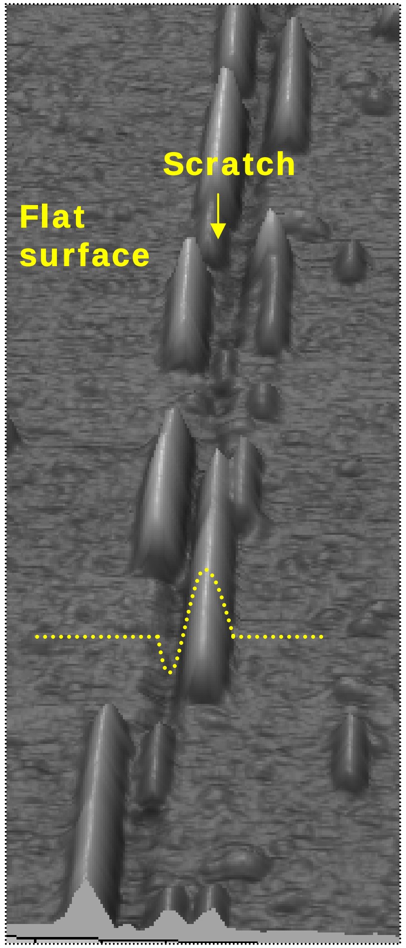


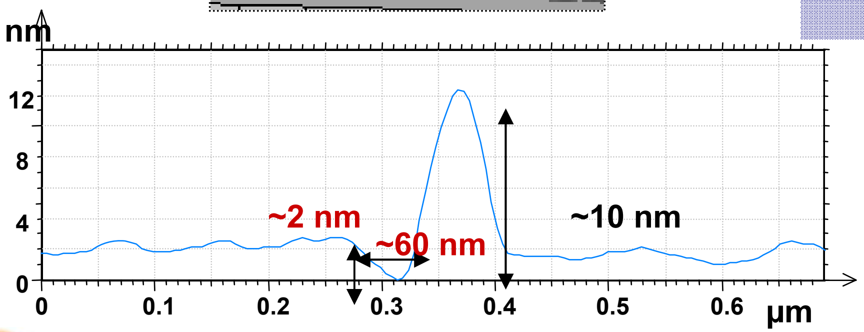
$\kappa<0$ concave

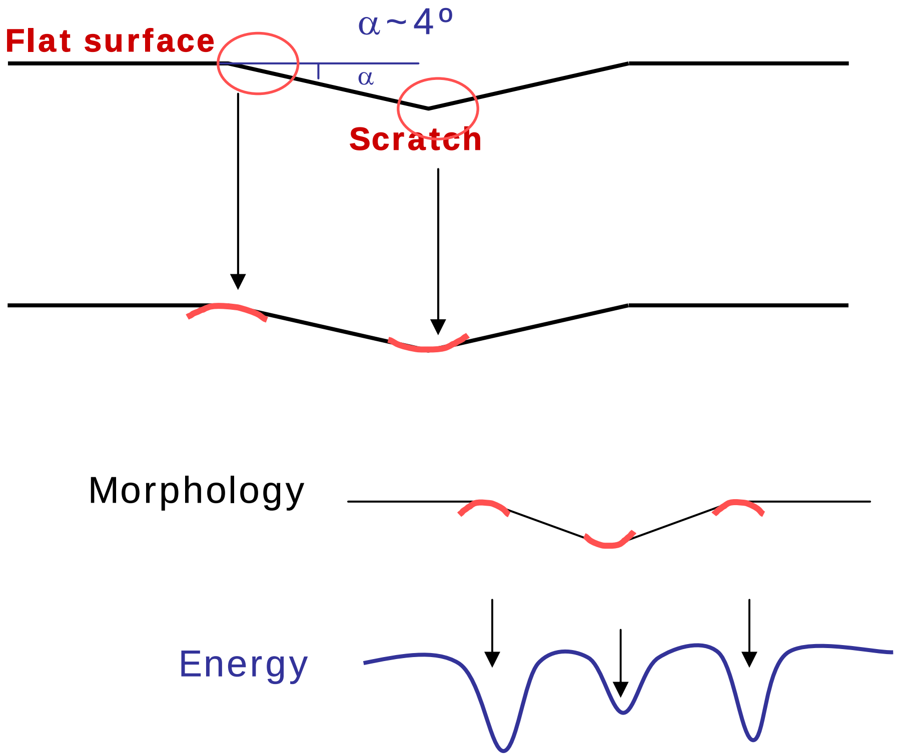
CGO / LAO grows under compressive strain

Concave and convex surfaces compete in lowering the local energy with respect to the flat substrate system's energy

Nanowall LOCATION







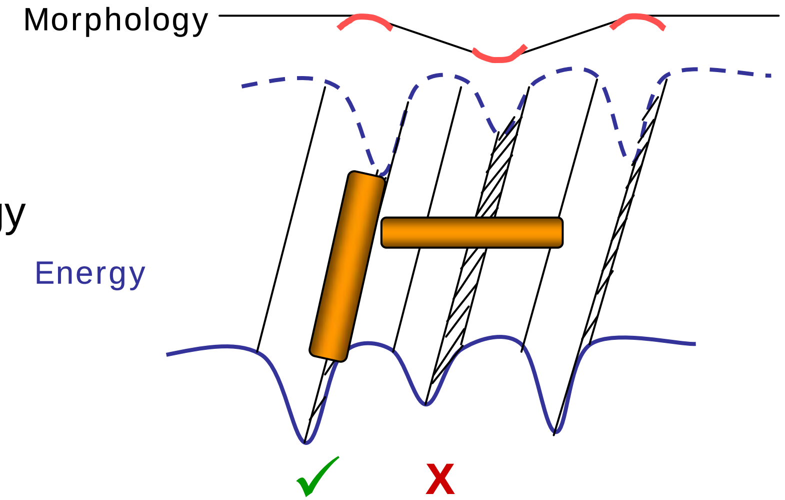
Competition between the **surface-energy** and **strain-energy** terms leads to multiple **local minima**

SUBSTRATE MORPHOLOGY INDUCED DIRECTED ORDERING

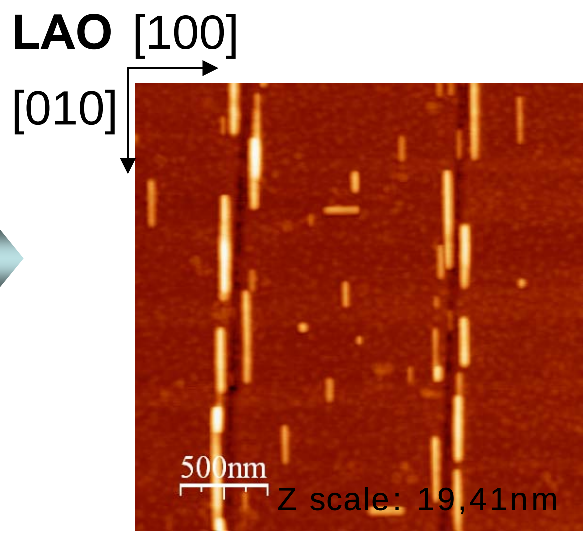
Nanowall ORIENTATION

Why do nanowalls align their long axis with the Scratch direction?

The orientation in which the nanowall maximizes its location at an energy minimum will be favoured



No “horizontal” nanowalls at the scratches



CONCLUSIONS

✓**CSD** has been shown a general method for generation of self assembled oxide nanoislands

✓Nanoindentation has successfully been used as a nanopatterning technique

✓Guided Self-Organized $Ce_{0.9}Gd_{0.1}O_{2-y}$ nanoisland growth has been evidenced

✓The substrate curvature effect on the different energy contributions has been proposed to be responsible for the results observed in the CGO/LAO system

-nanowall location at scratch edges is evidenced
-pre-existing nanowall orientation balance is broken

The nanoislands´kinetic evolution, under study, seems to give very rich phenomena suggesting further influence of the nanoindentation parameters

THANK YOU!