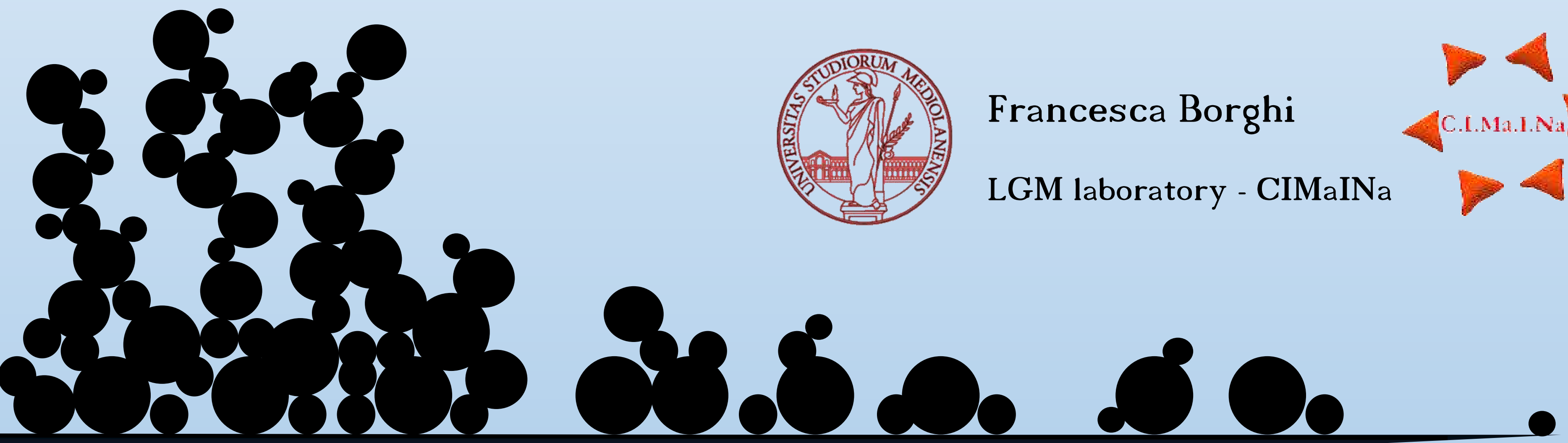
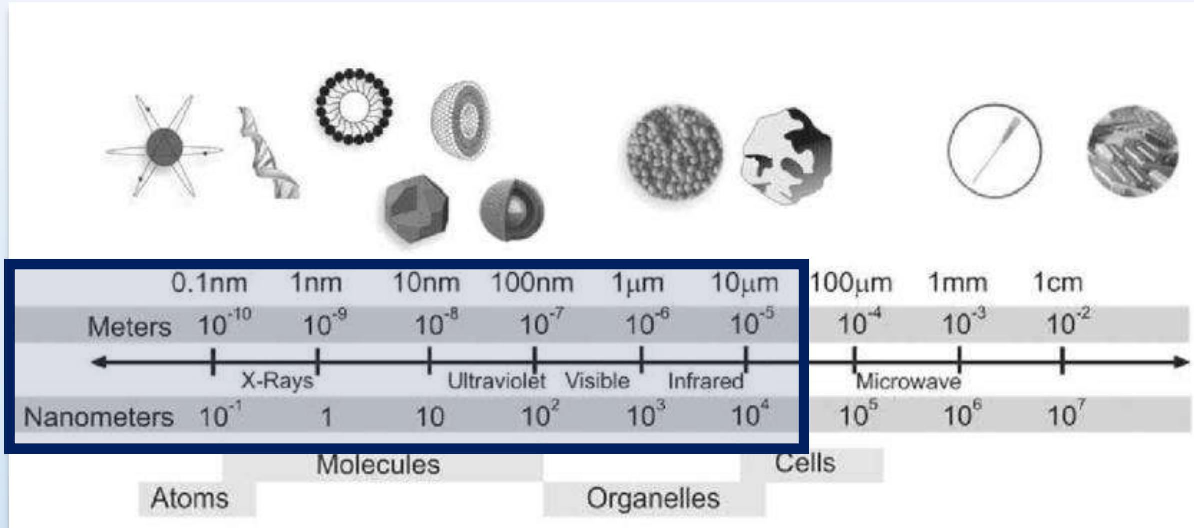
Investigation of the early stages of growth of nanostructured zirconia produced by Supersonic Cluster Beam Deposition: from sub-monolayer to thin film regime

Francesca Borghi

LGM laboratory - CIMaINa

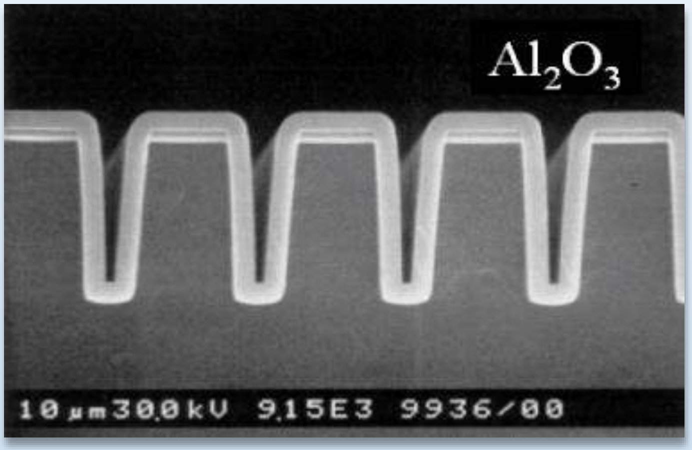


THIN FILMS



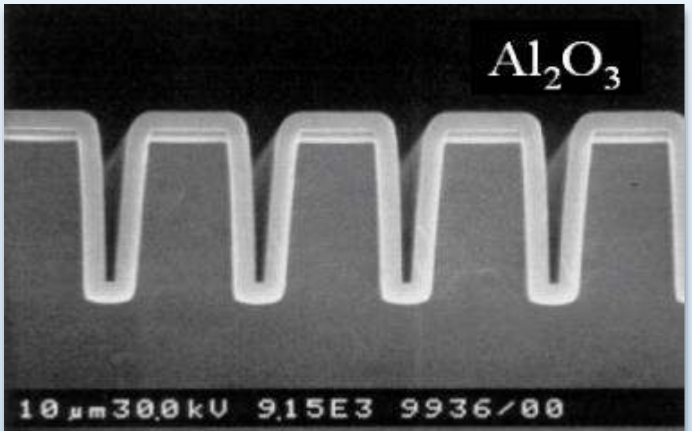
0.1nm
1nm
10nm
100nm
1μm
10μm
100μm
1mm
1cm
Meters
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
X-Rays
Ultraviolet
Visible
Infrared
Microwave
Nanometers
10^{-1}
1
10
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
Molecules
Cells
Atoms
Organelles

THIN FILMS

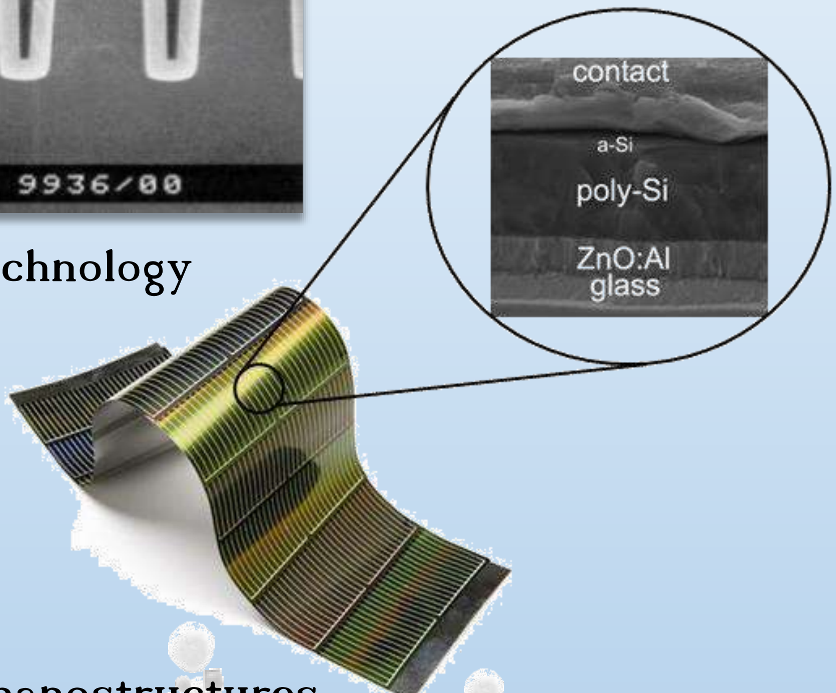


Semiconductor technology

THIN FILMS

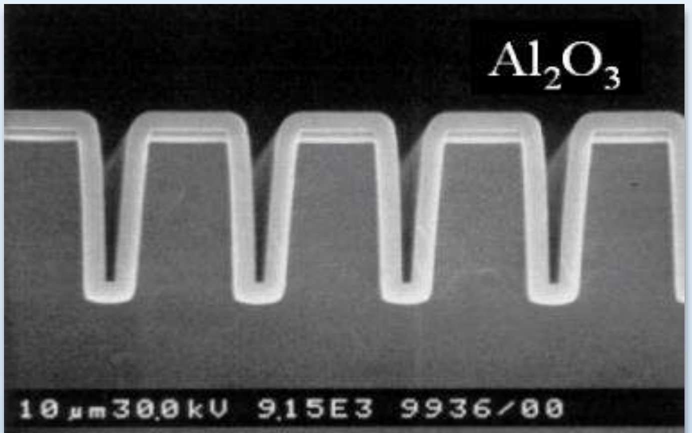


Semiconductor technology

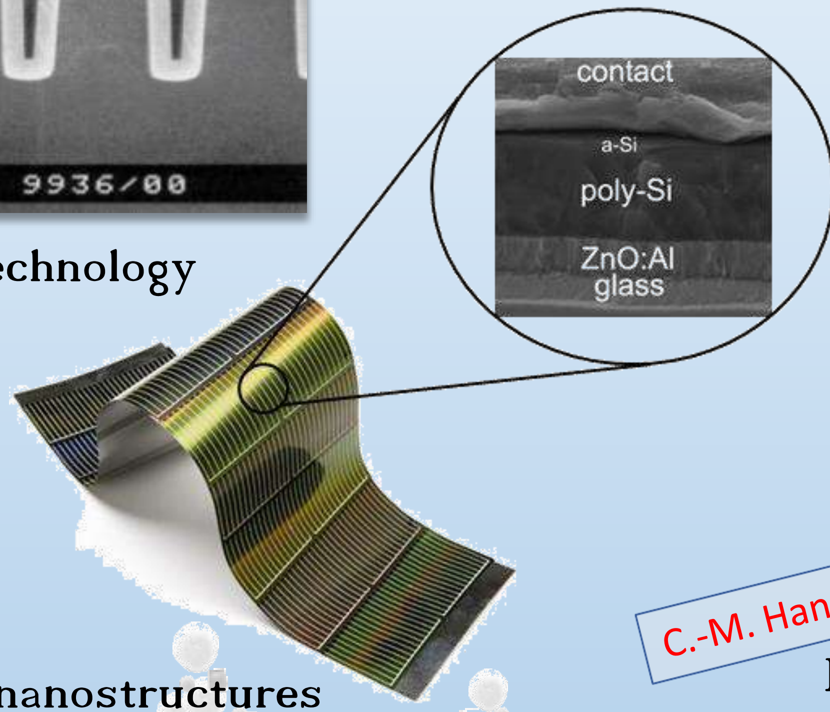


Plasmonic nanostructures

THIN FILMS

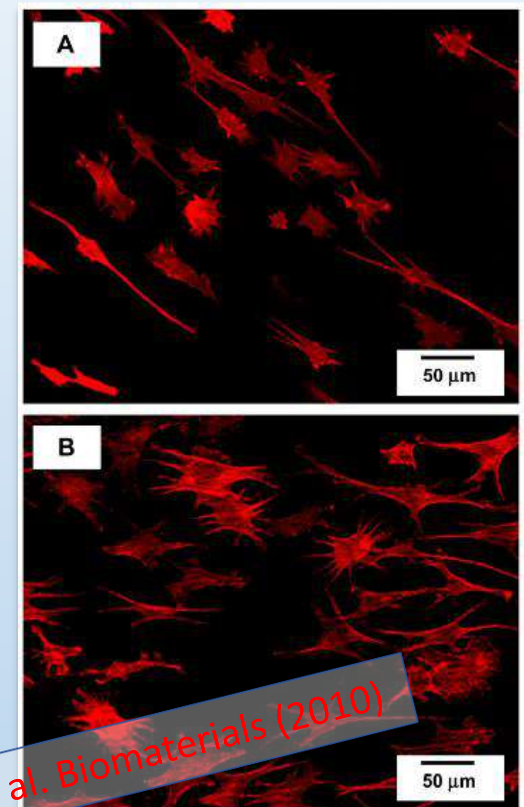


Semiconductor technology



Plasmonic nanostructures

Biomedicine

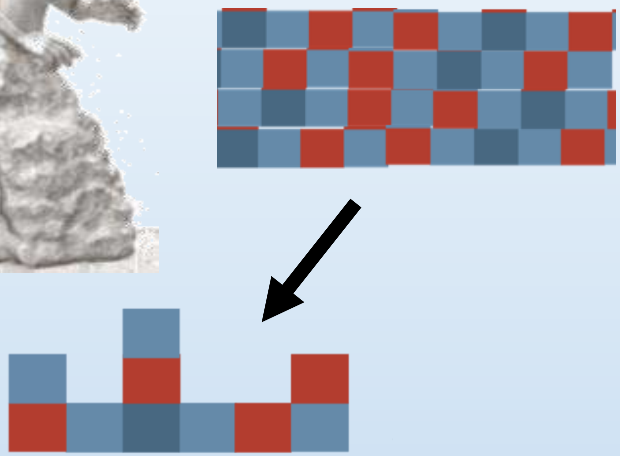


C.-M. Han et al. Biomaterials (2010)

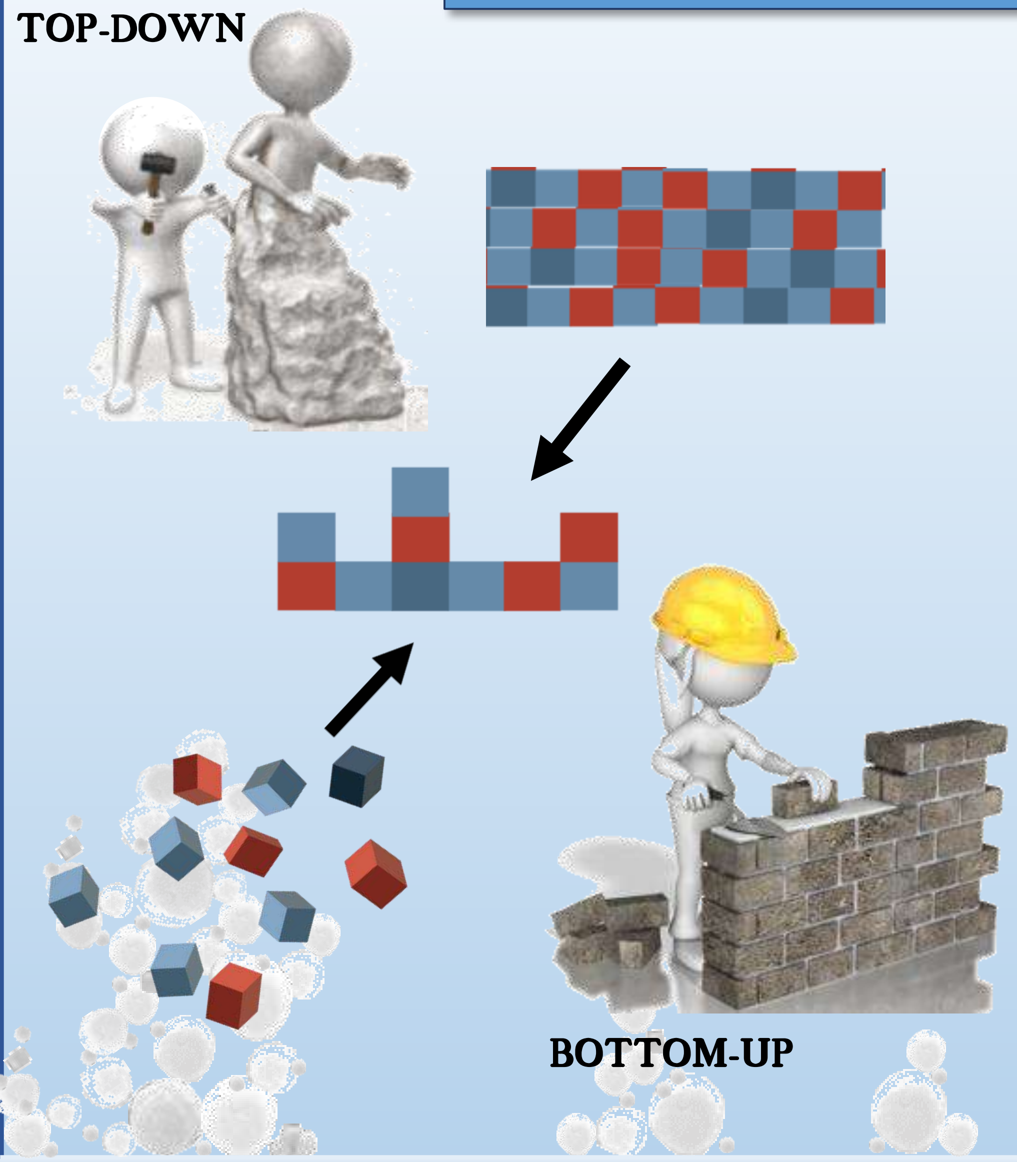
MC_3T_3-E1 cells cultured on (A) as-machined and (B) Ti-coated PEEK

THIN FILMS DEPOSITION TECHNIQUES

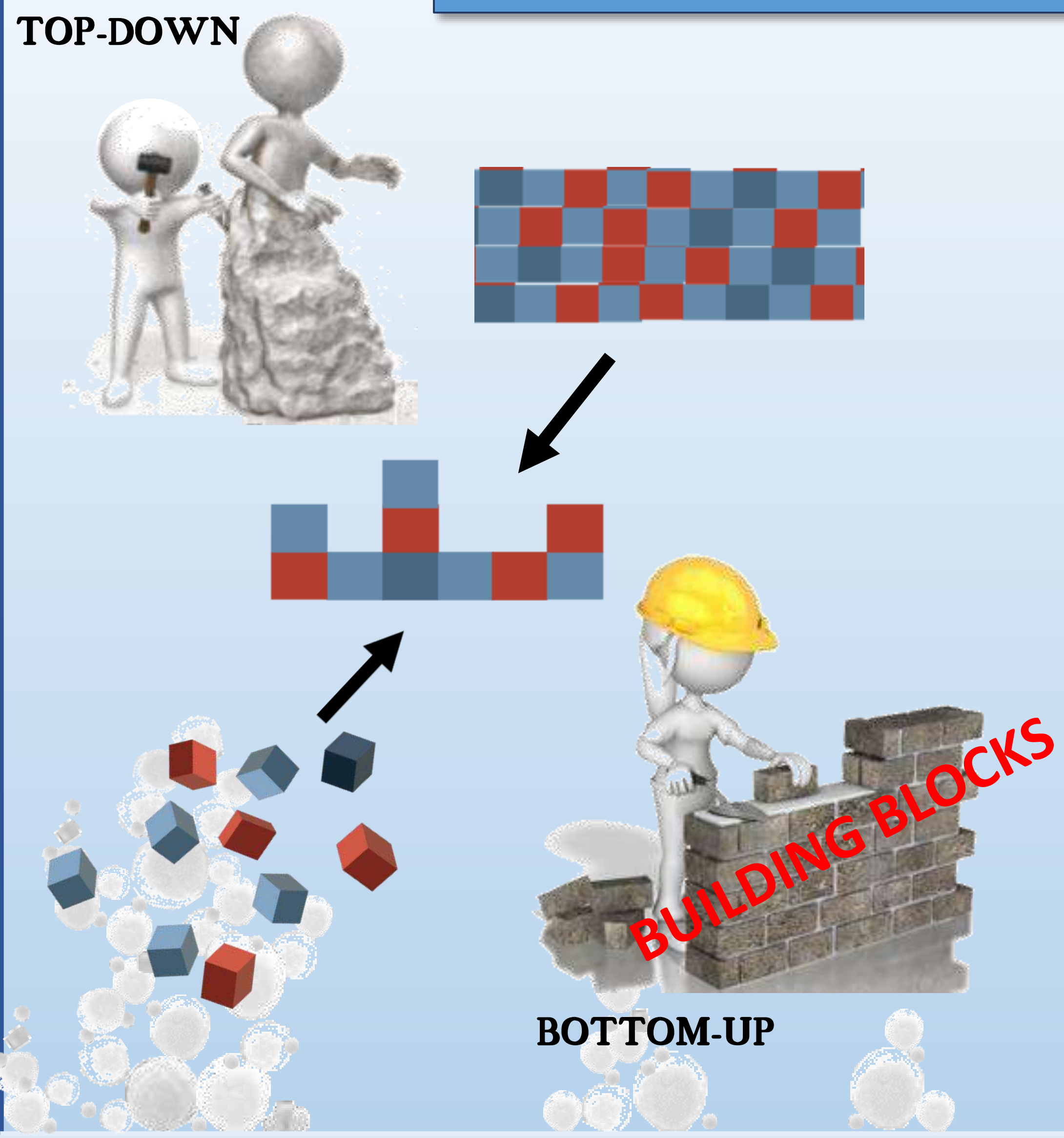
TOP-DOWN



THIN FILMS DEPOSITION TECHNIQUES



THIN FILMS DEPOSITION TECHNIQUES



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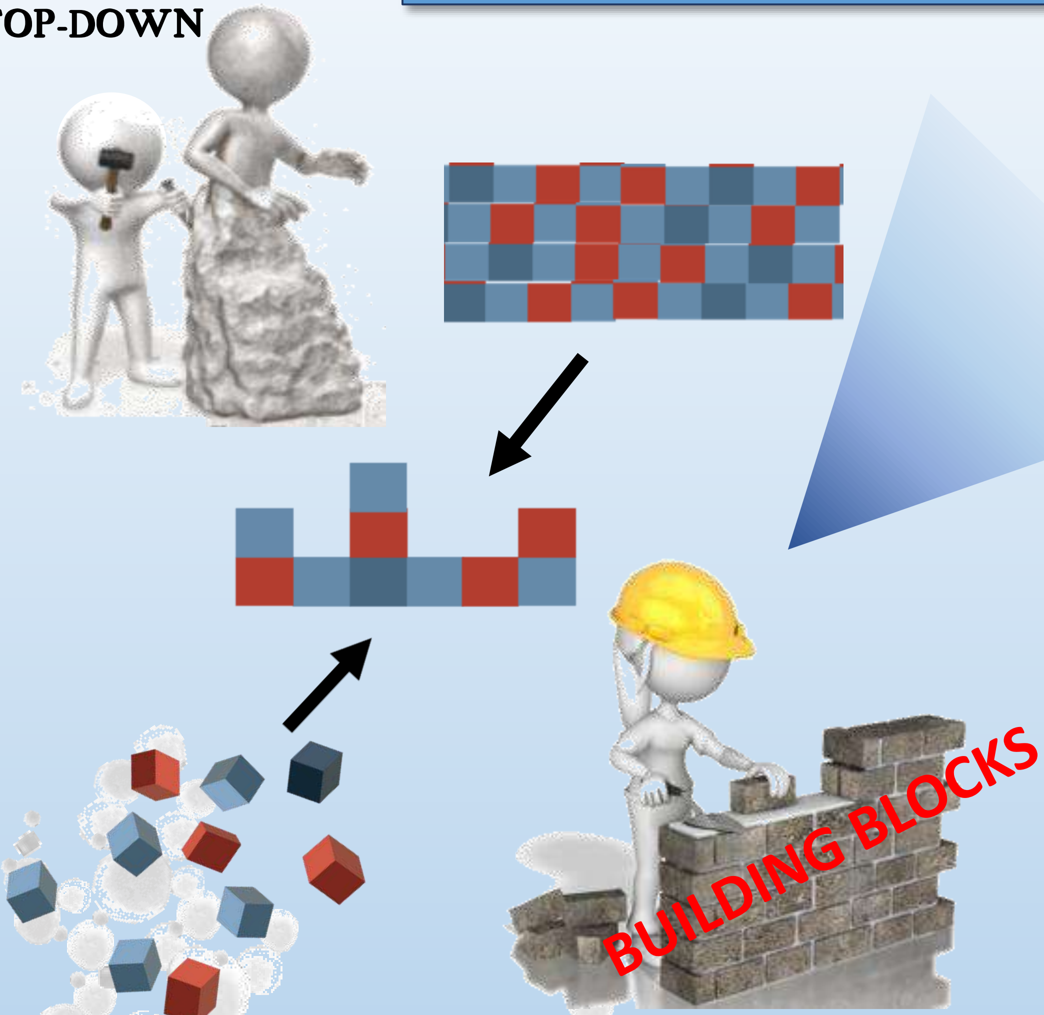


BOTTOM-UP

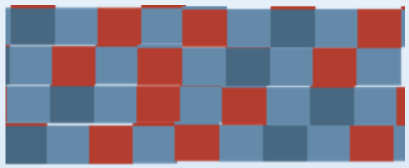
PHYSICAL VAPOUR DEPOSITION
(PVD)

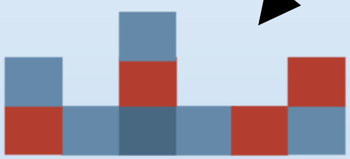
CHEMICAL VAPOUR DEPOSITION
(CVD)

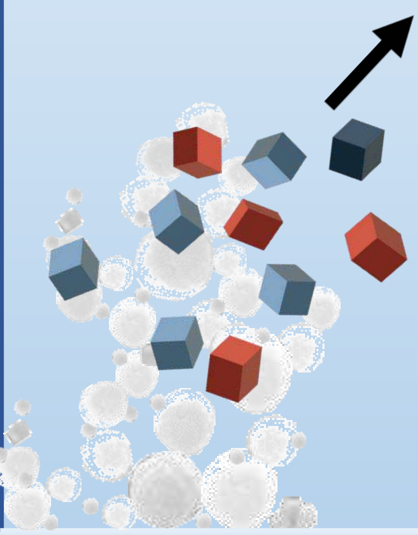
ASSEMBLING
of PRECURSORS
from GAS PHASE
onto a SUBSTRATE

THIN FILMS DEPOSITION TECHNIQUES

TOP-DOWN







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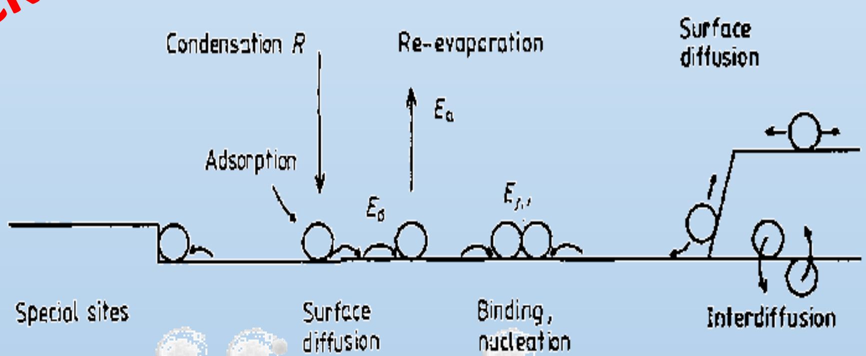
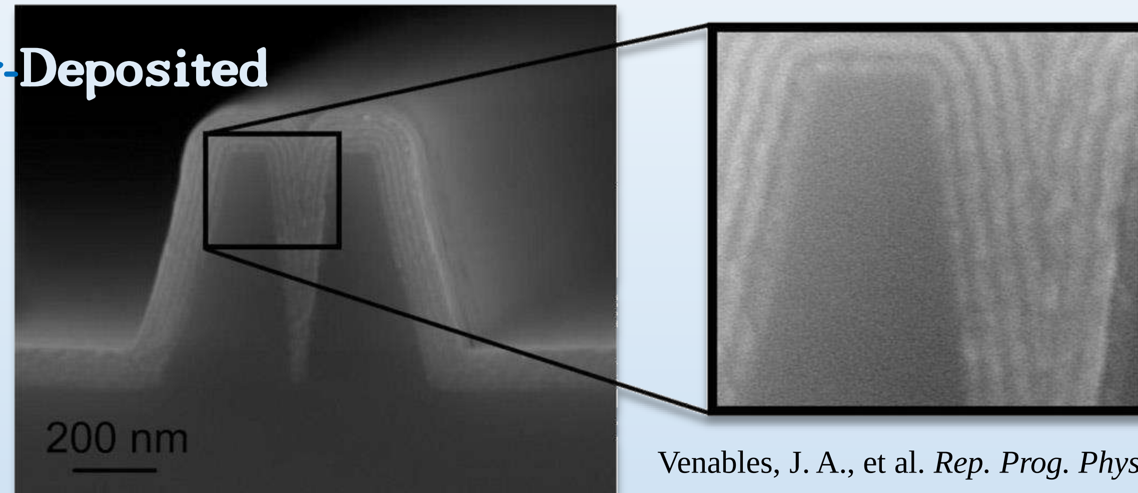


BOTTOM-UP APPROACHES

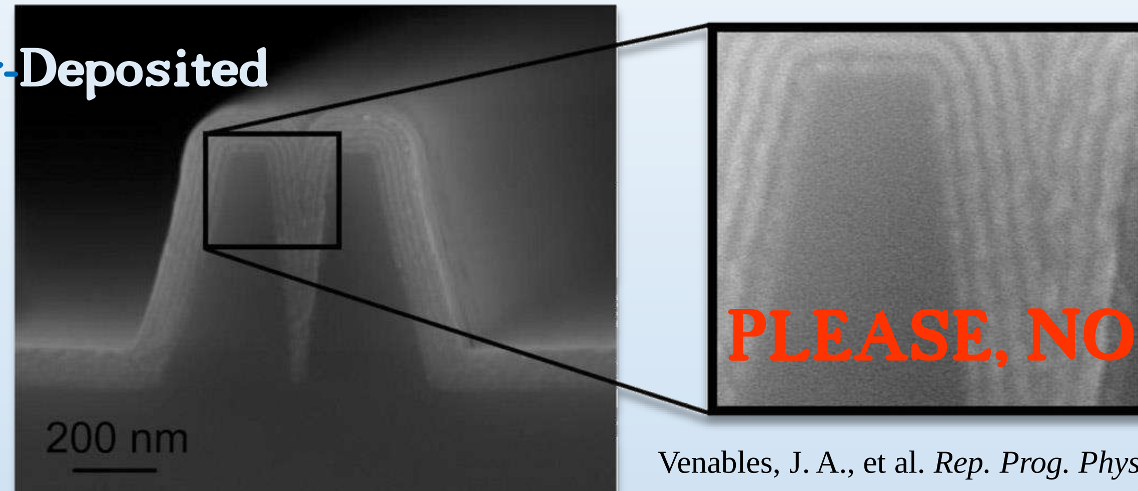
Atomic-Layer-Deposited thin films



Venables, J. A., et al. *Rep. Prog. Phys.* **47,** 399 (1984).

BOTTOM-UP APPROACHES

Atomic-Layer-Deposited thin films



PLEASE, NO DEFECTS!

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BOTTOM-UP APPROACHES

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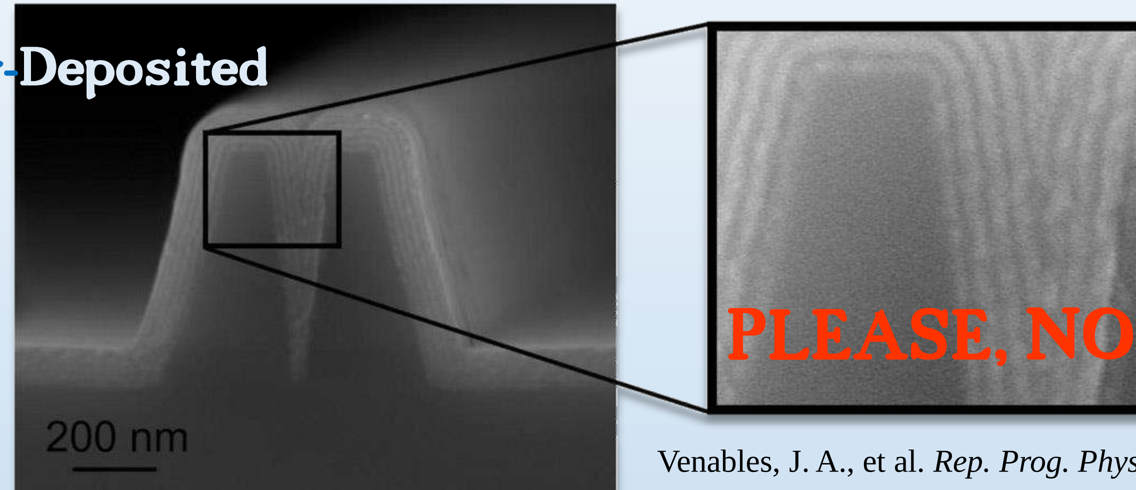

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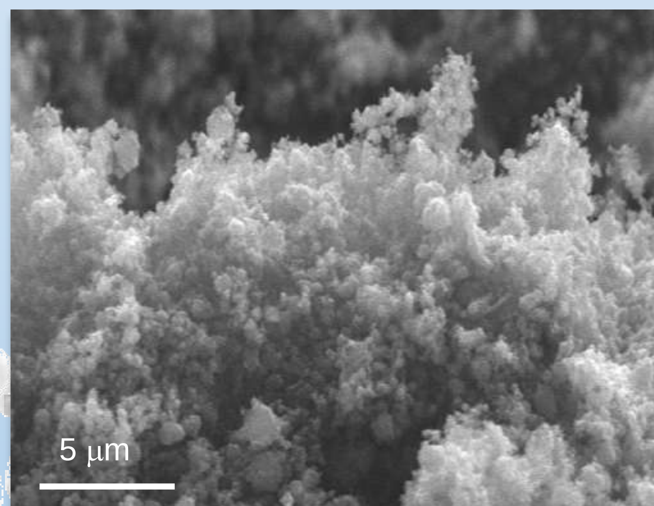
Nanostructured clusters-assembled thin films



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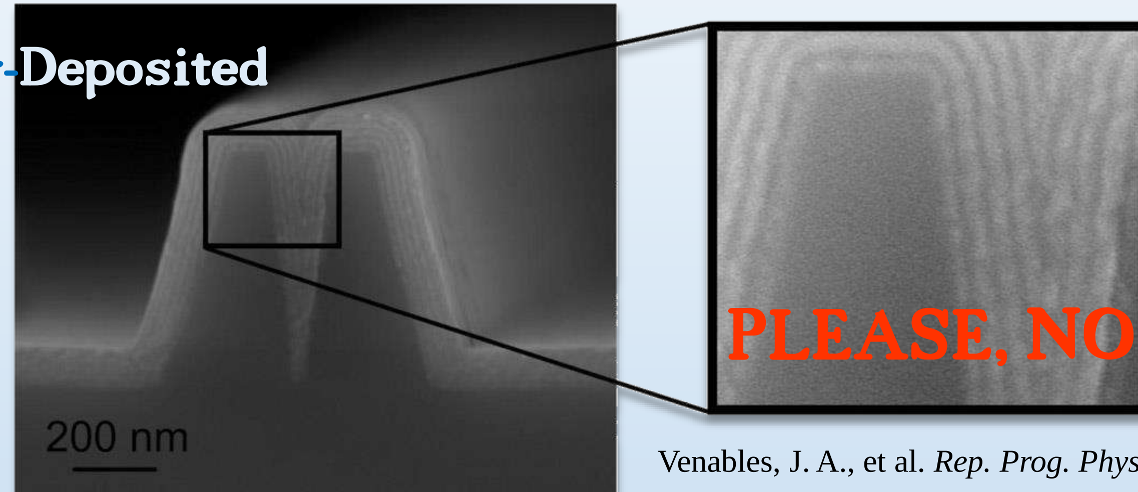

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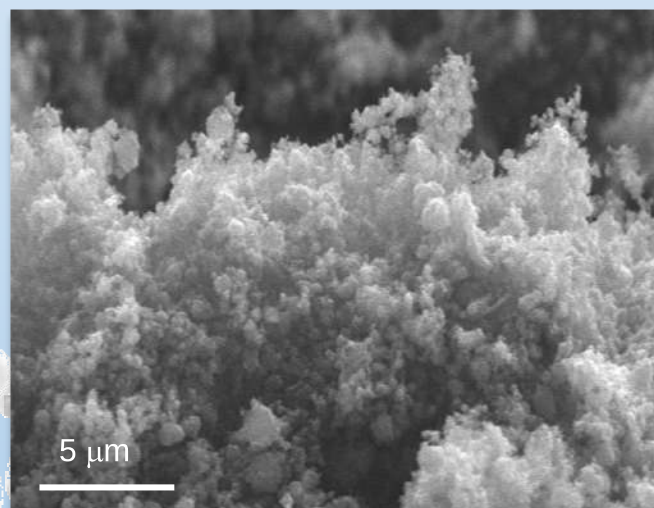
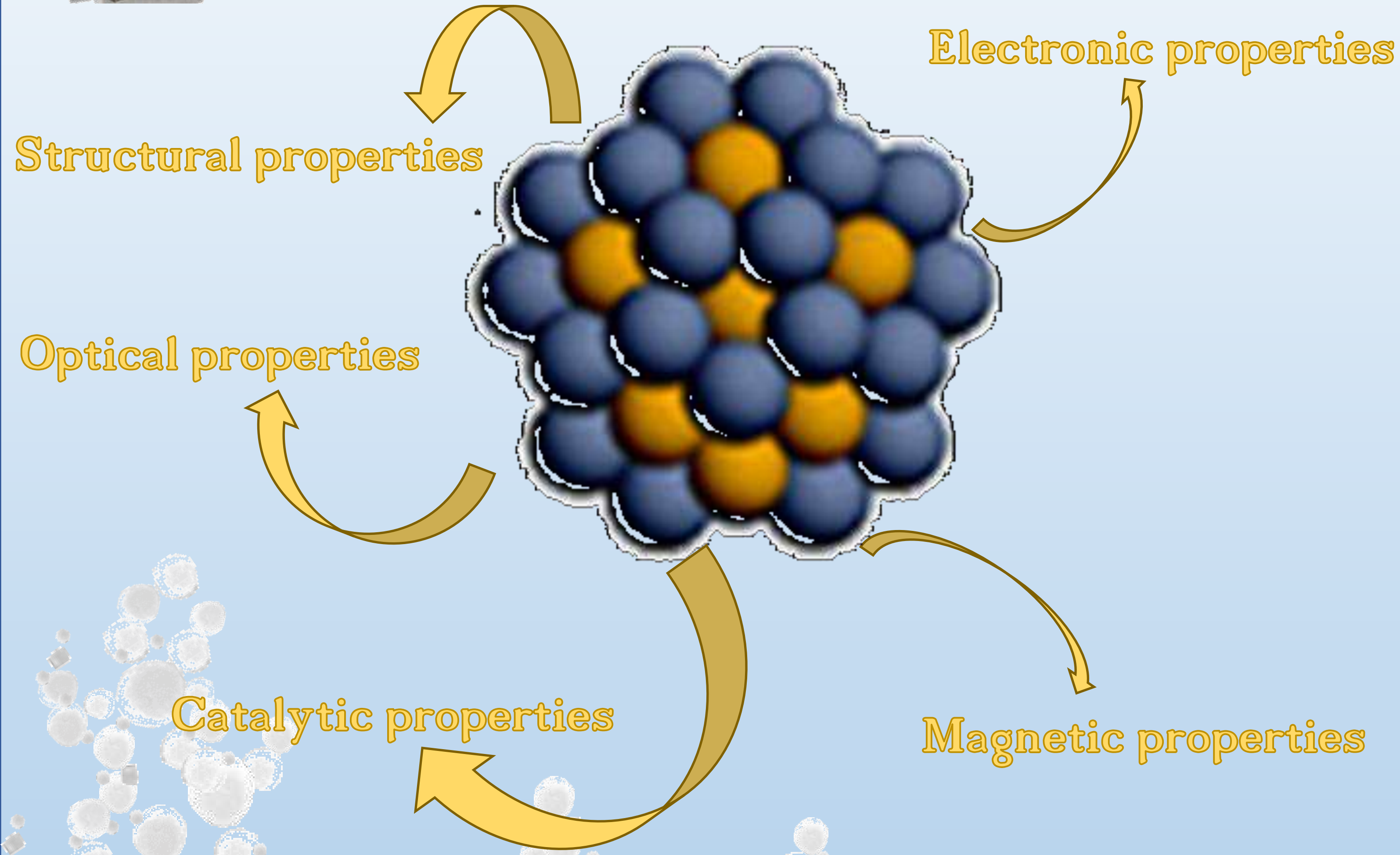


Controlled properties by disorder organized at the nano/meso scale

DEPOSITION OF CLUSTERS



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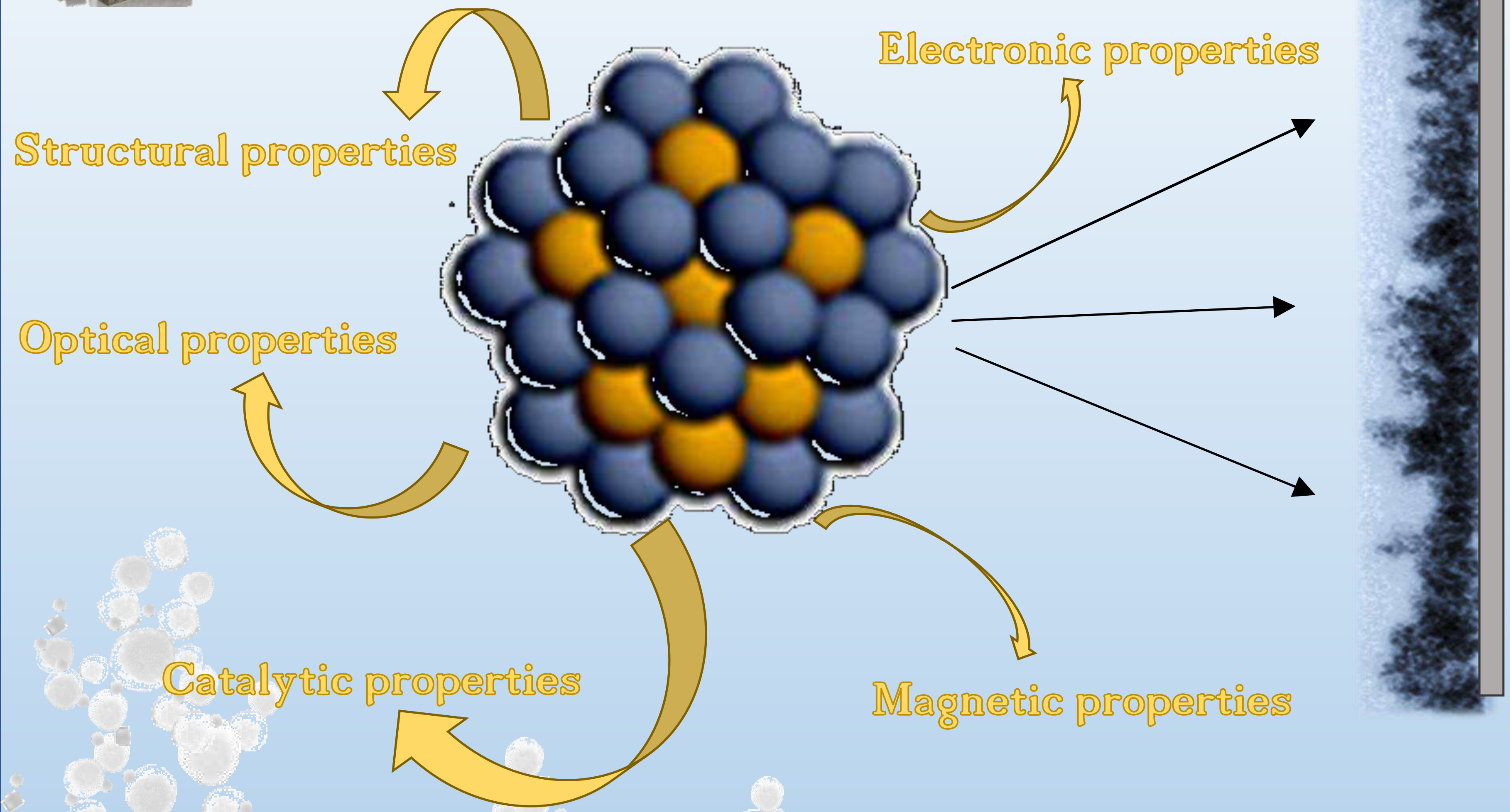

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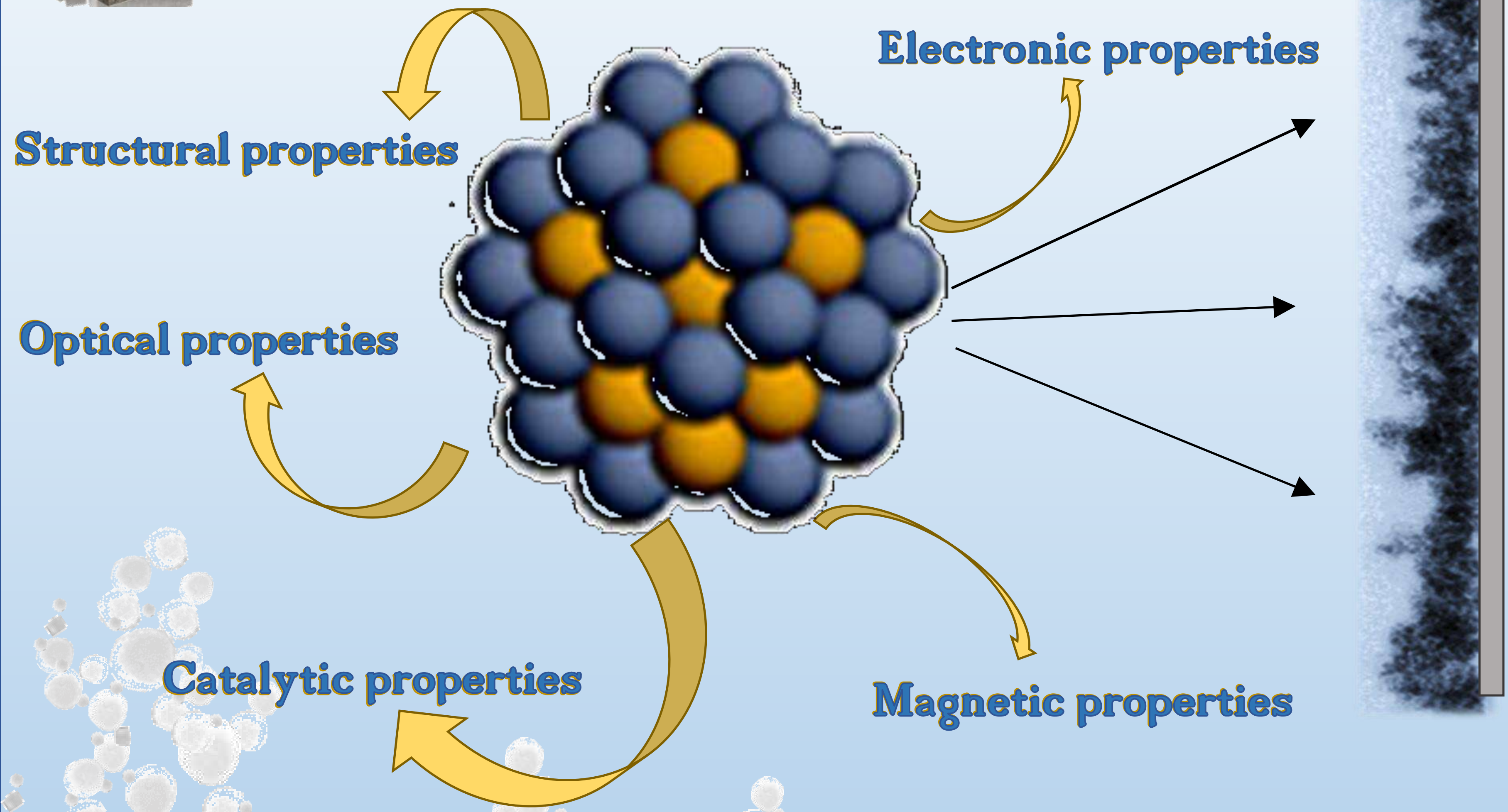
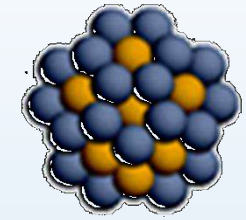
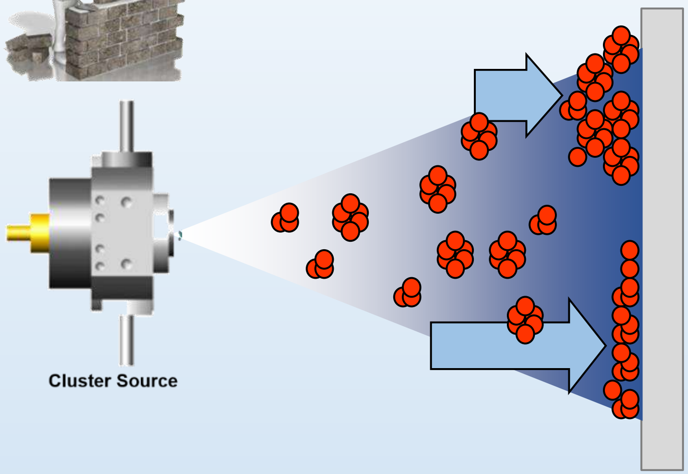


From STRUCTURAL to FUNCTIONAL properties





$\varepsilon << 1$

Memory effect

$\varepsilon >> 1$

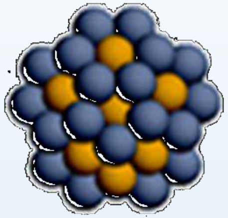
Fragmentation

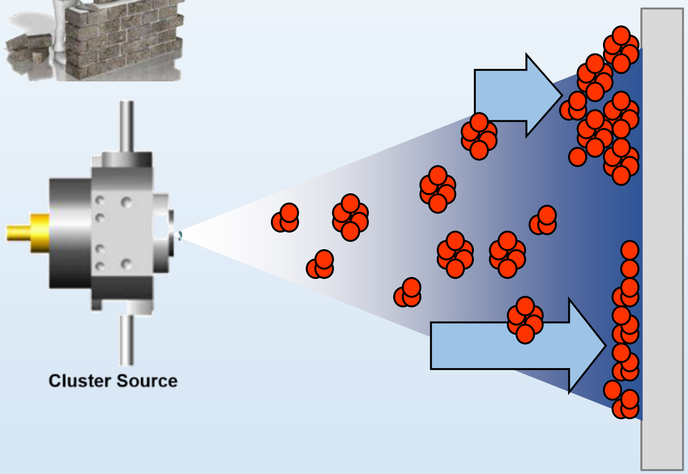
Pulsed Microplasma Cluster Source (PMCS)

$$\varepsilon = \frac{E_{kin}^{cluster} / N_{cluster}}{E_{coh}^{cluster}}$$

$E_{kin} < 1\,\mathrm{eV/atom}$

From STRUCTURAL to FUNCTIONAL properties





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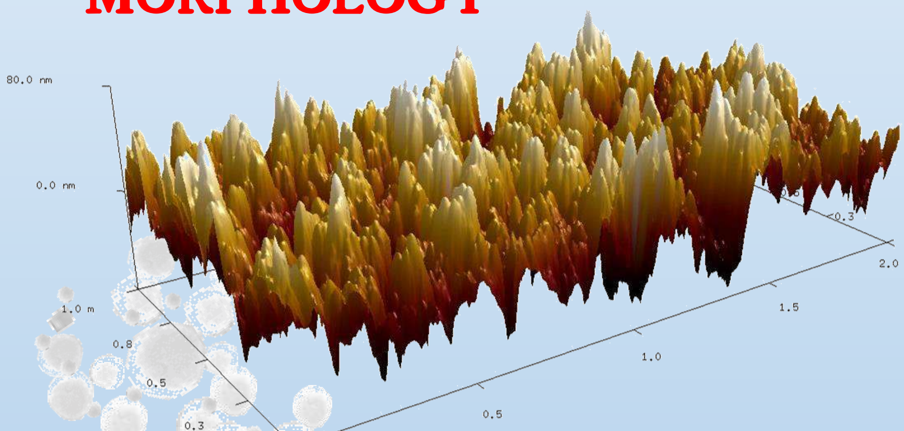
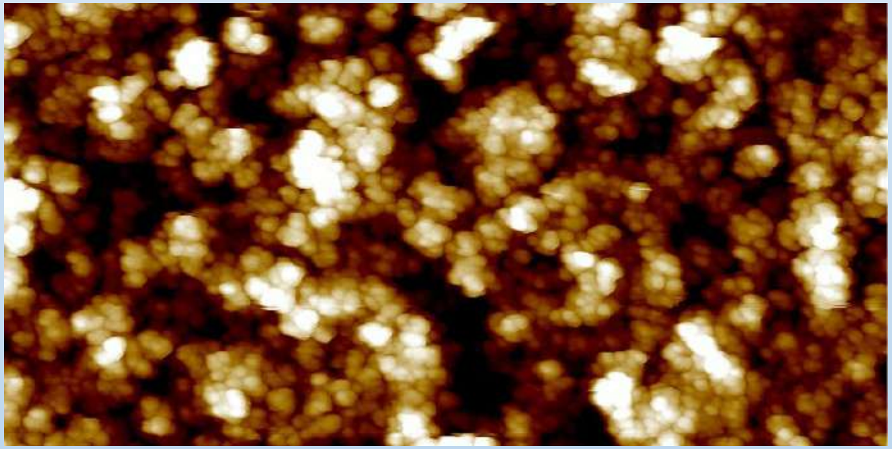
MORPHOLOGY



2µm x 1µm x 0.1µm



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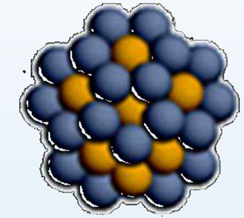

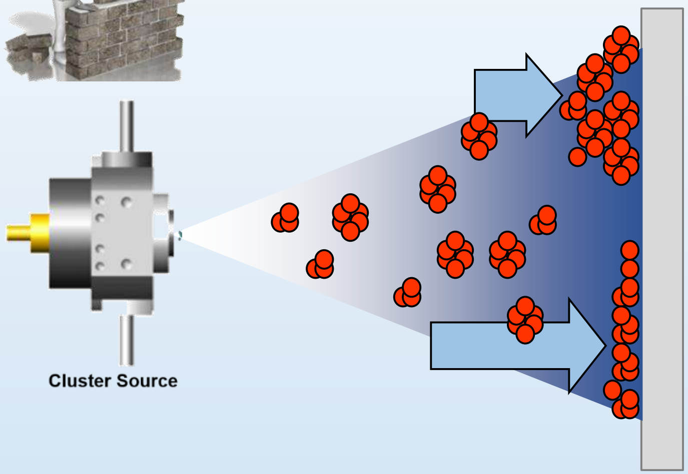

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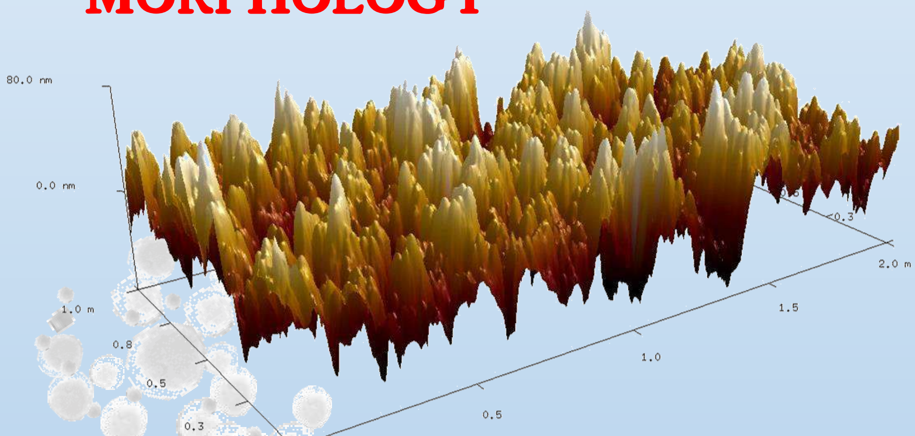

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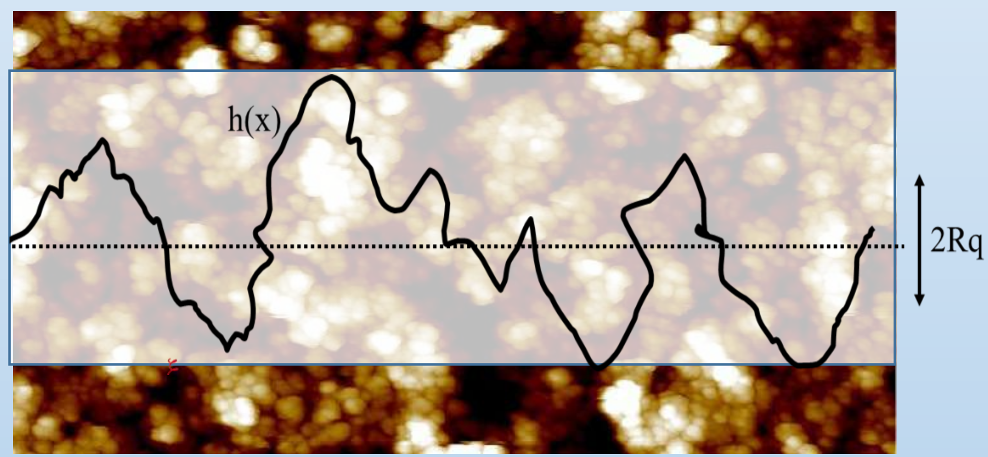

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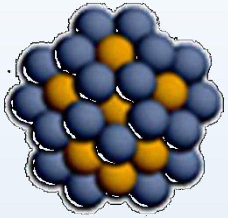

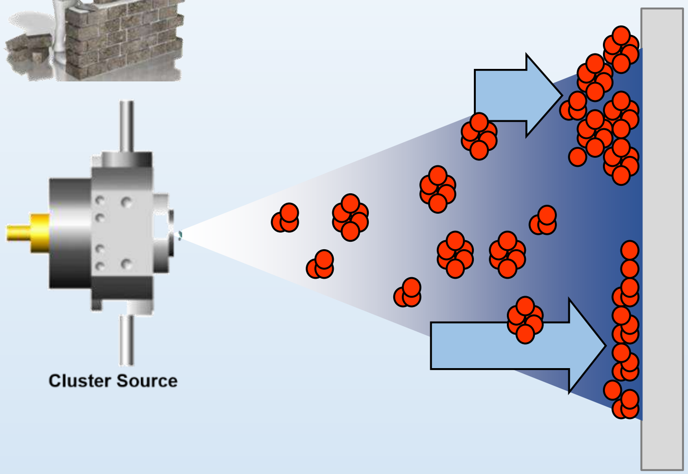

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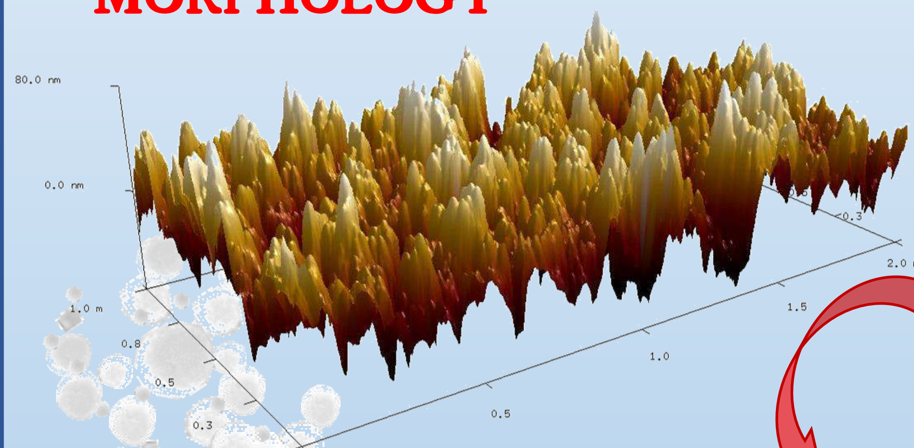
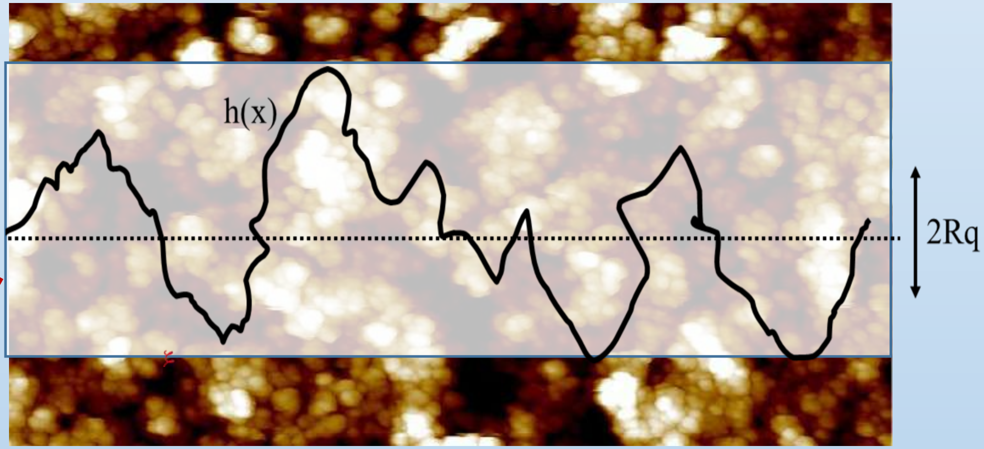


2μm x 1μm x 0.1μm

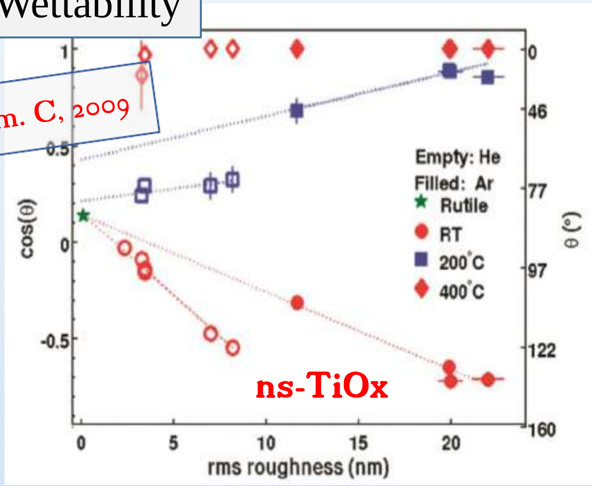


FUNCTIONAL PROPERTIES

From STRUCTURAL to FUNCTIONAL properties

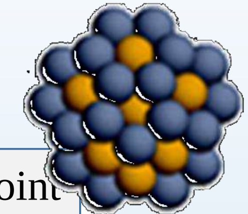
Wettability

A. Podestà, J. Phys. Chem. C, 2009

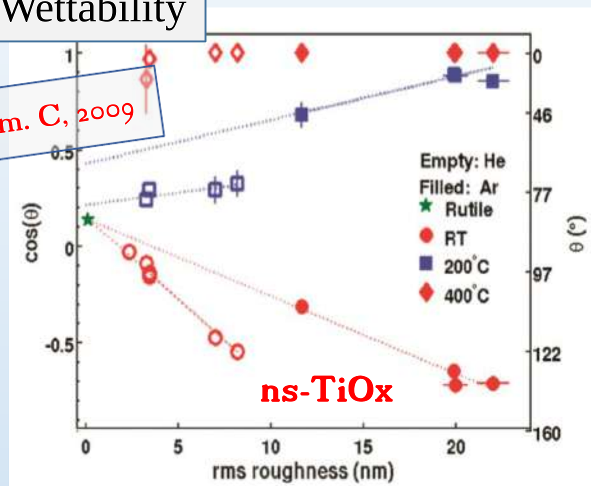


MORPHOLOGY

From STRUCTURAL to FUNCTIONAL properties

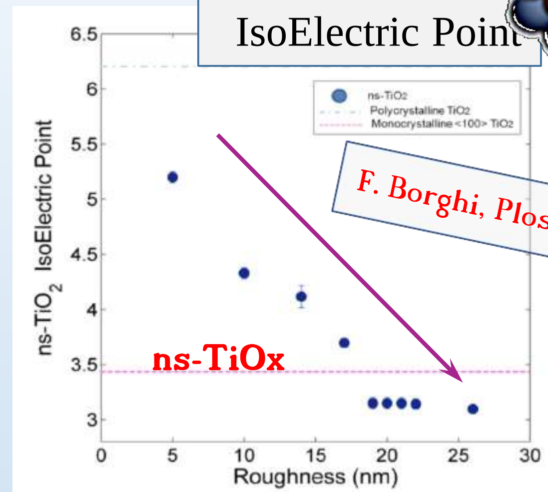


Wettability



A. Podestà, J. Phys. Chem. C, 2009

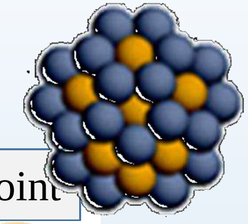
IsoElectric Point



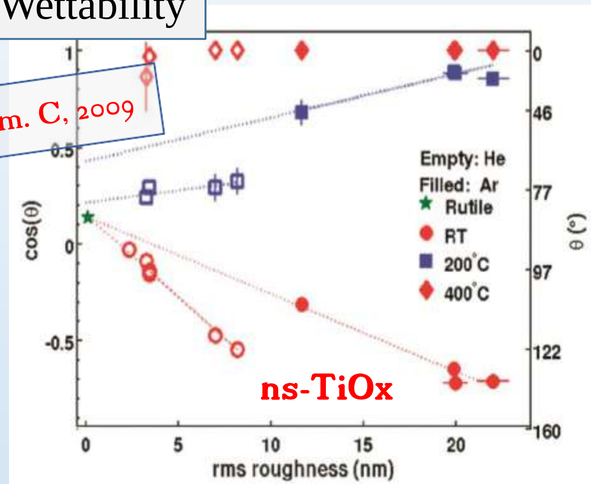
F. Borghi, PlosOne, 2013

MORPHOLOGY

From STRUCTURAL to FUNCTIONAL properties



Wettability



A. Podestà, J. Phys. Chem. C, 2009

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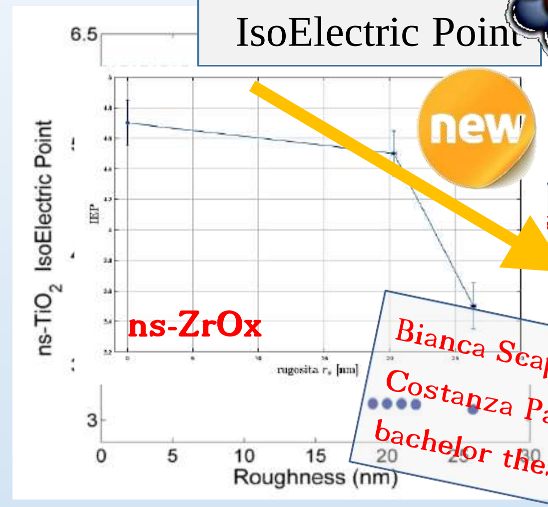


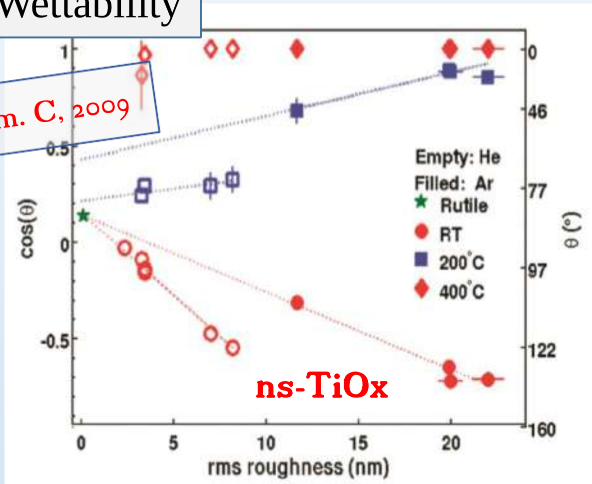
One, 2013

Bianca Scaparra & Costanza Paternoster bachelor thesis

MORPHOLOGY

From STRUCTURAL to FUNCTIONAL properties

Wettability



A. Podestà, J. Phys. Chem. C, 2009

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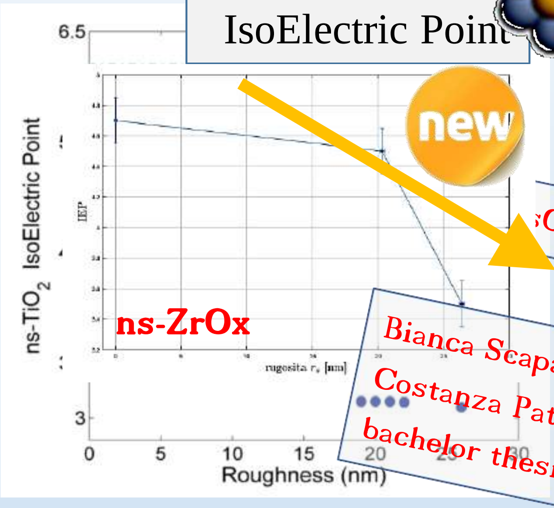
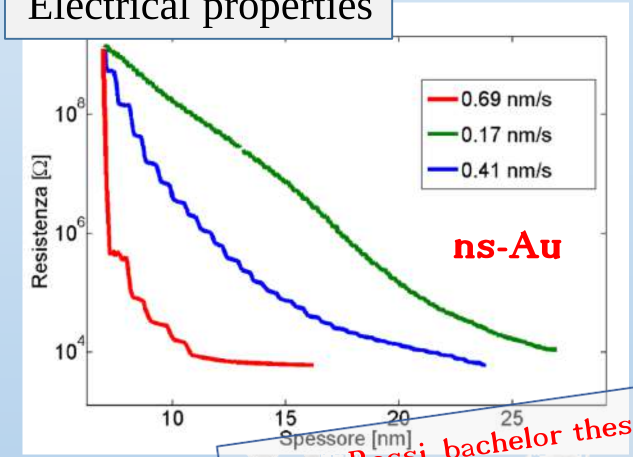


…sOne, 2013

Bianca Scaparra & Costanza Paternoster bachelor thesis

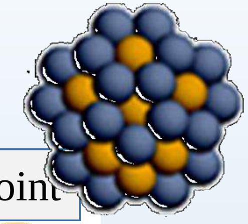
MORPHOLOGY

Electrical properties

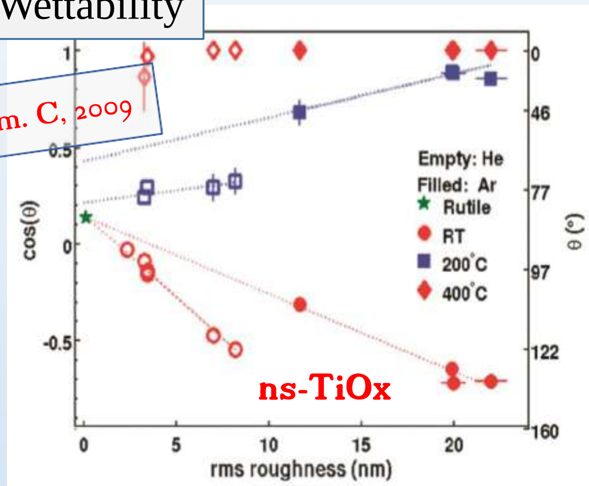


Matteo Rossi, bachelor thesis 2016

From STRUCTURAL to FUNCTIONAL properties



Wettability



A. Podestà, J. Phys. Chem. C, 2009

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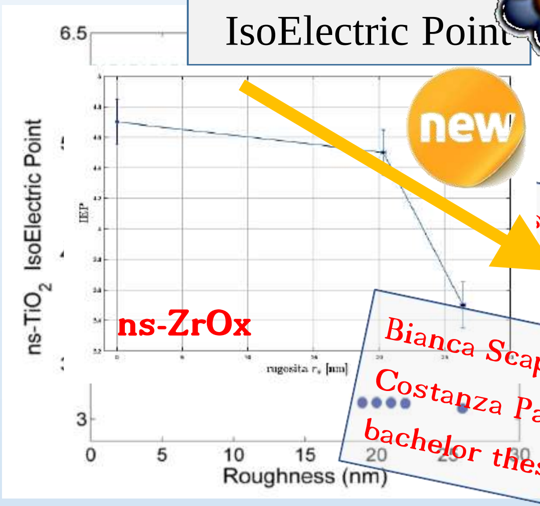

…One, 2013

Bianca Scaparra & Costanza Paternoster bachelor thesis

MORPHOLOGY

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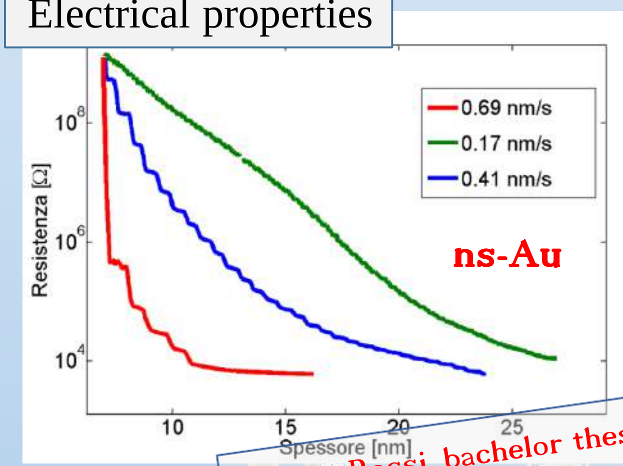
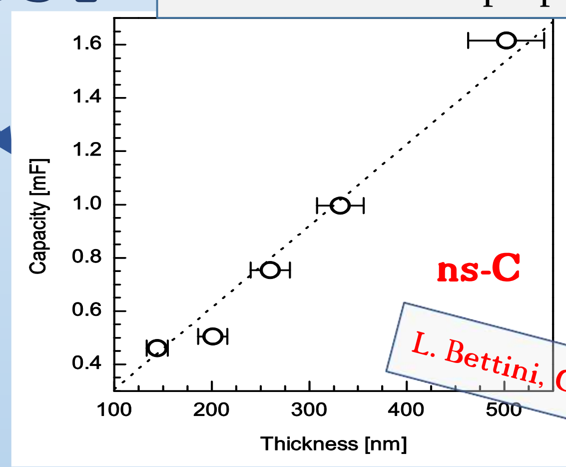


Matteo Rossi, bachelor thesis 2016

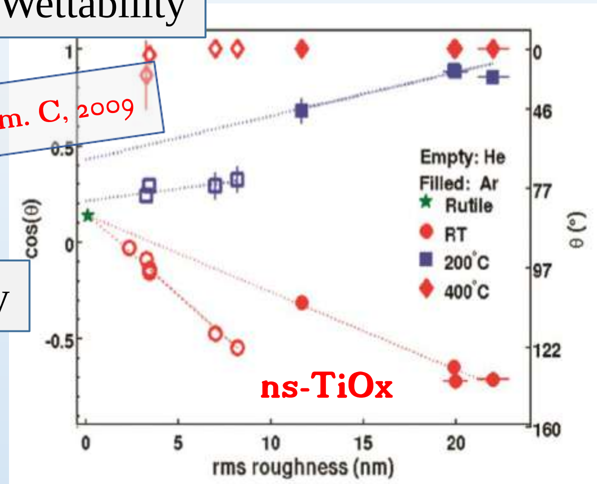
Electrochemical properties



L. Bettini, Carbon, 2013

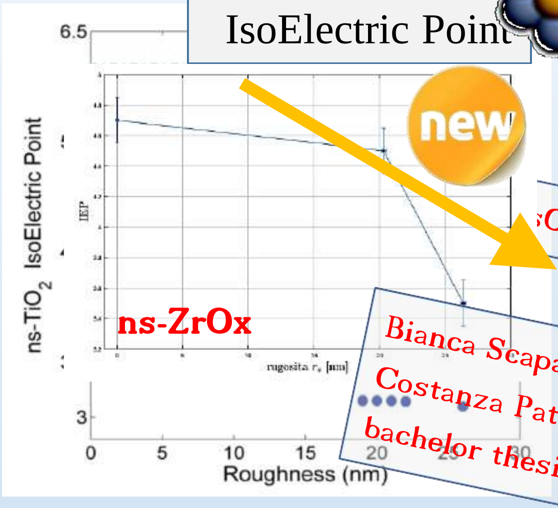
From STRUCTURAL to FUNCTIONAL properties

Wettability



A. Podestà, J. Phys. Chem. C, 2009

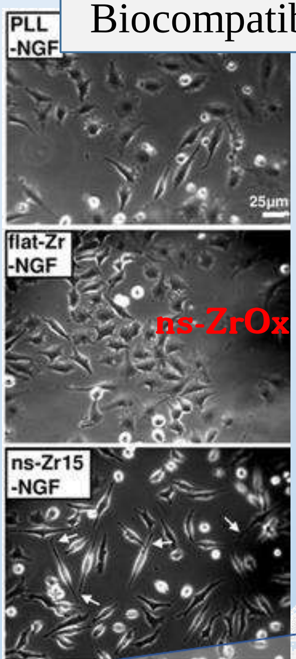
IsoElectric Point



PLoS One, 2013

Bianca Scaparra & Costanza Paternoster bachelor thesis

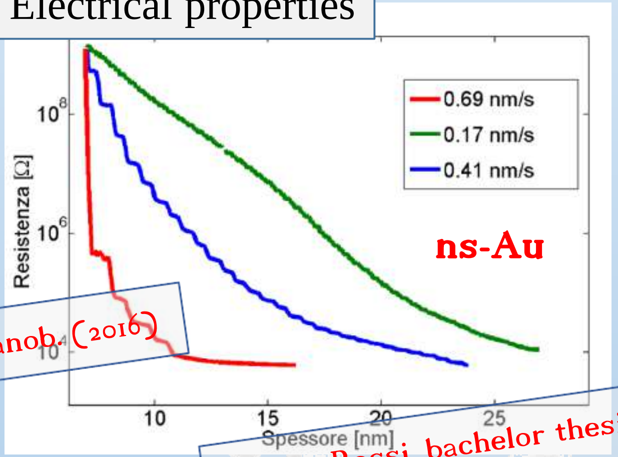
Biocompatibility



C. Schulte, et al, J. of Nanob. (2016)

MORPHOLOGY

Electrical properties



Matteo Rossi, bachelor thesis 2016

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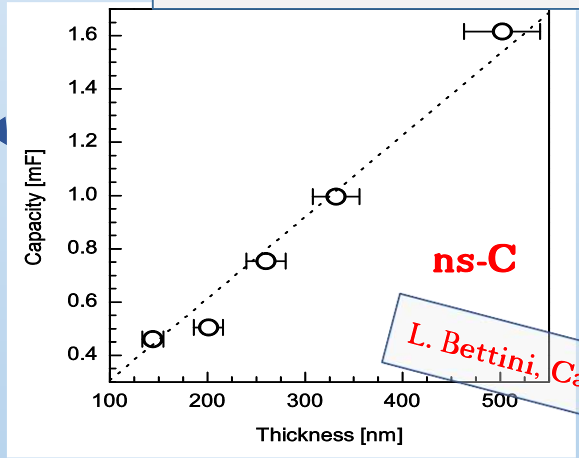
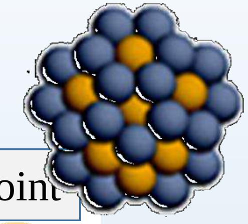


L. Bettini, Carbon, 2013

From STRUCTURAL to FUNCTIONAL properties



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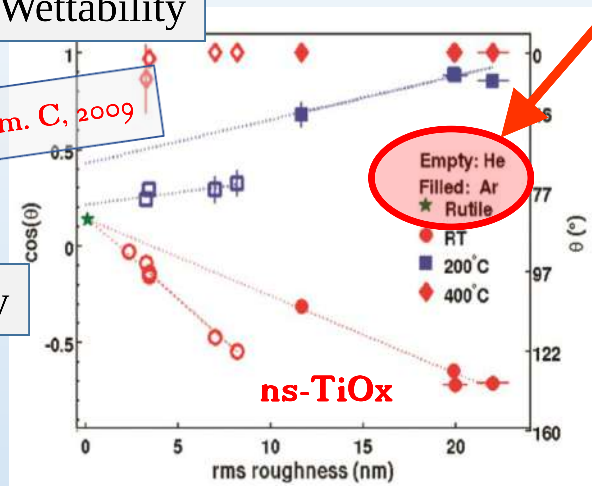
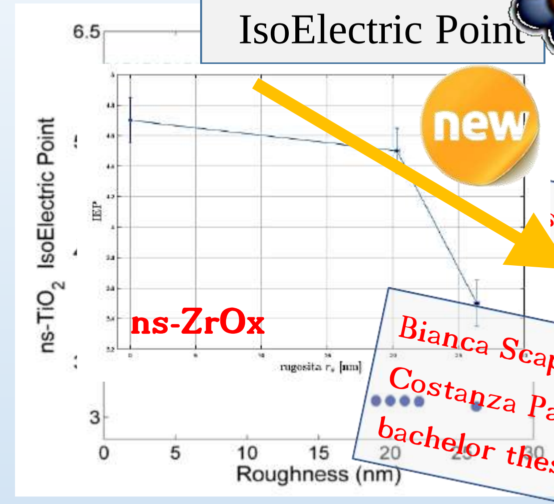


A. Podestà, J. Phys. Chem. C, 2009

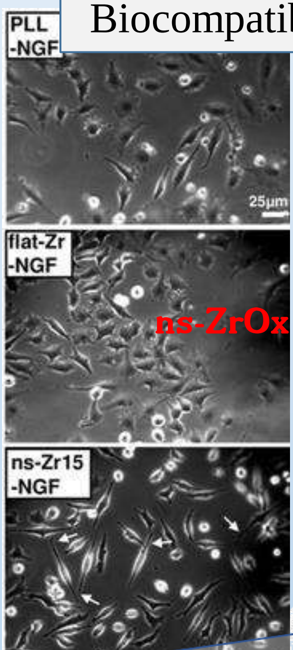
IsoElectric Point



PLoS One, 2013

Bianca Scaparra & Costanza Paternoster bachelor thesis

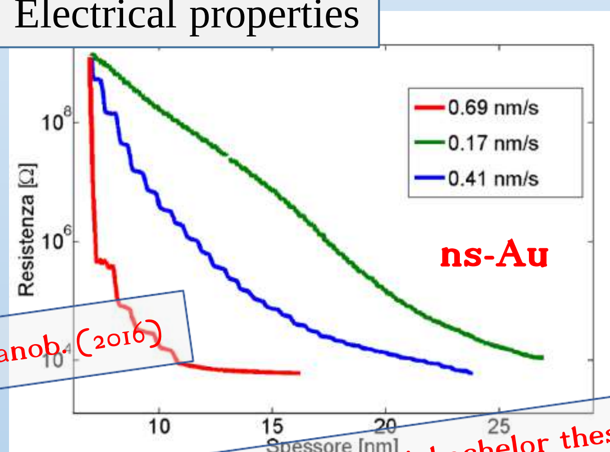
Biocompatibility



C. Schulte, et al, J. of Nanob. (2016)

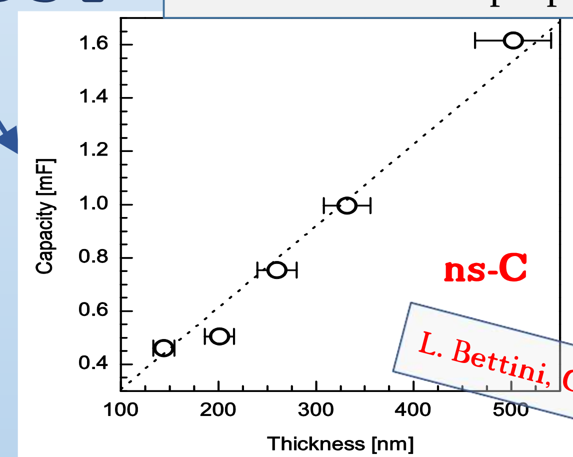
MORPHOLOGY

Electrical properties



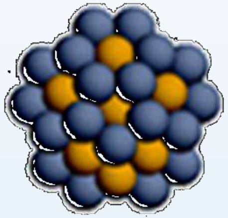
Matteo Rossi, bachelor thesis 2016

Electrochemical properties



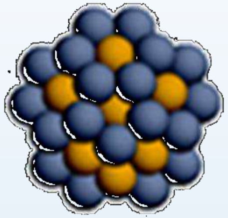
L. Bettini, Carbon, 2013

GROWTH PROCESS



Which are the parameters that control the morphological properties of thin film and their evolution?

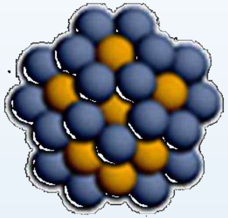
GROWTH PROCESS



Which are the parameters that control the morphological properties of thin film and their evolution?

DESCRIBE

GROWTH PROCESS



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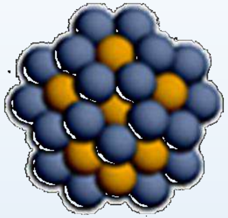
DESCRIBE

CONTROL

GROWTH PROCESS



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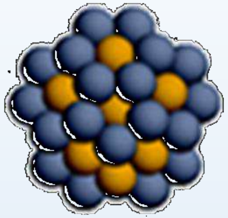
GROWTH PROCESS



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CONTROL

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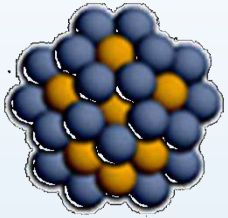
STRUCTURAL → FUNCTIONAL properties

GROWTH PROCESS



Which are the parameters that control the morphological properties of thin film and their evolution?

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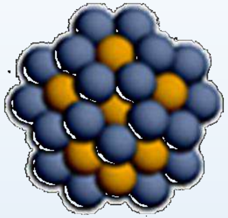
STRUCTURAL → FUNCTIONAL properties

From the early stages, few clusters on the surface

STATE OF ART



EXPERIMENTS and THEORY

Barabási, A.-L. & Stanley, H. E. *Fractal Concepts in Surface Growth*. (Cambridge University Press, 1995)

Jensen, P. *Rev. Mod. Phys.* (1999)

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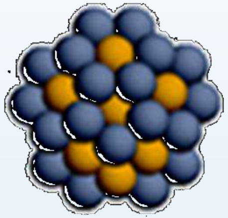

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Vandamme, et al. J. Phys. Condens. Matter, (2003)

Yoon, B. et al., Surf. Sci. , (1999)

Bouwen, W. et al., Rev. Sci. Instrum., (2000)

Bouwen, W. et al. Thin Solid Films, (1999)

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ENGINEER

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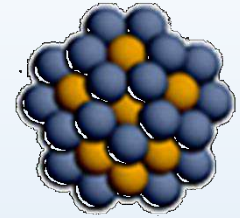

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DESCRIBE

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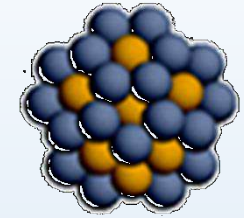
Bouwen, W. et al. Thin Solid Films, (1999)

Too complex system for theoretical framework

Low stability and deposition rate of cluster sources

ENGINEER

STATE OF ART



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DESCRIBE

Too complex system for theoretical framework

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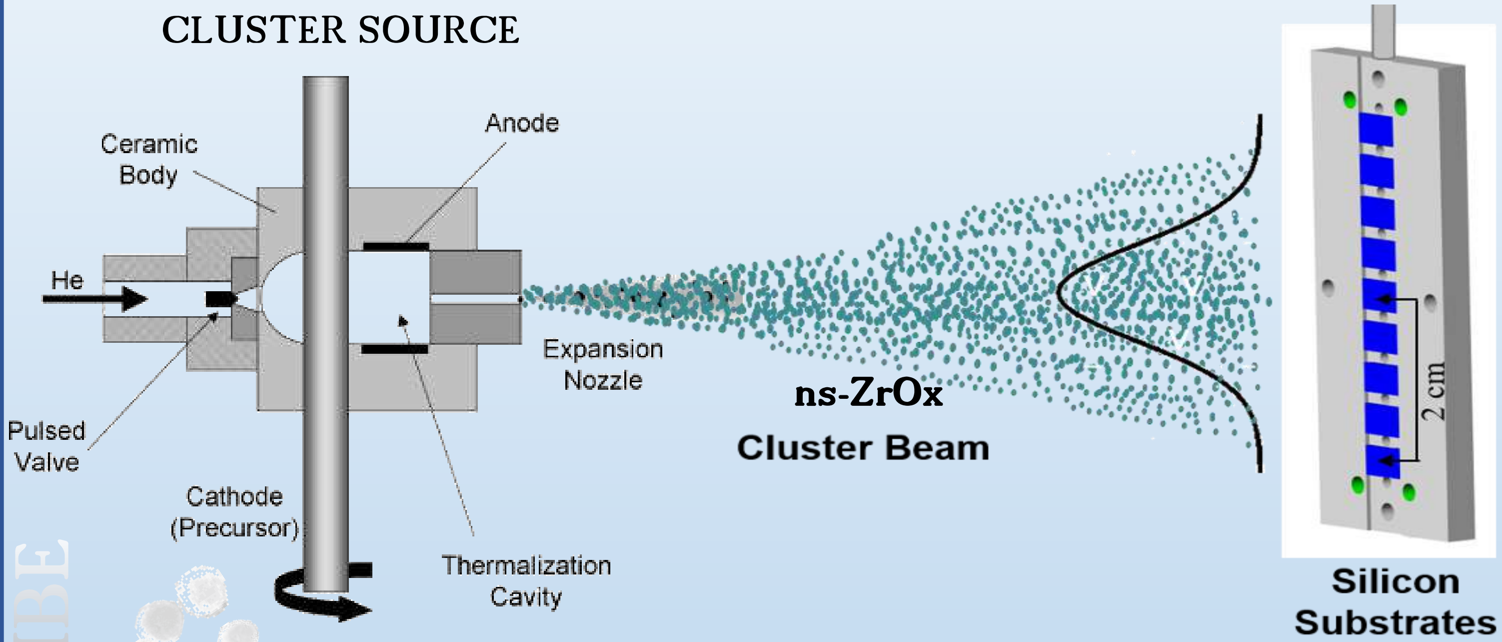
Bouwen, W. et al. Thin Solid Films, (1999)

Low stability and deposition rate of cluster sources

Do NOT focus on single defect but on the MESO/MACRO effects of disorder

ENGINEER

Supersonic Cluster Beam Deposition of NS-ZrOx Thin Film



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DESCRIBE

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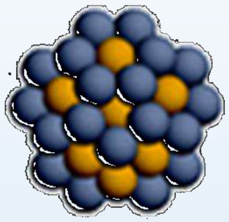
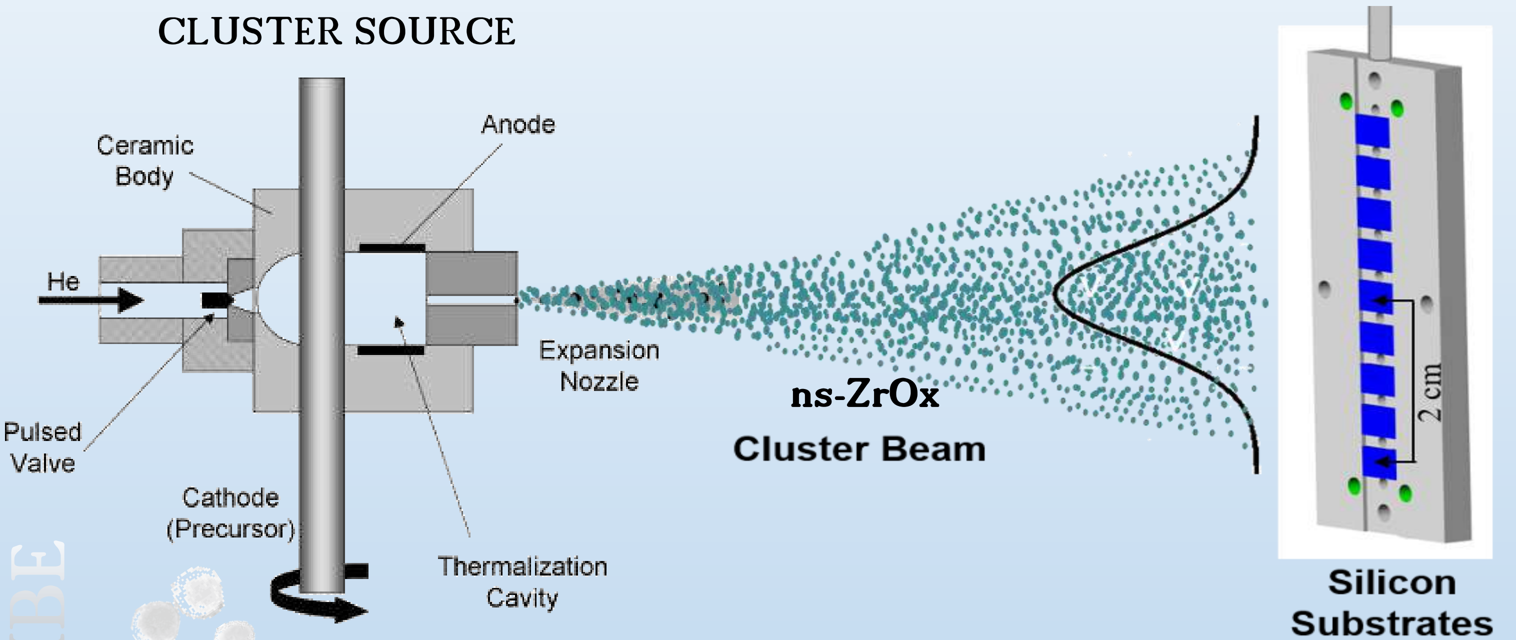


CONTROL

CLUSTER SOURCE



At **room temperature**

On fragments of polished **Si wafers** (~ 1x0,5 cm²)

With **Helium** or **Argon** as carrier gas

DESCRIBE

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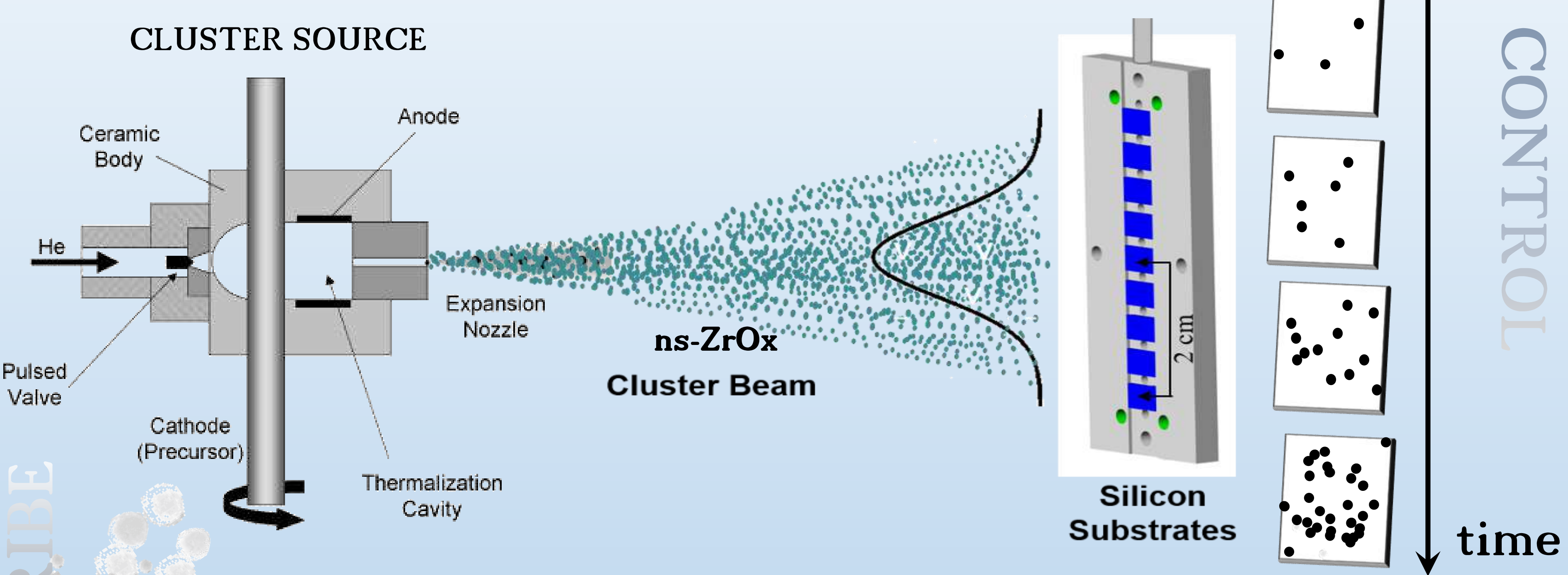

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With **Helium** or **Argon** as carrier gas

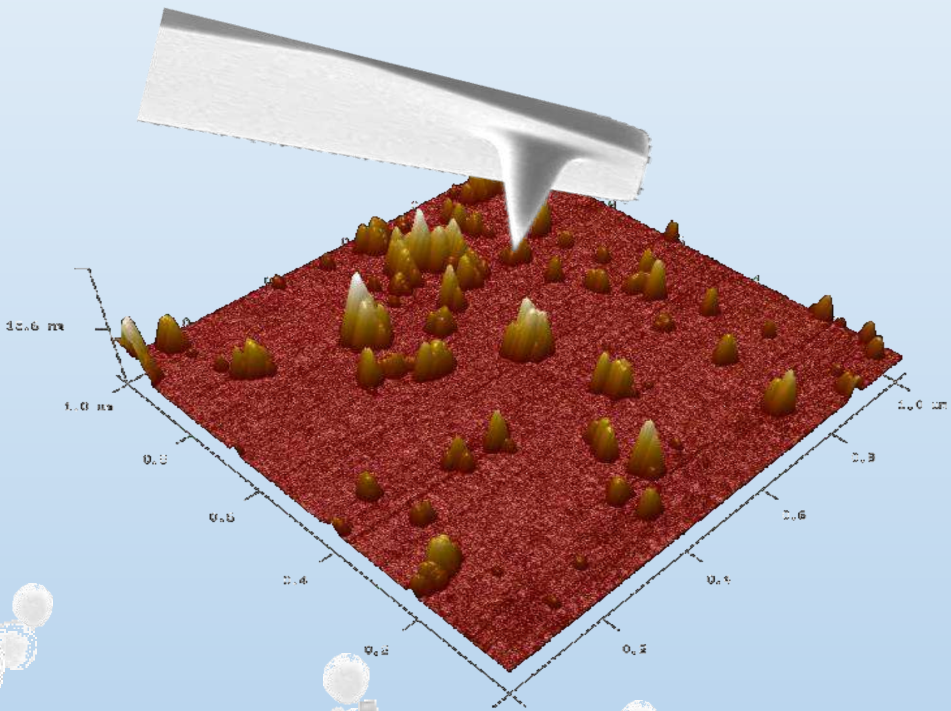
DESCRIBE

K. Wegner, Journal of Phys. D Appl. Phys. (2006)

ENGINEER

Characterization of NS-ZrOx Thin Film

Atomic Force Microscopy



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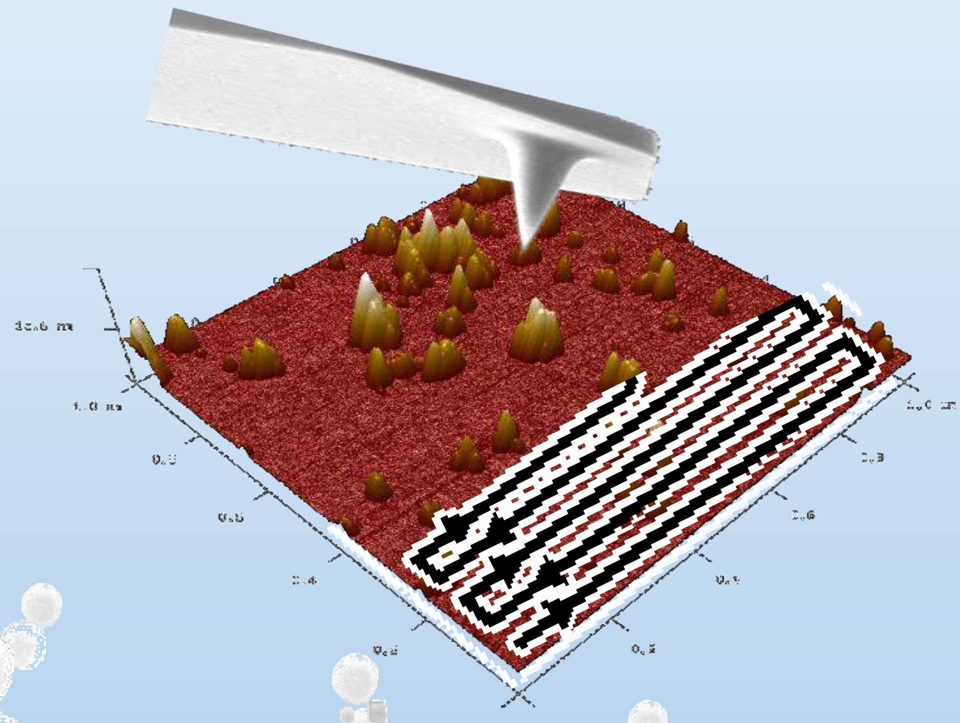

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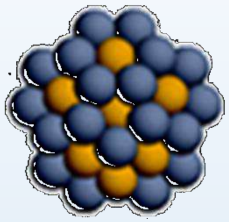
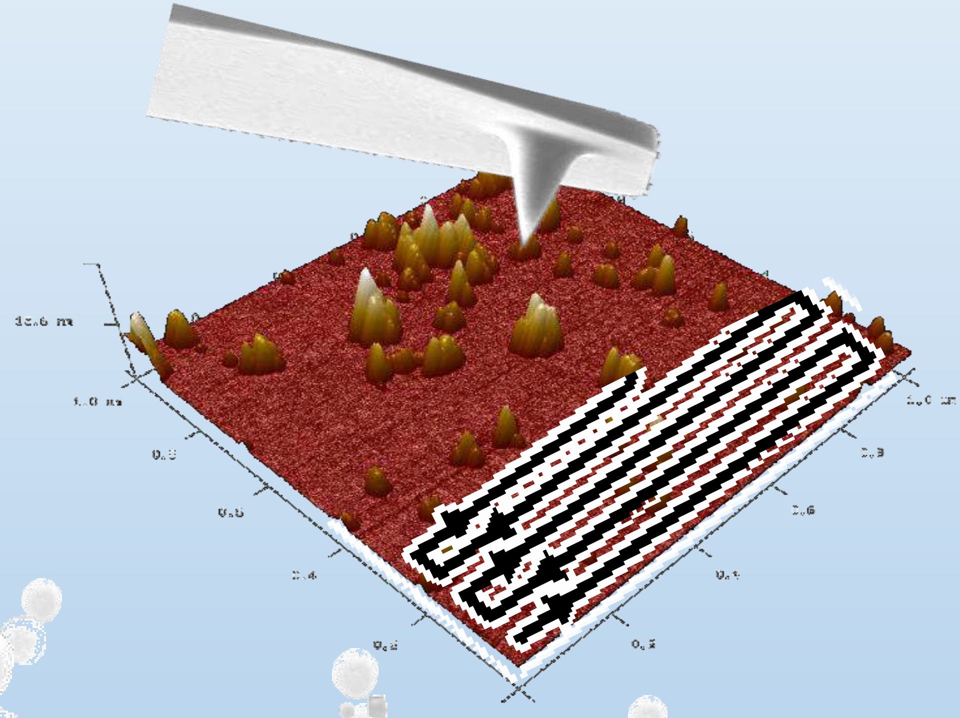
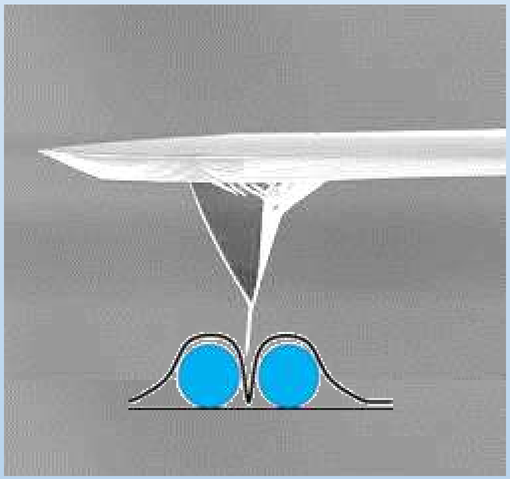


Atomic Force Microscopy





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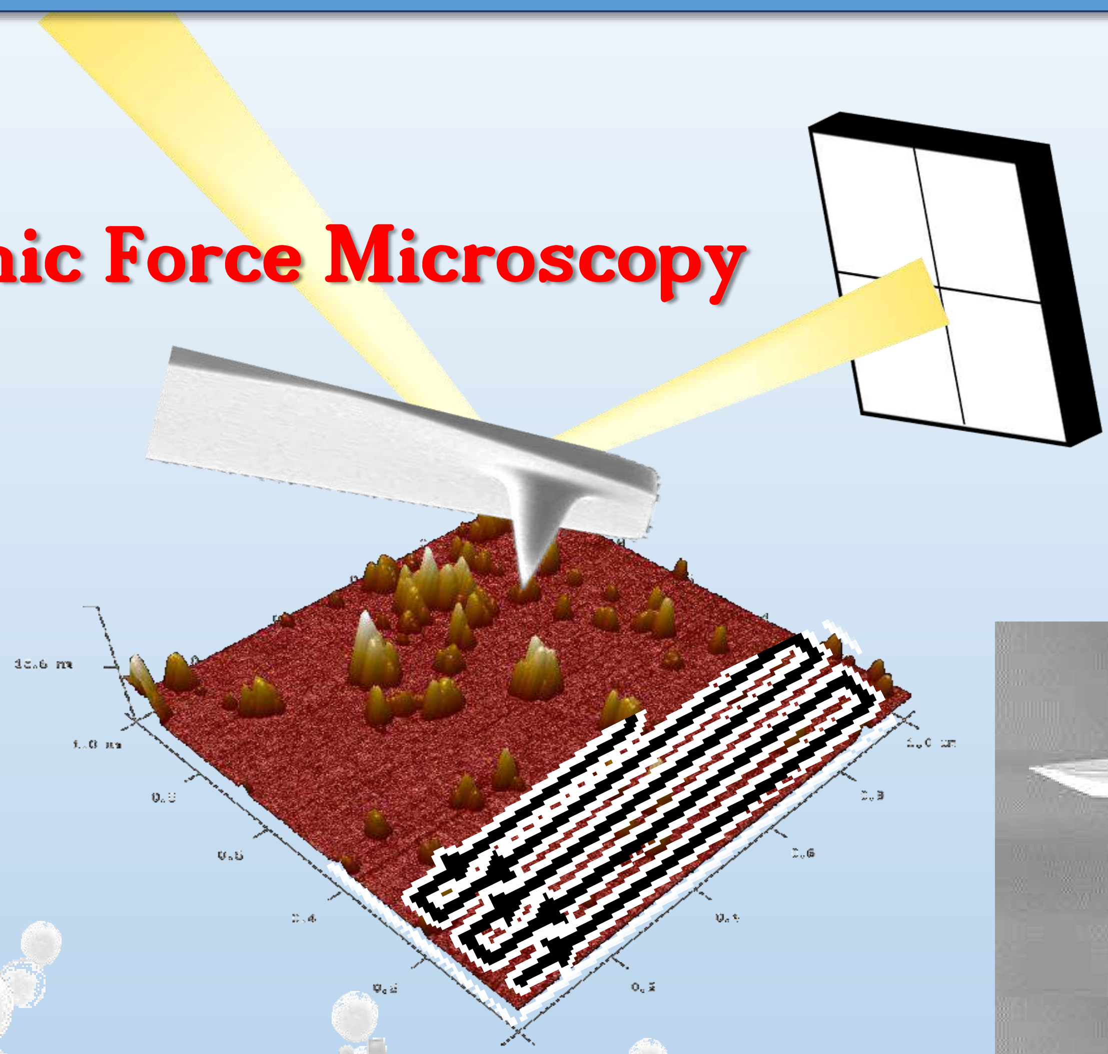

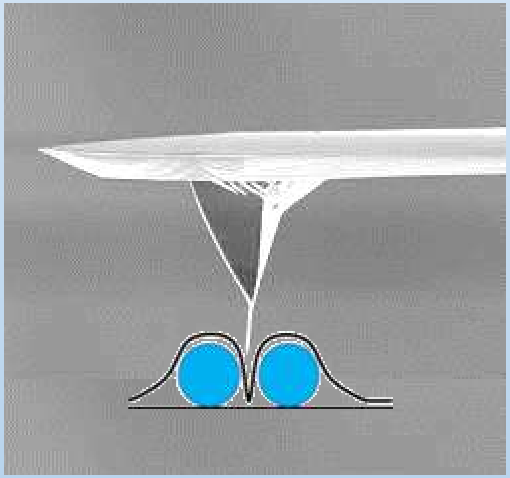

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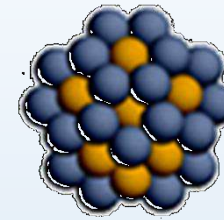
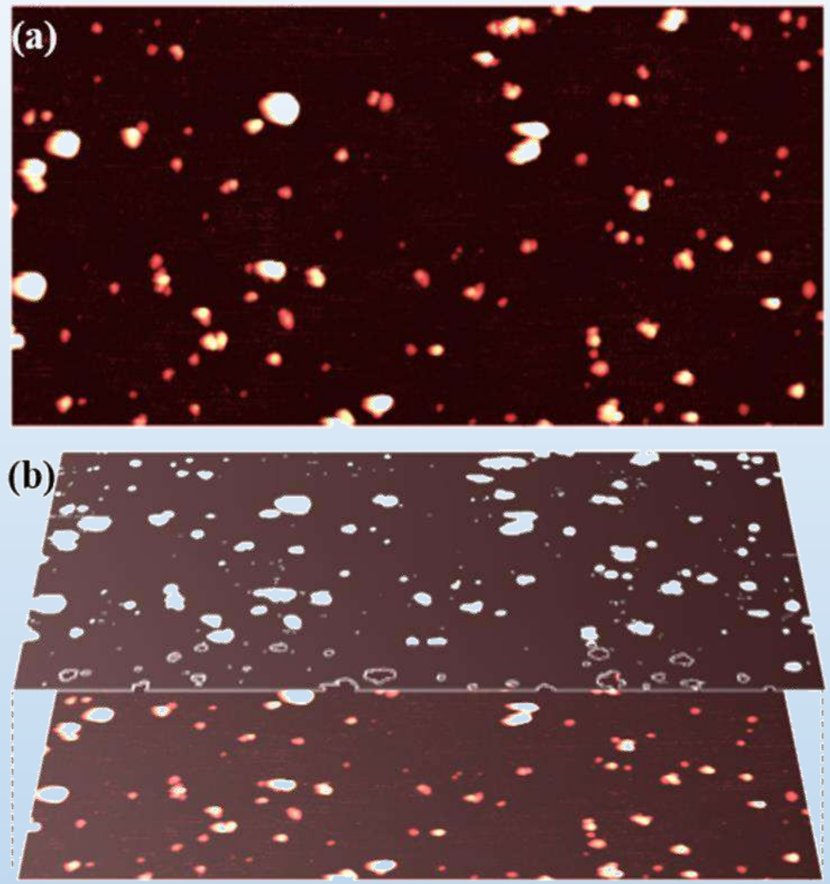
DESCRIBE

ENGINEER

EVALUATION OF THE GEOMETRICAL PROPERTIES





2µm x 1µm x 0.005µm

CONTROL

DESCRIBE

F. borghi, et al., Arxiv, submitted to Phys. Rev. B

ENGINEER

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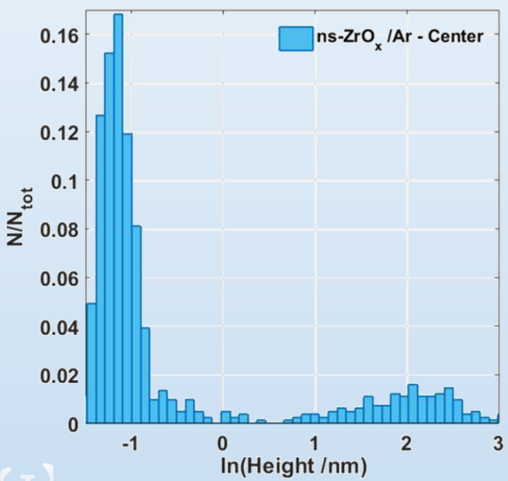

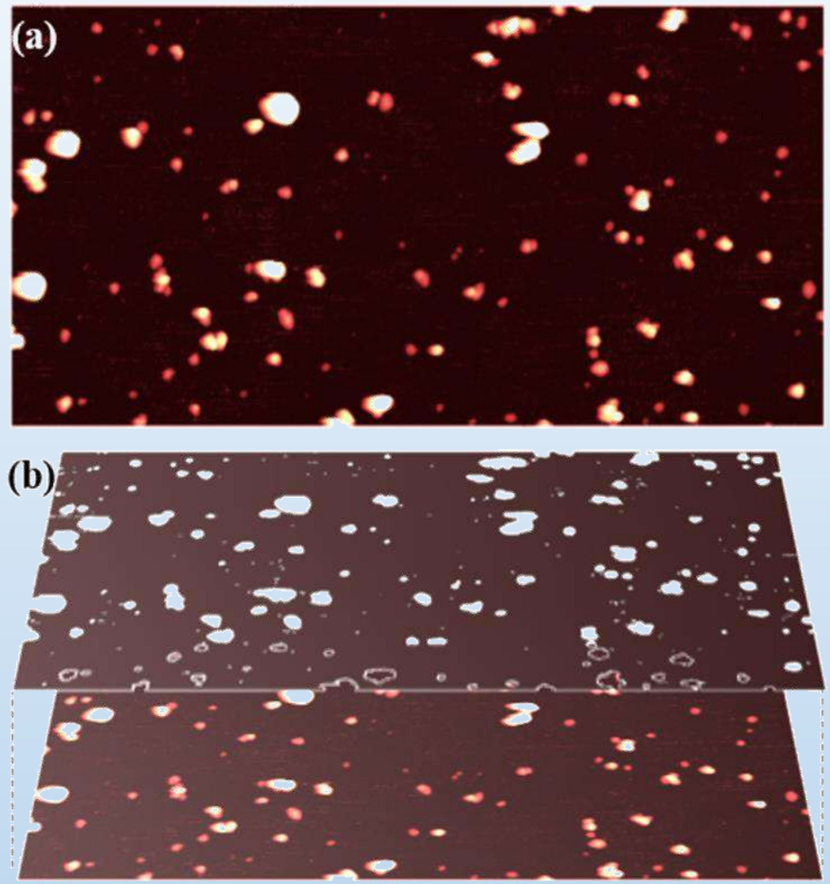

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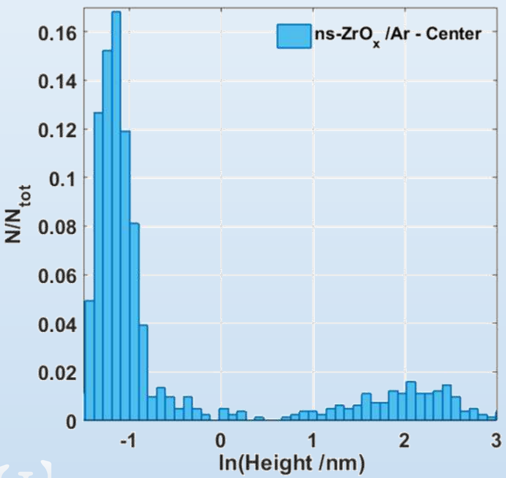

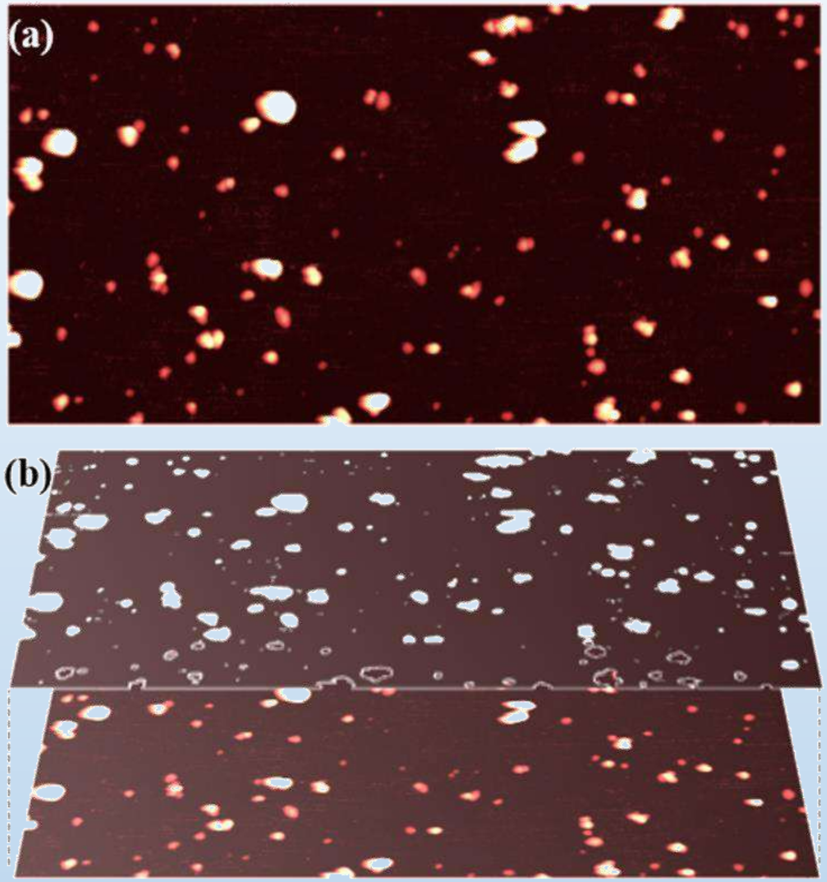

2µm x 1µm x 0.005µm

Coverage: ratio between the area occupied by clusters on the surface and the scanned area

CONTROL

DESCRIBE

ENGINEER

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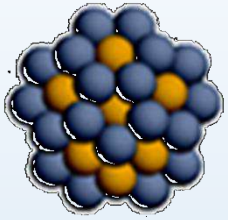
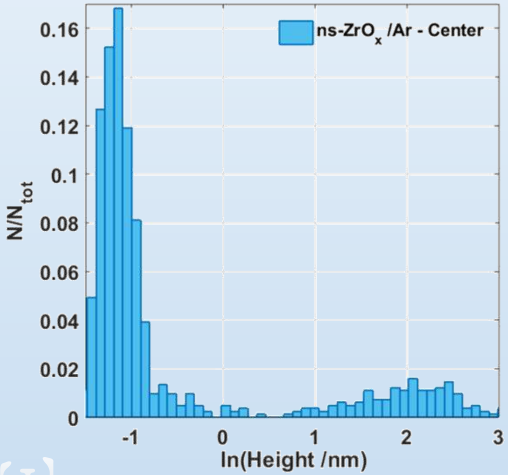
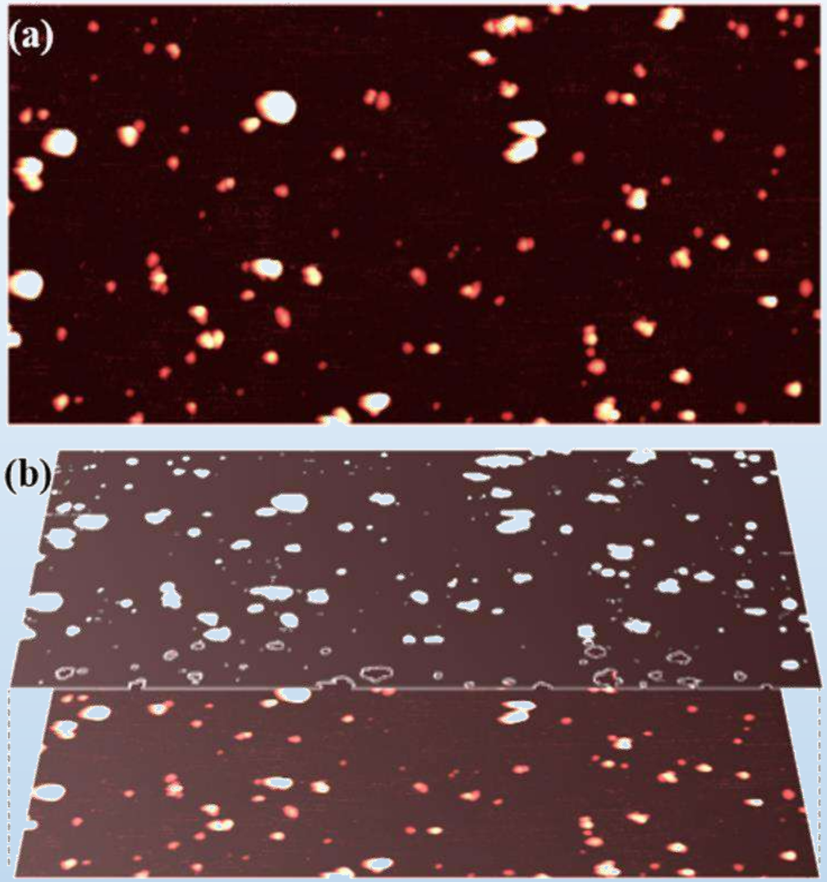
EVALUATION OF THE GEOMETRICAL PROPERTIES

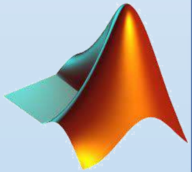






2μm x 1μm x 0.005μm

CONTROL



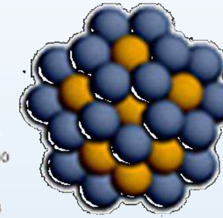
DESCRIBE

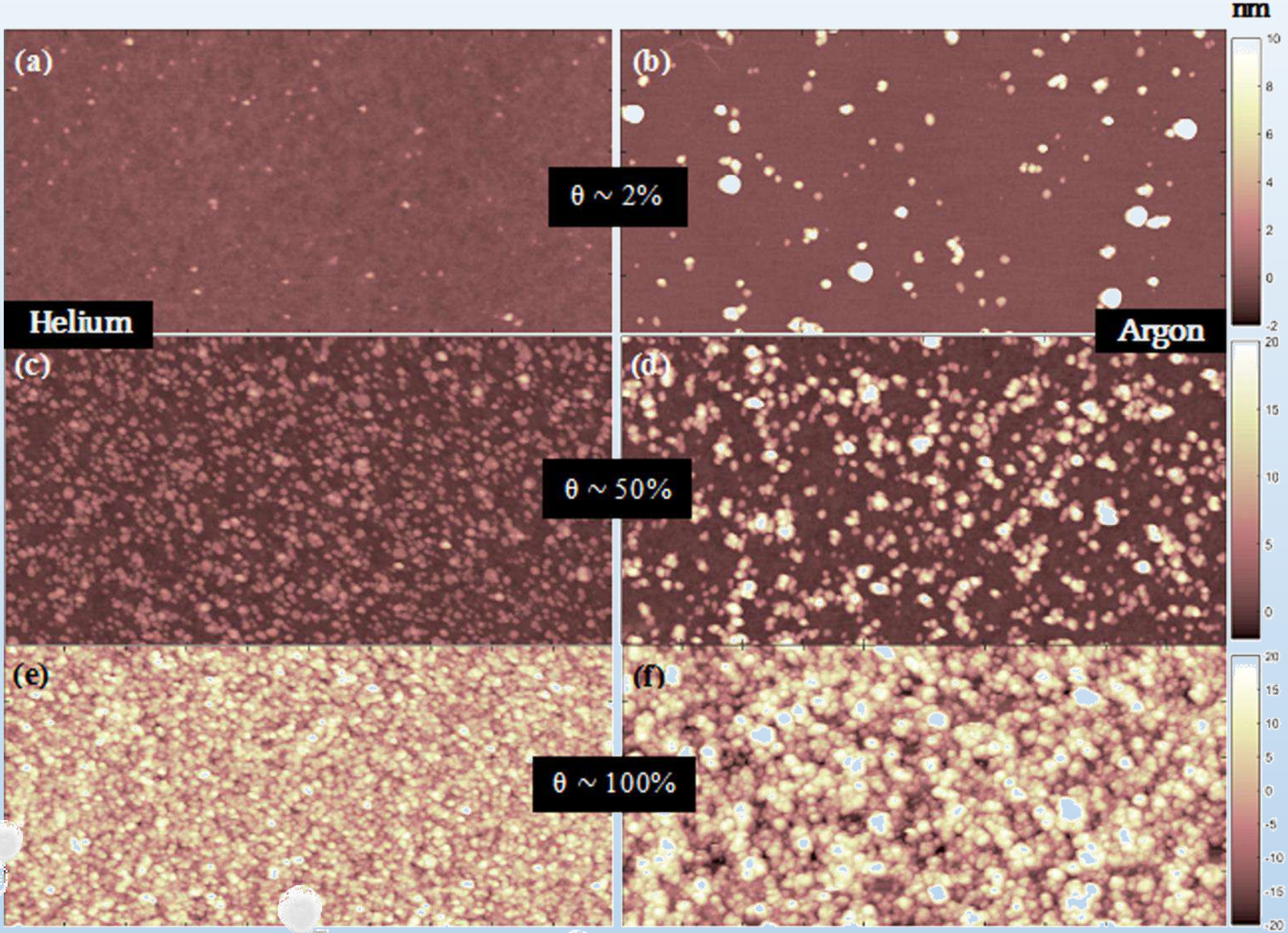
Coverage: ratio between the area occupied by clusters on the surface and the scanned area

Objects with dimension in z-direction different from the dimensions of primeval incident cluster have been called **islands**

ENGINEER

SURFACE EVOLUTION





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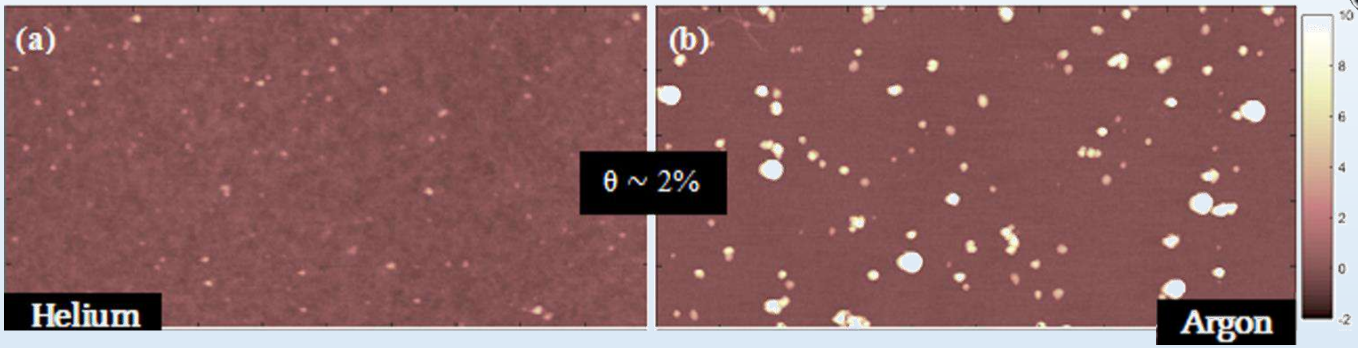
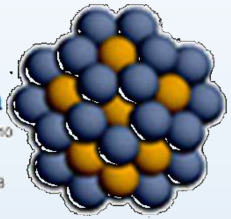
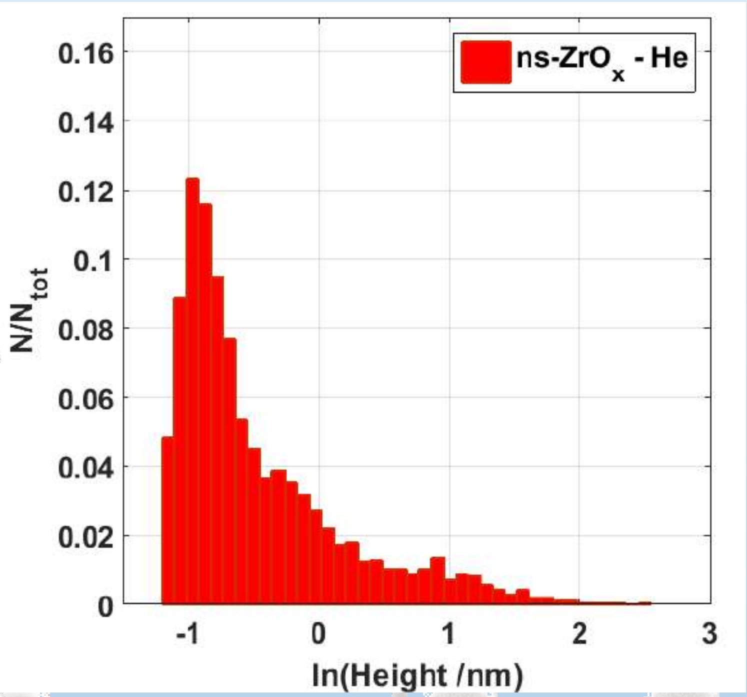
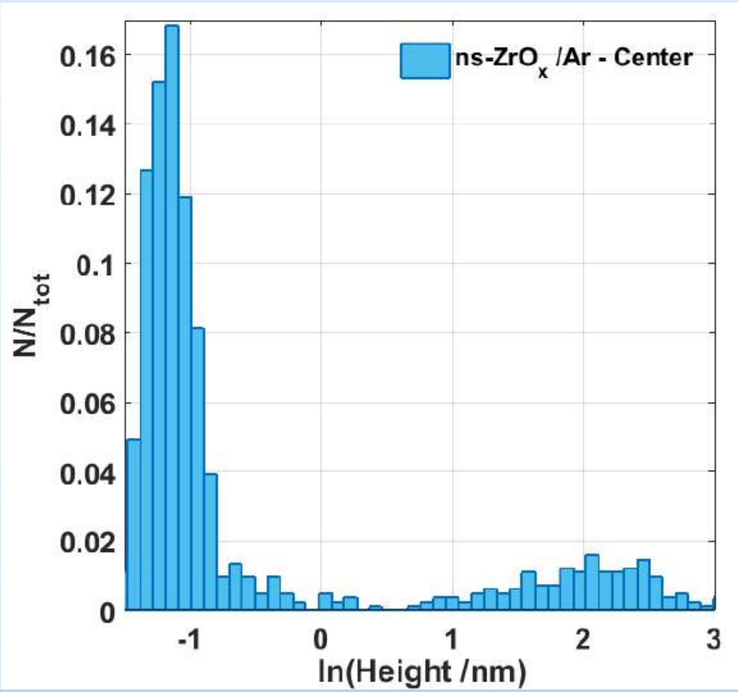
Ns-ZrOx CLUSTER SIZE DISTRIBUTION









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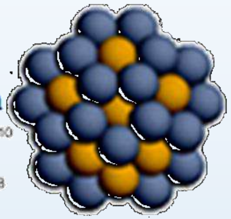

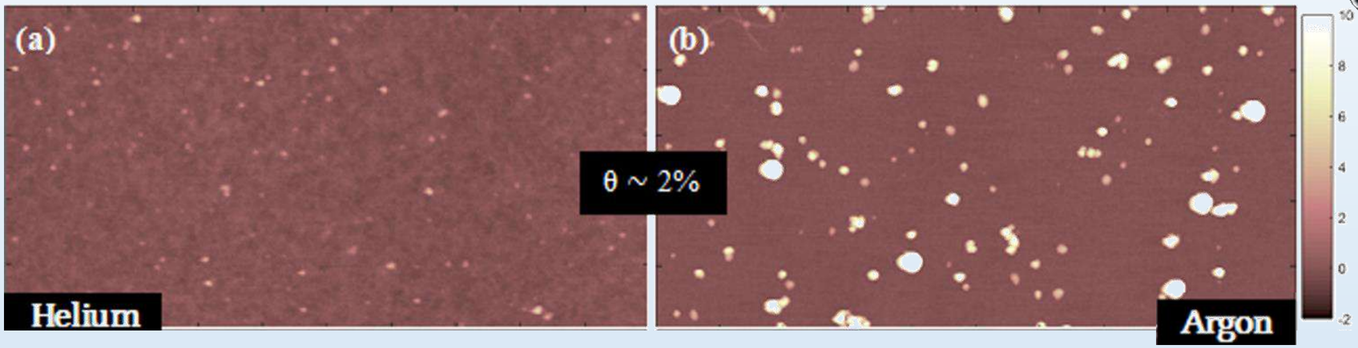

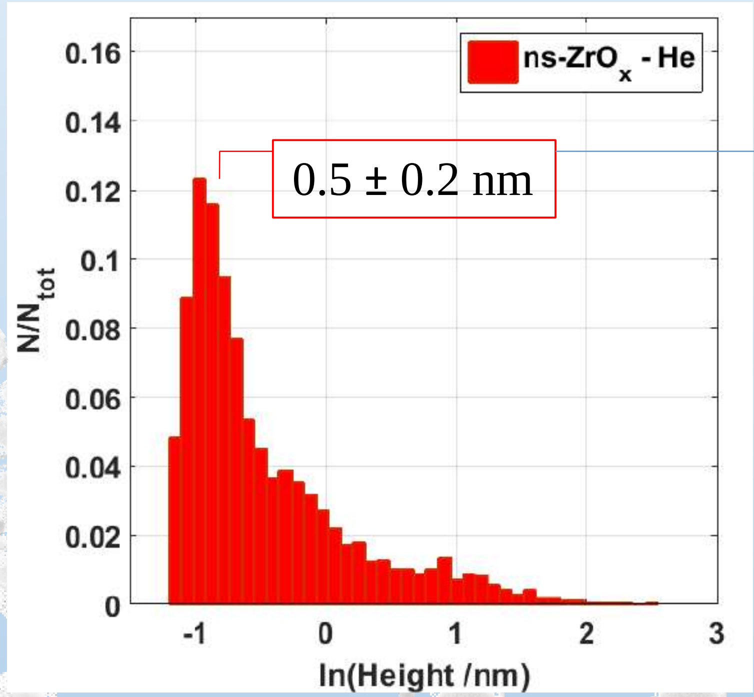

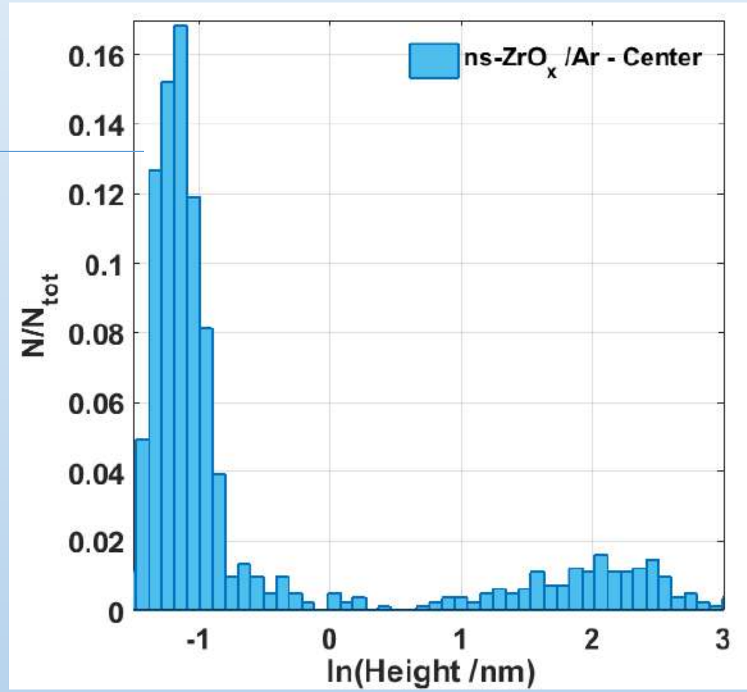

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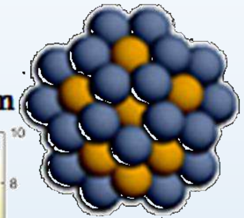

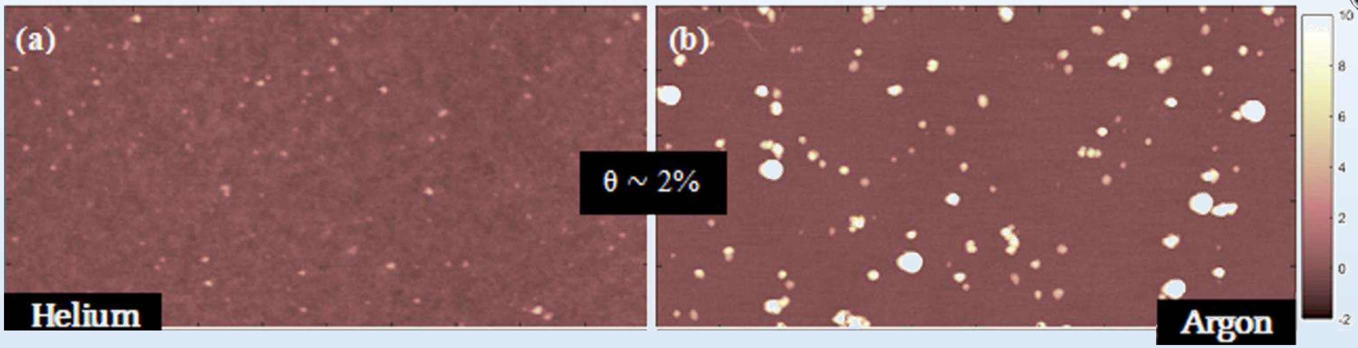

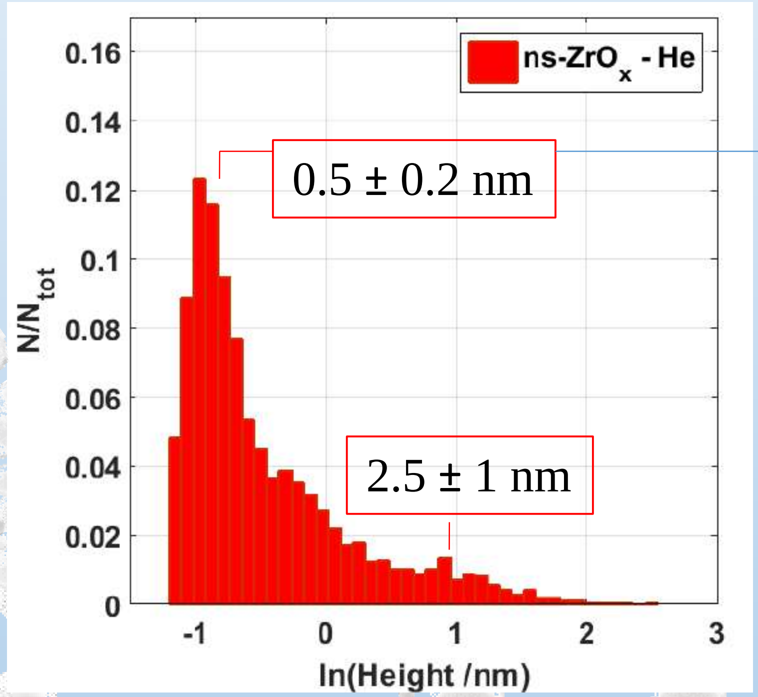

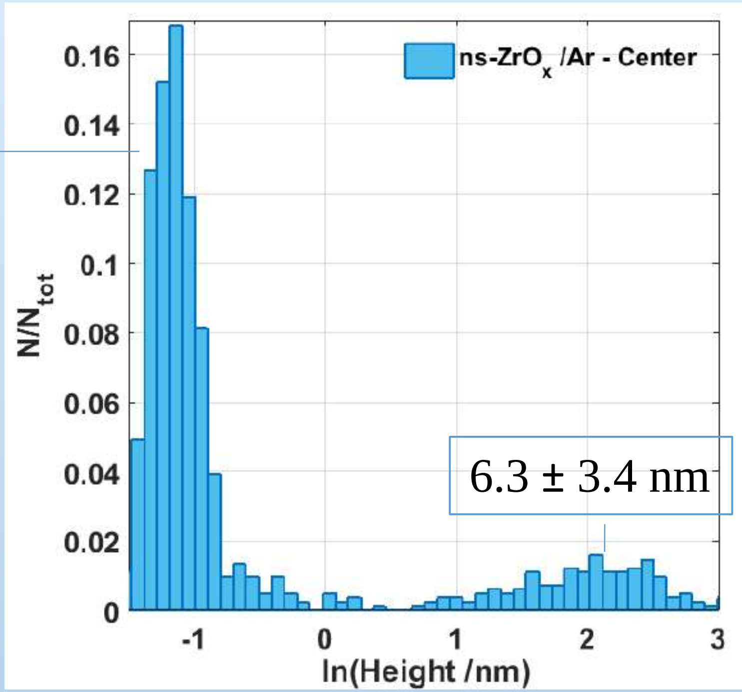

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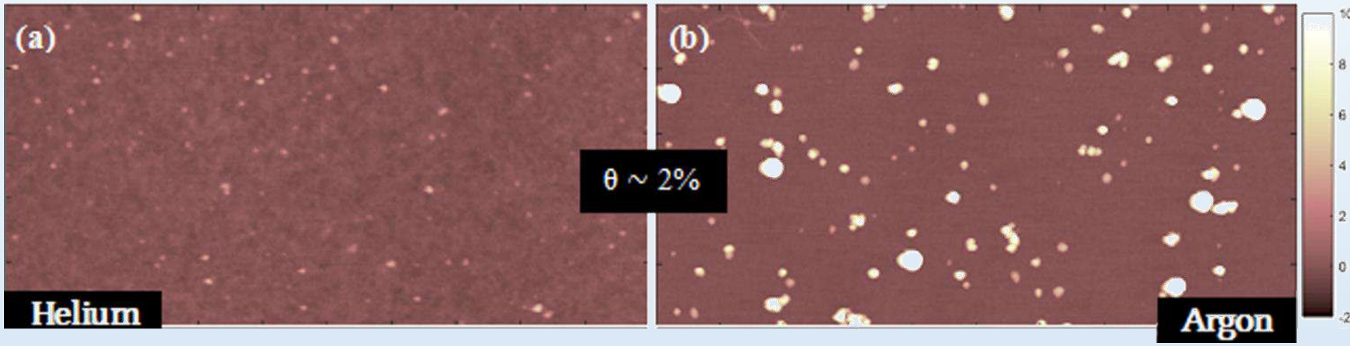

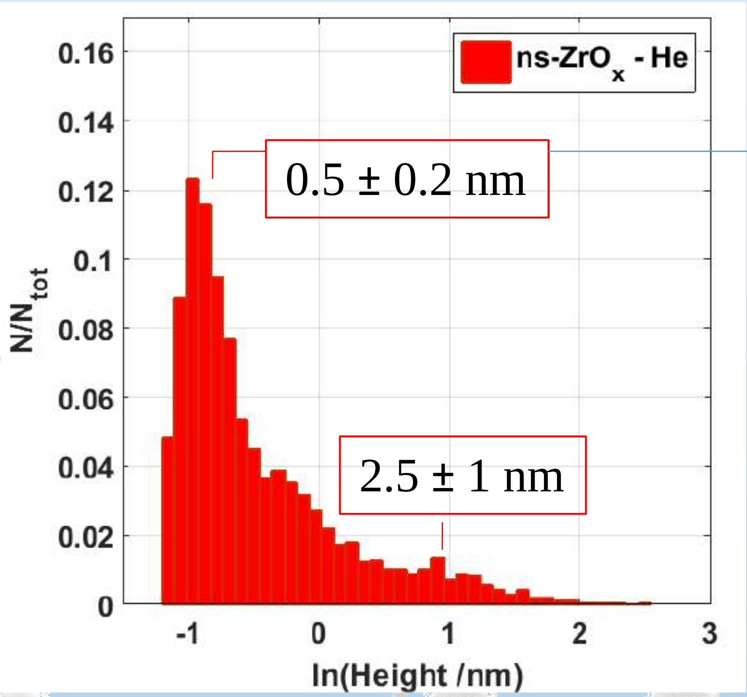

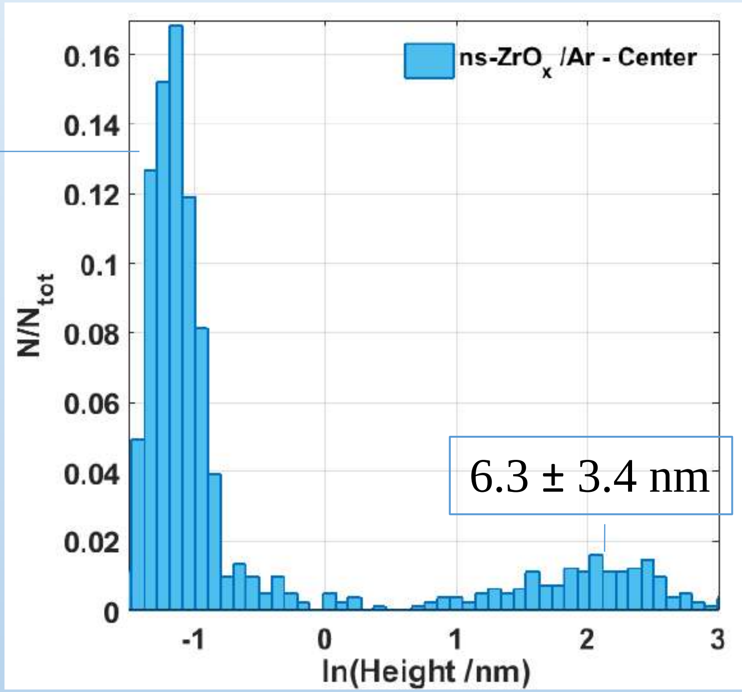

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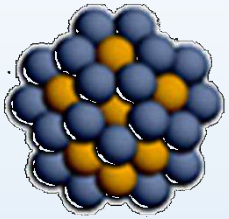
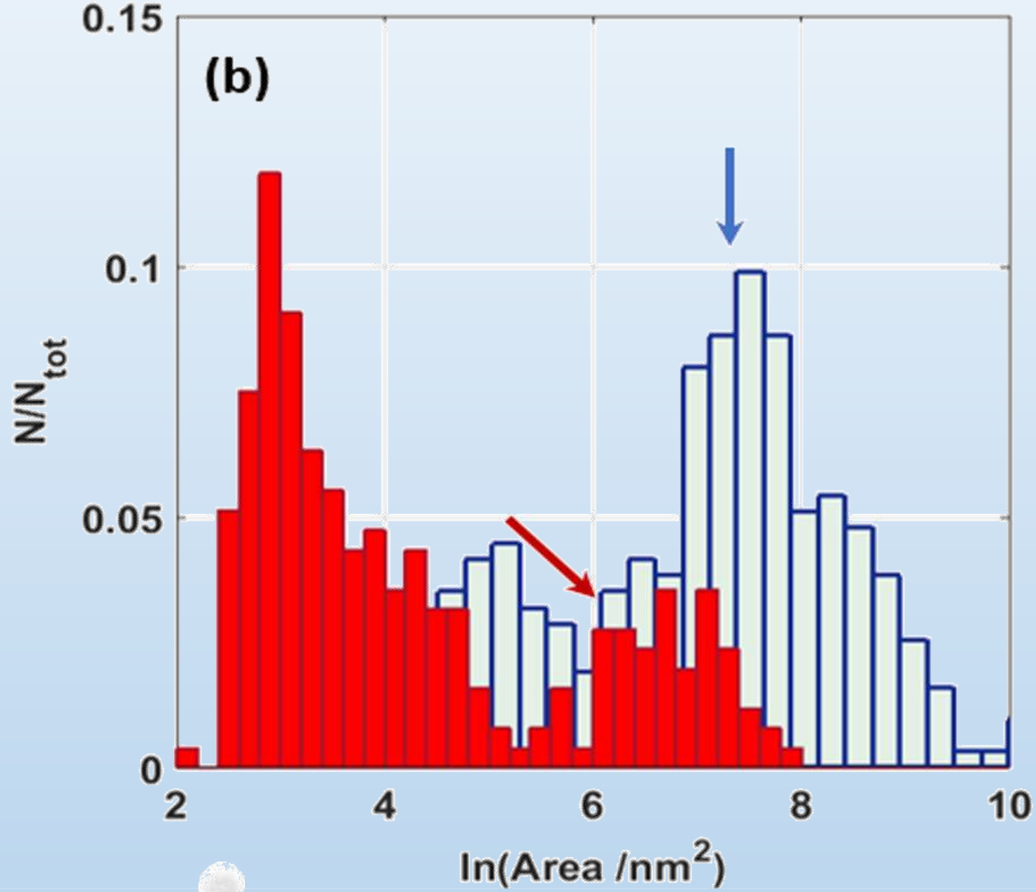
F. borghi, et al., Arxiv, submitted to Phys. Rev. B

A. Podestà, J. of Appl. Phys., 2015

ENGINEER

SURFACE EVOLUTION





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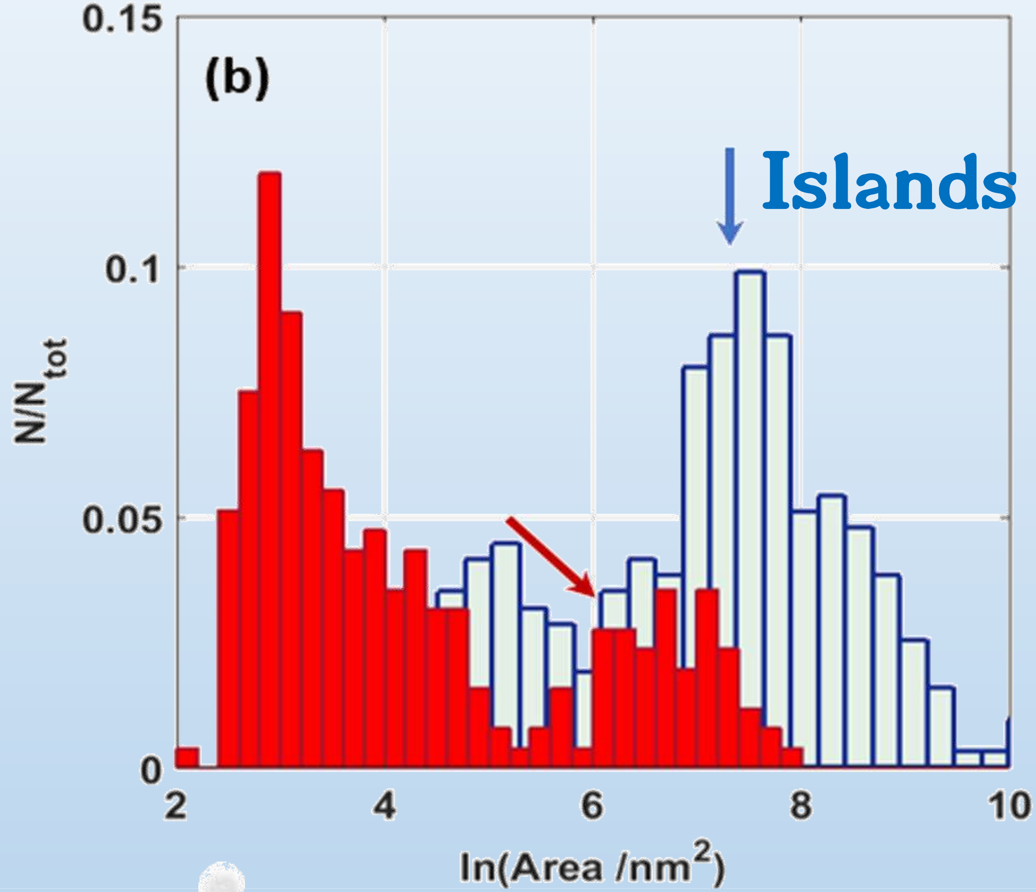
SURFACE EVOLUTION



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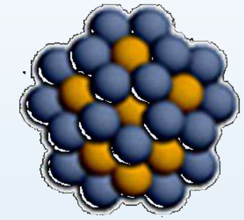
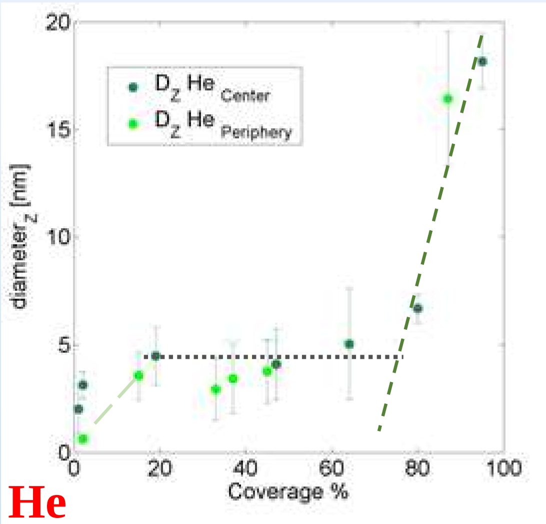
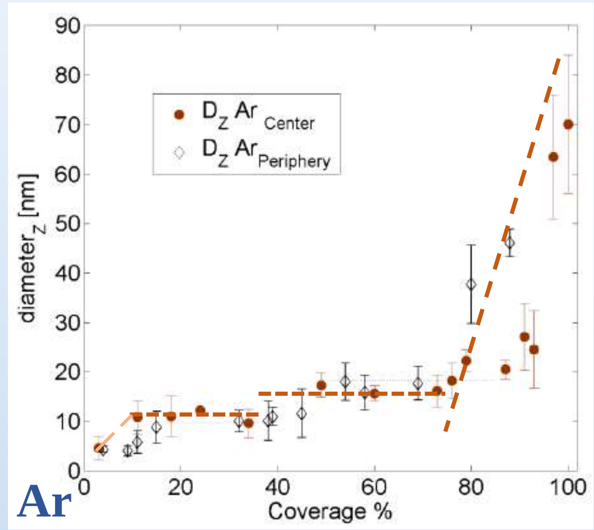
HEIGHT EVOLUTION







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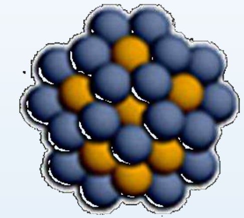
HEIGHT EVOLUTION



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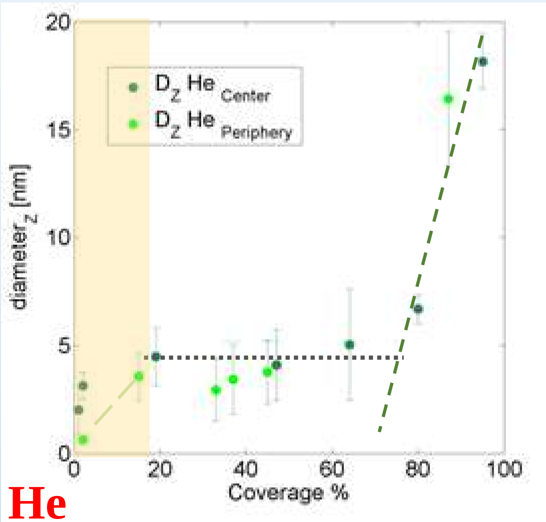

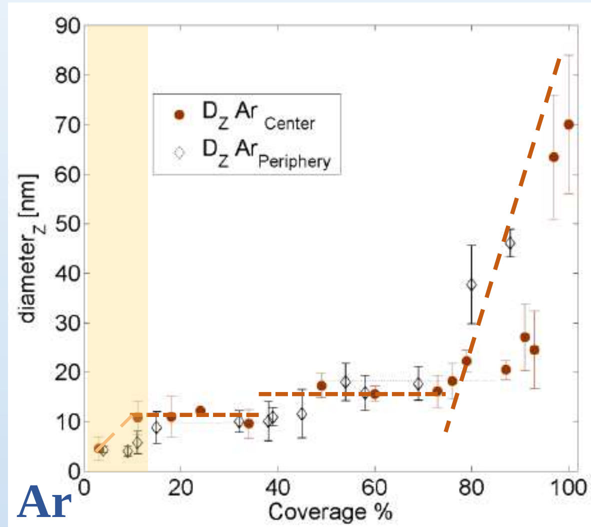

0 - 10 % : coalescence and fast nucleation processes

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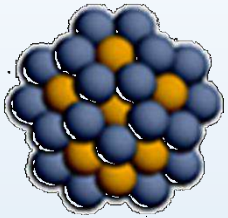
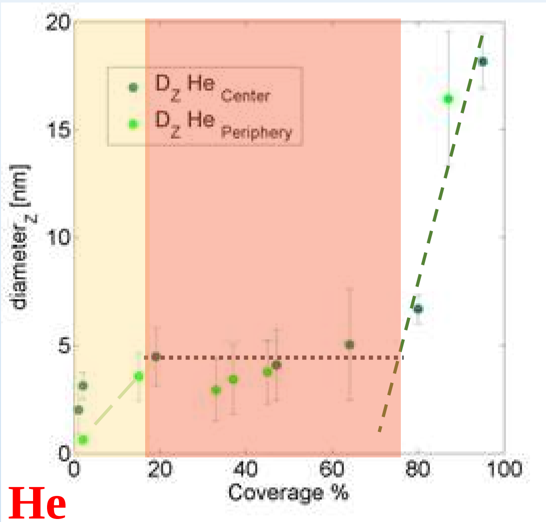
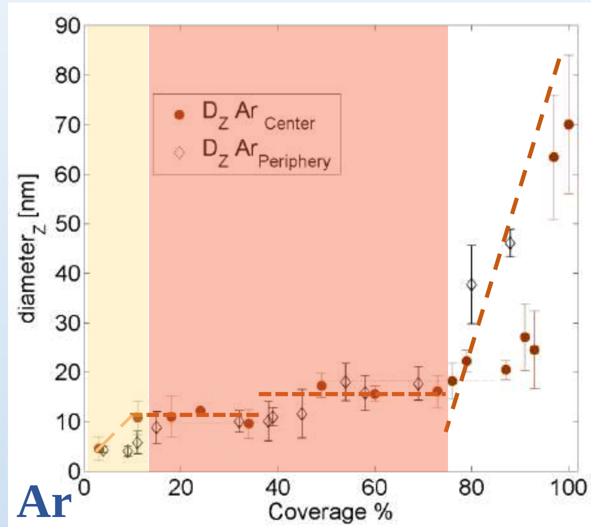
HEIGHT EVOLUTION







CONTROL

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10 - 70 %: (He) x-y juxtaposition and nucleation of new islands, (Ar) stepwise around coverage of 50%

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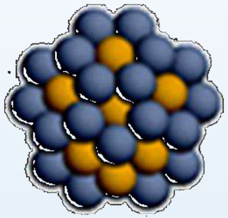

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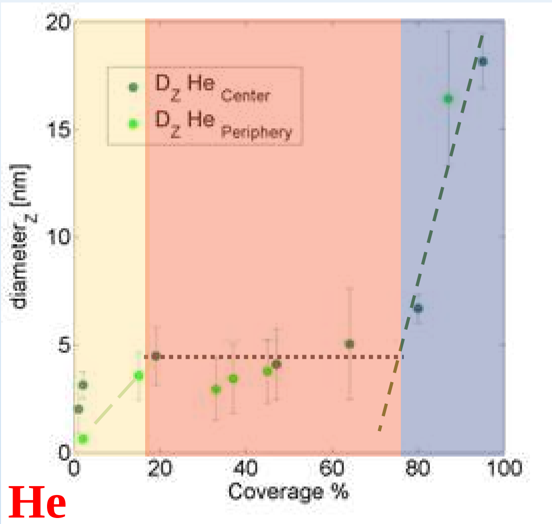

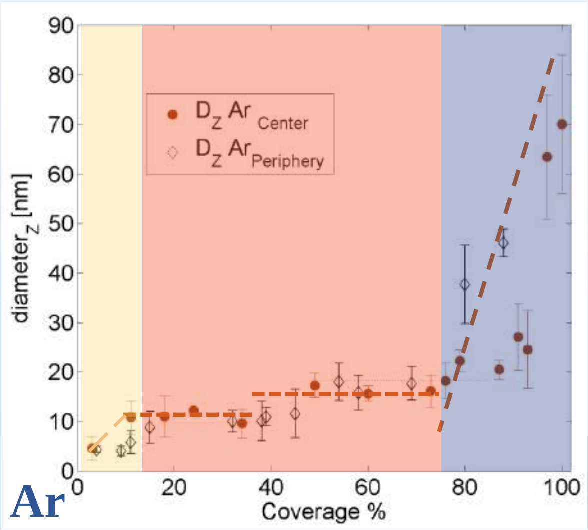

0 - 10 % : coalescence and fast nucleation processes

10 - 70 %: (He) x-y juxtaposition and nucleation of new islands, (Ar) stepwise around coverage of 50%

70 - 100 % : Starting point of **ballistic deposition** (without diffusion and coalescence)

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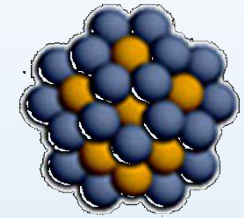
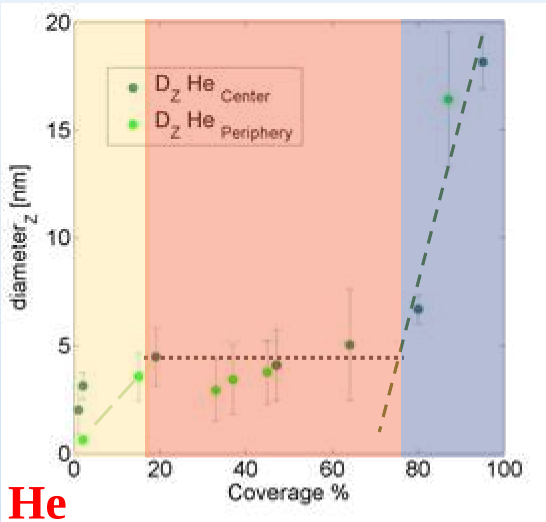
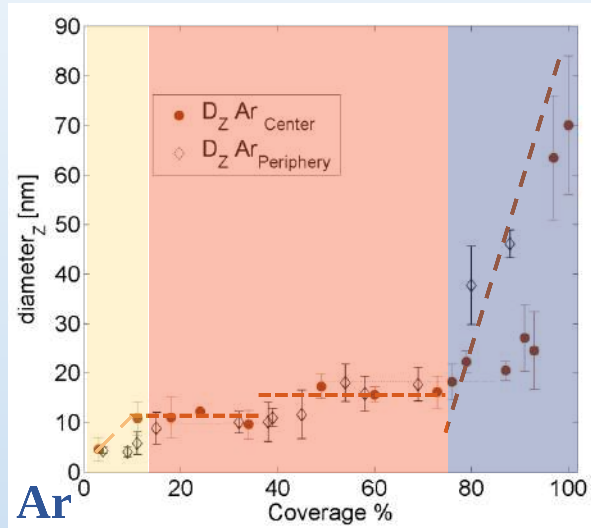
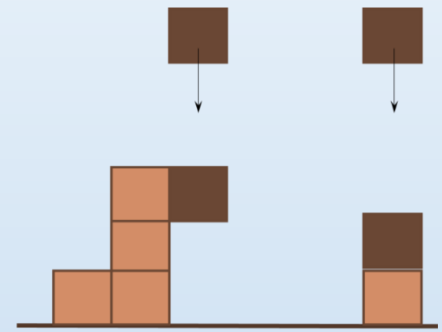
HEIGHT EVOLUTION







Sticking probability =1



nearest neighbor B. D.

CONTROL

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DESCRIBE

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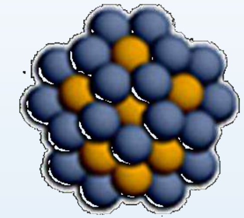
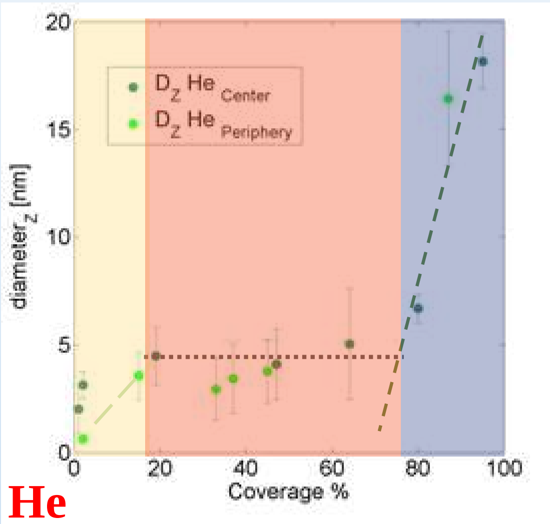
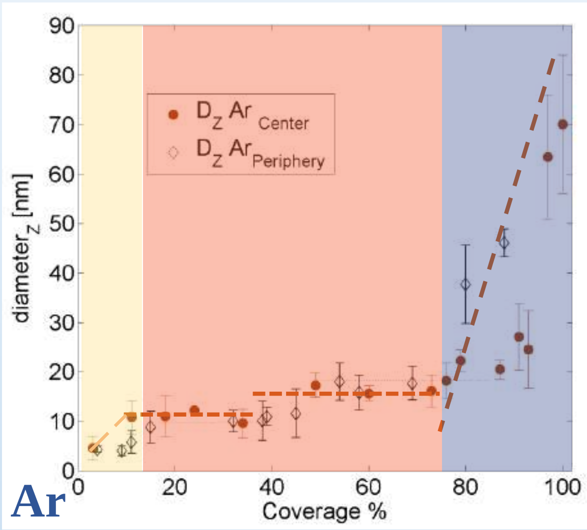
HEIGHT EVOLUTION







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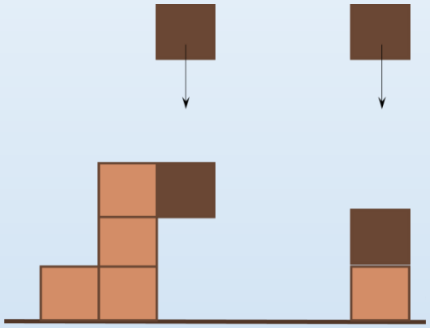
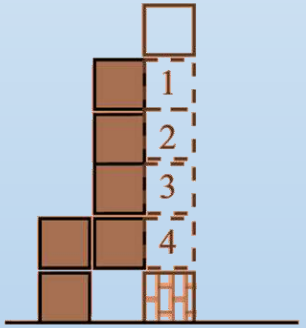


nearest neighbor B. D.

Sticking probability ≠1



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Robledo, A. *et al. Phys. Rev. E* **83**, 051604 (2011)

F. borghi, et al., Arxiv, submitted to Phys. Rev. B

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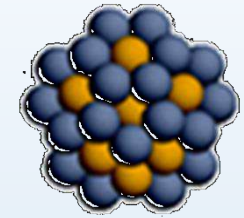
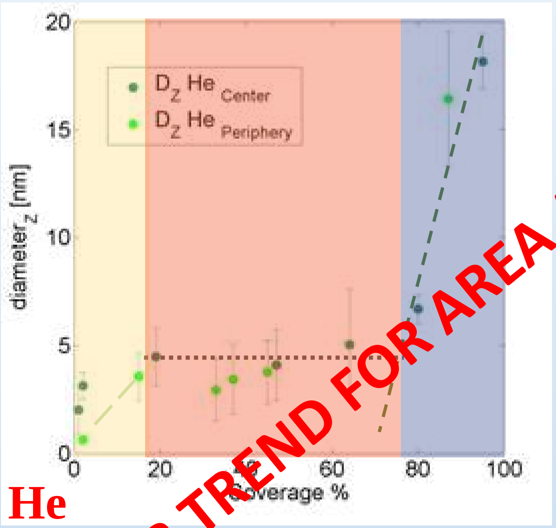
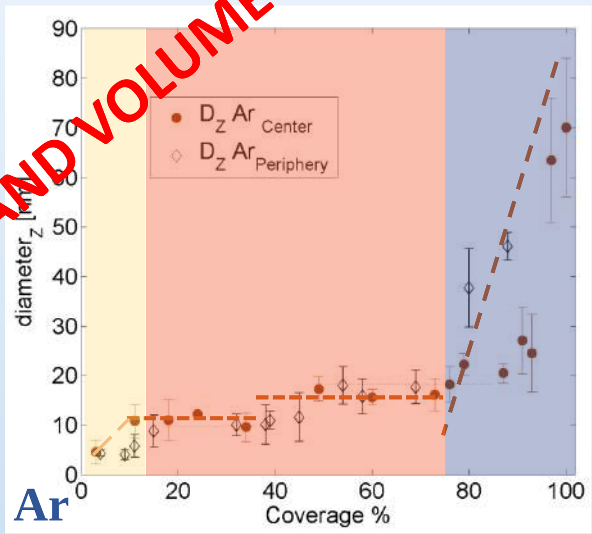
HEIGHT EVOLUTION

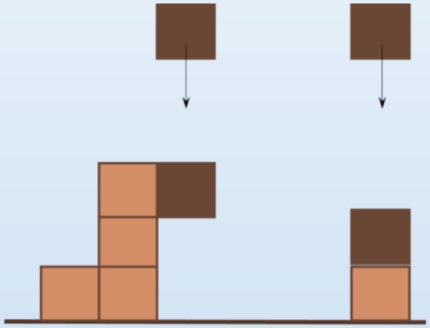






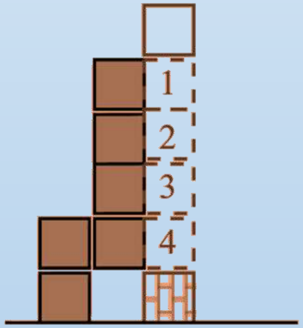
SIMILAR TREND FOR AREA AND VOLUME!

Sticking probability =1



nearest neighbor B. D.

Sticking probability ≠1



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Robledo, A. *et al. Phys. Rev. E* **83**, 051604 (2011)

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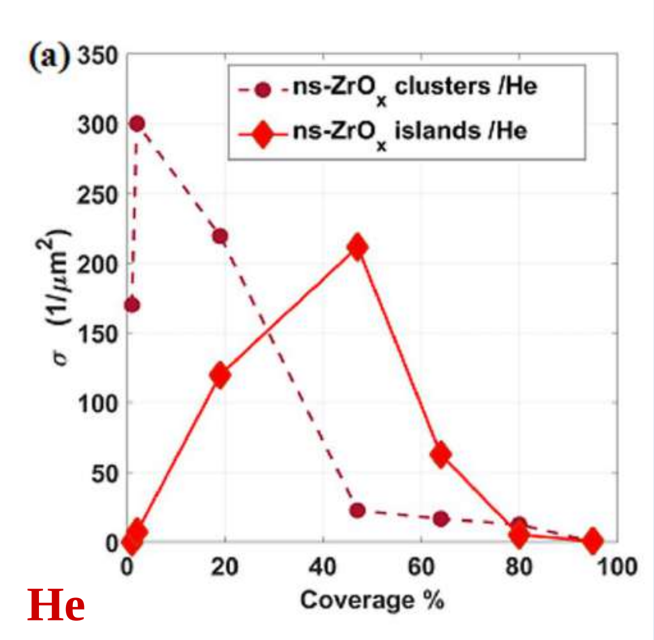
DENSITY OF CLUSTERS AND ISLANDS



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DENSITY OF CLUSTERS AND ISLANDS

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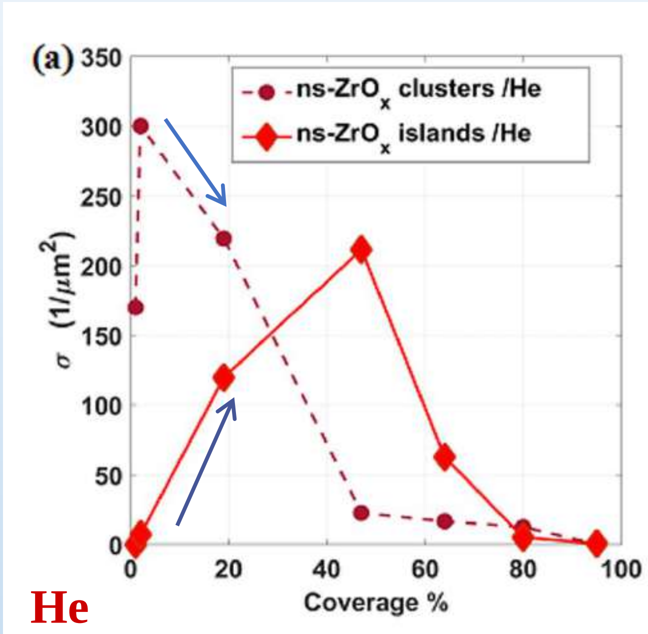

Nucleation events

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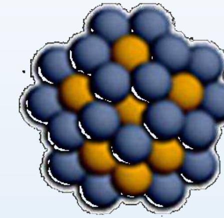
DENSITY OF CLUSTERS AND ISLANDS



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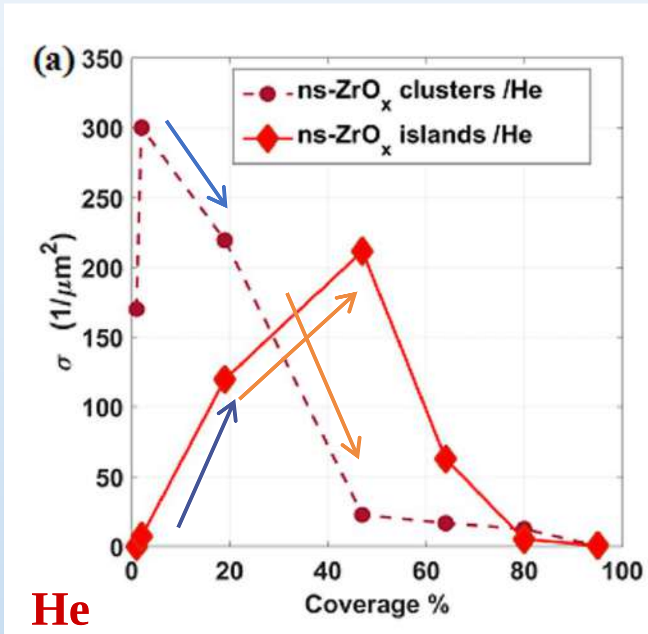

Nucleation events

Competition between
nucleation events
and island growth

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F. borghi, et al., Arxiv, submitted to Phys. Rev. B

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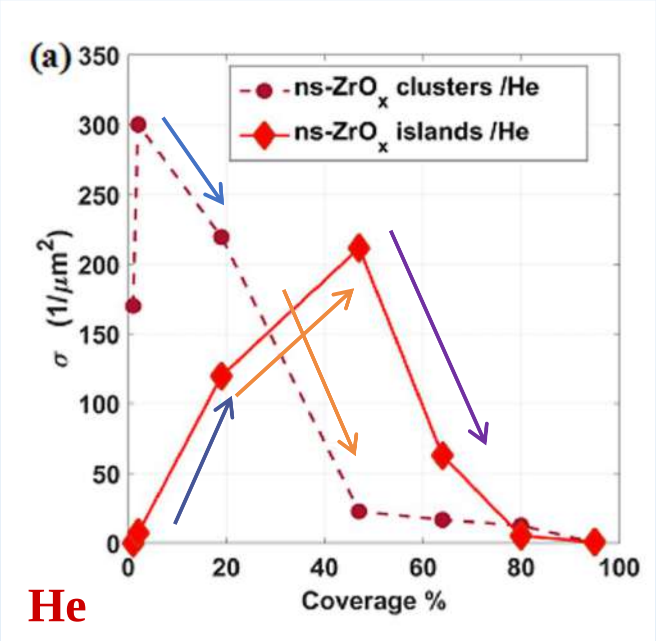
DENSITY OF CLUSTERS AND ISLANDS



Nucleation events

Competition between nucleation events and island growth

Islands coalescence

CONTROL

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DENSITY OF CLUSTERS AND ISLANDS

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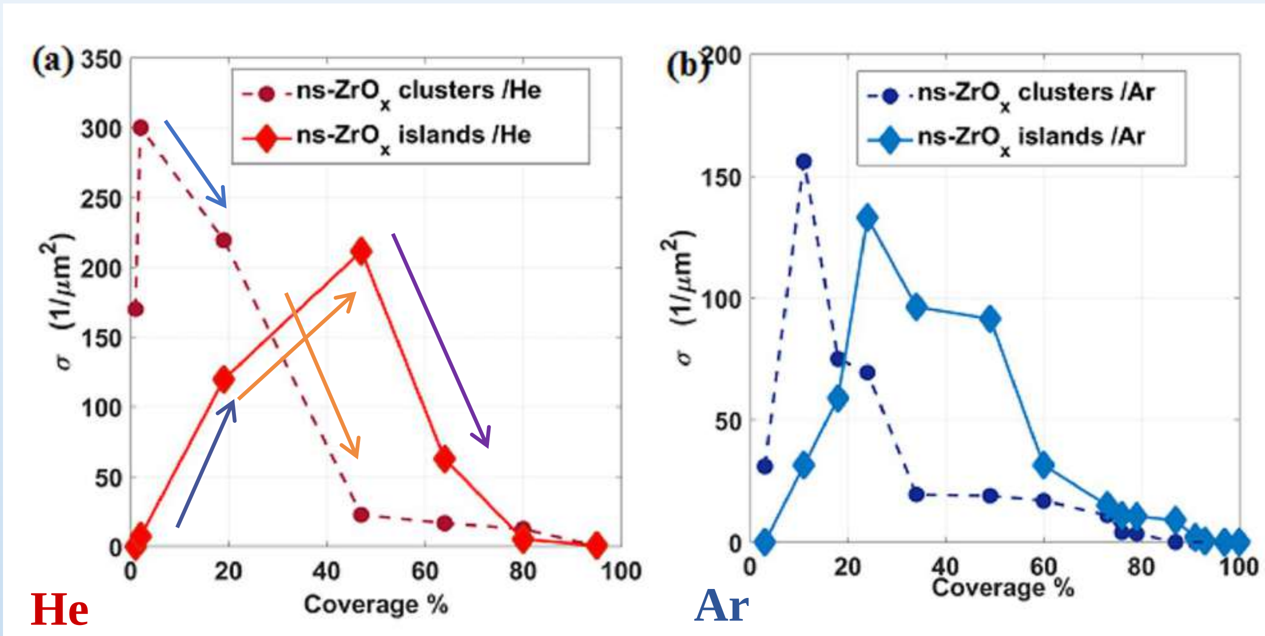

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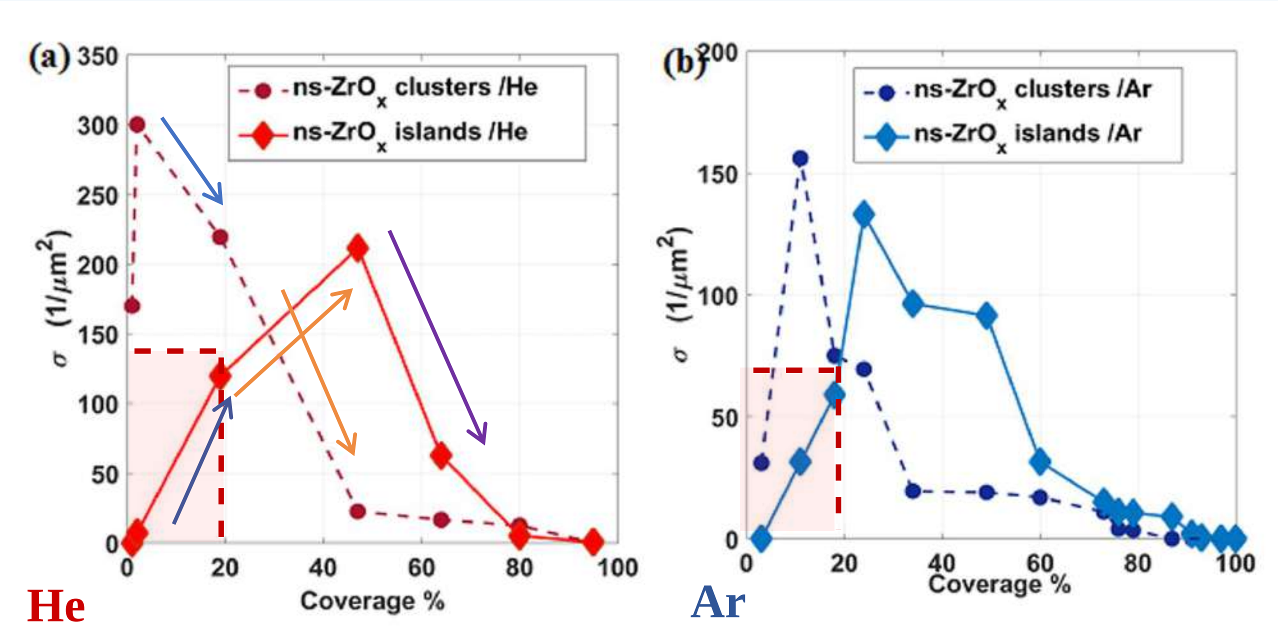

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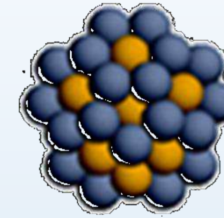
DENSITY OF CLUSTERS AND ISLANDS



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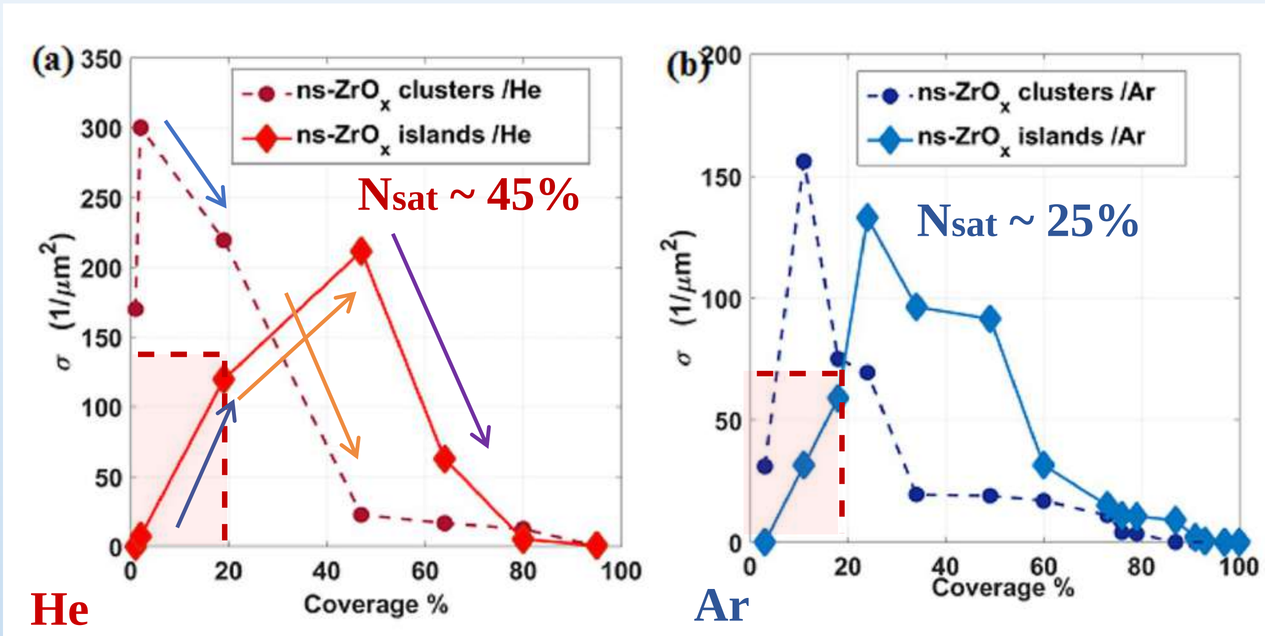

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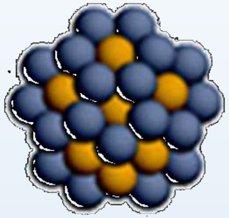
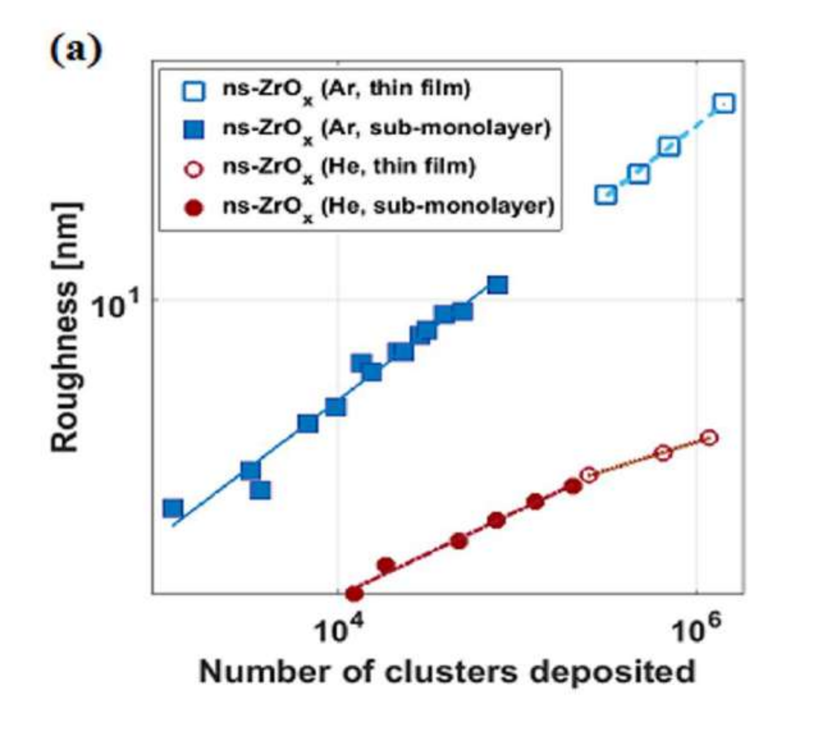
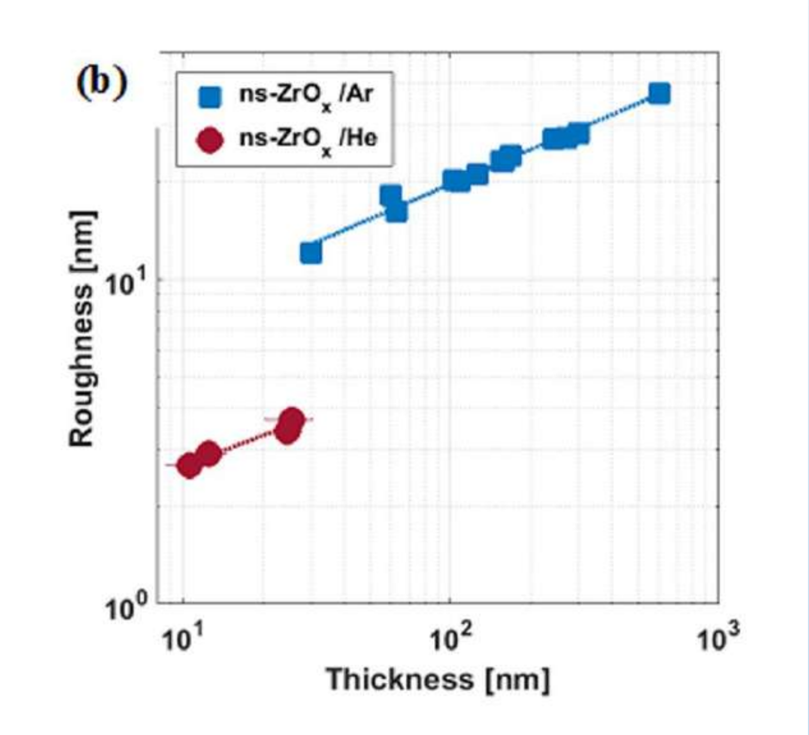
From SUB-MONOLAYER to THIN FILM REGIME



$Rq \sim h^{\beta}$ β - *growth exponent*





CONTROL

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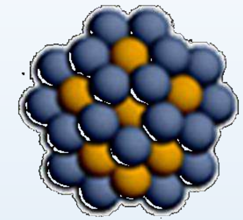
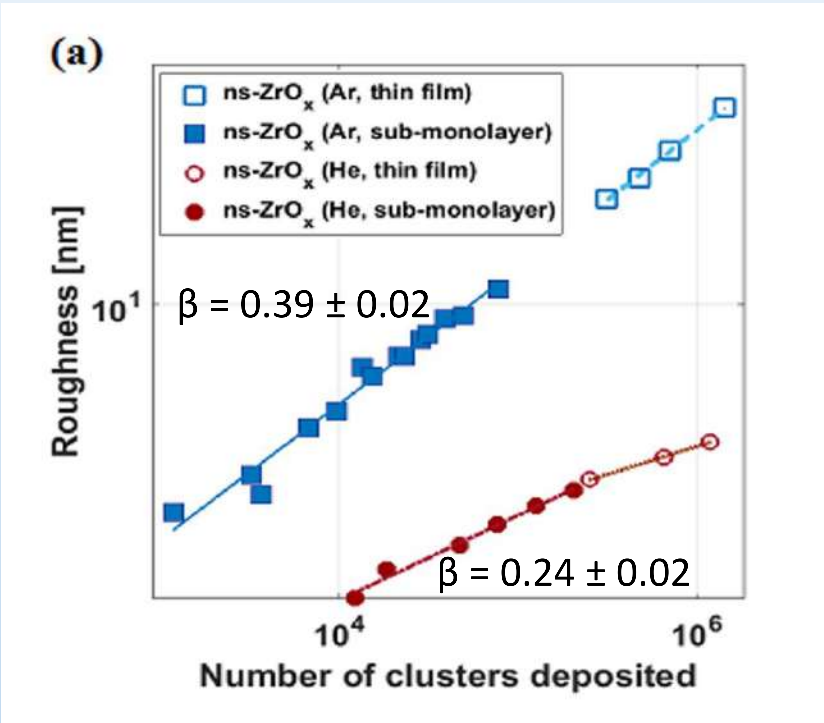
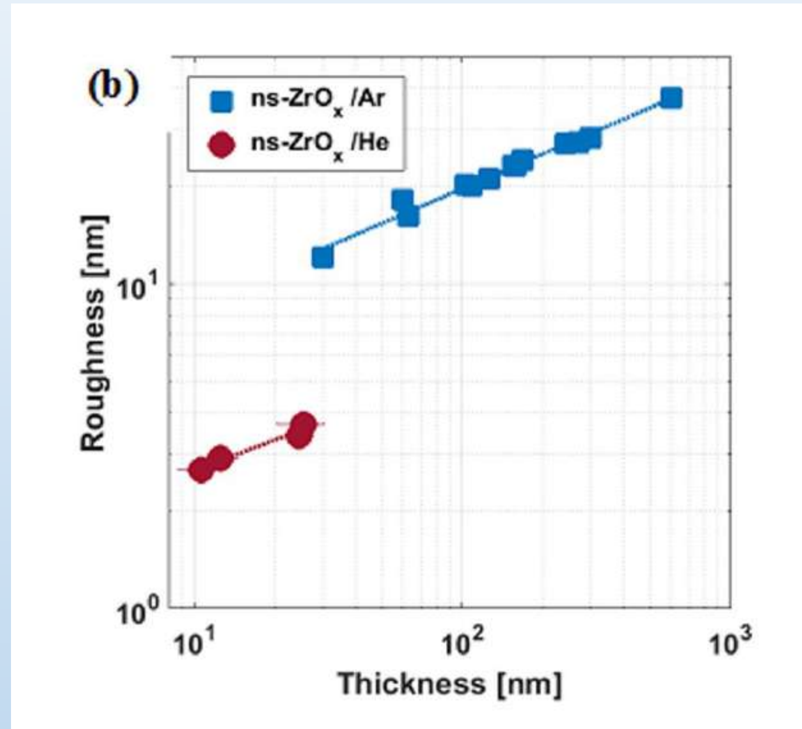
From SUB-MONOLAYER to THIN FILM REGIME



$$Rq \sim h^{\beta} \qquad \beta \text{ - } \textit{growth exponent}$$





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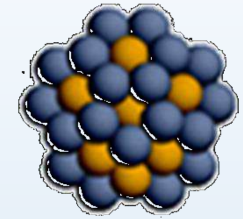

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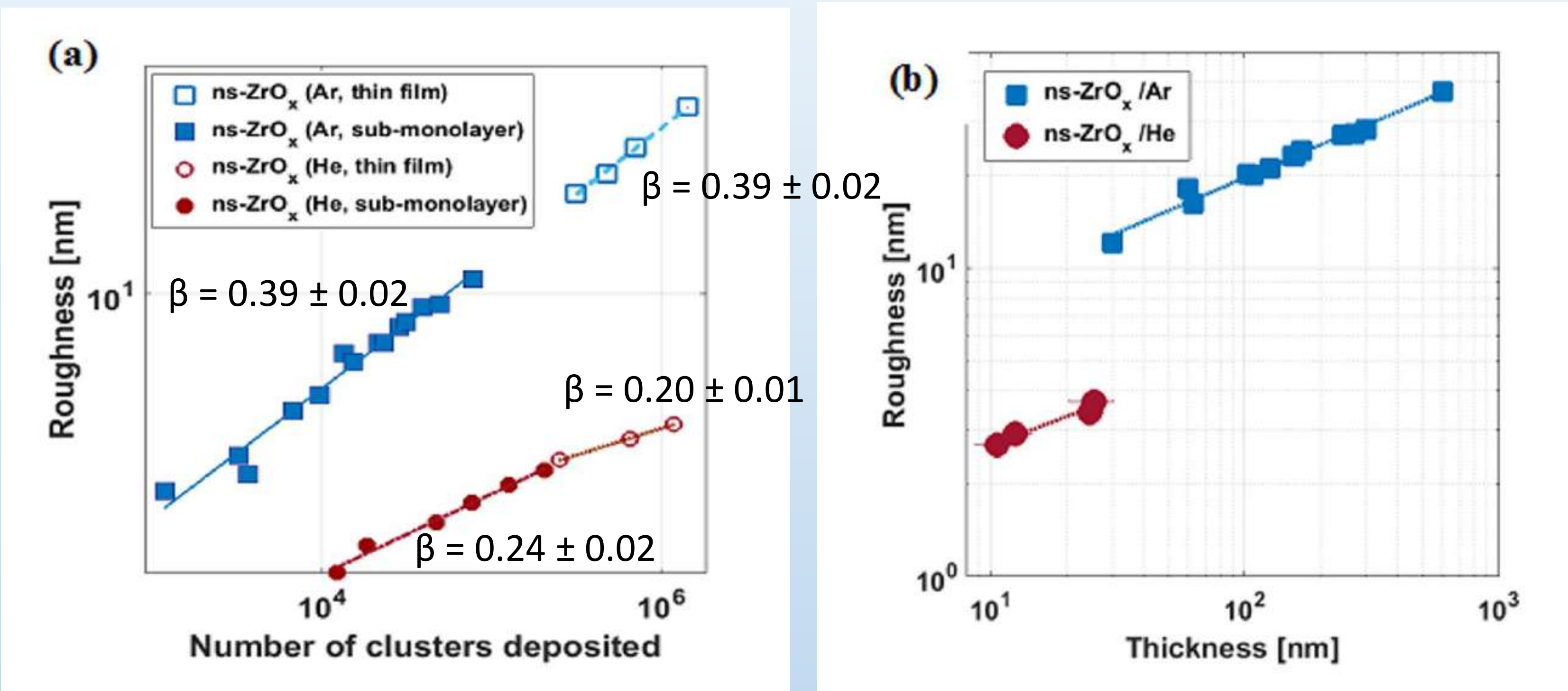

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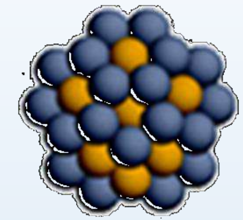

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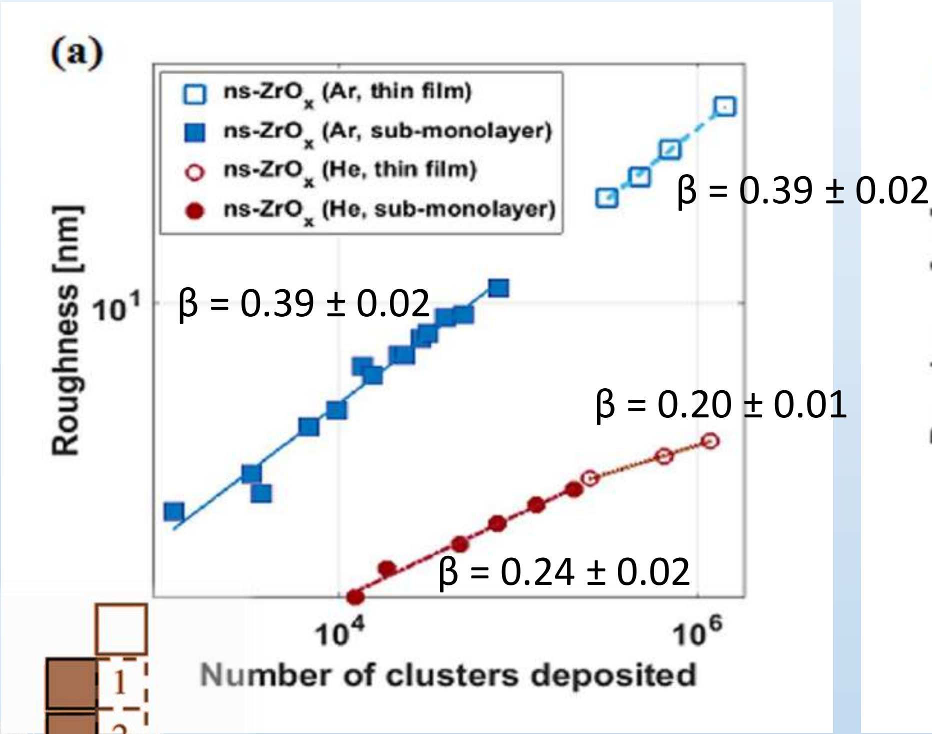

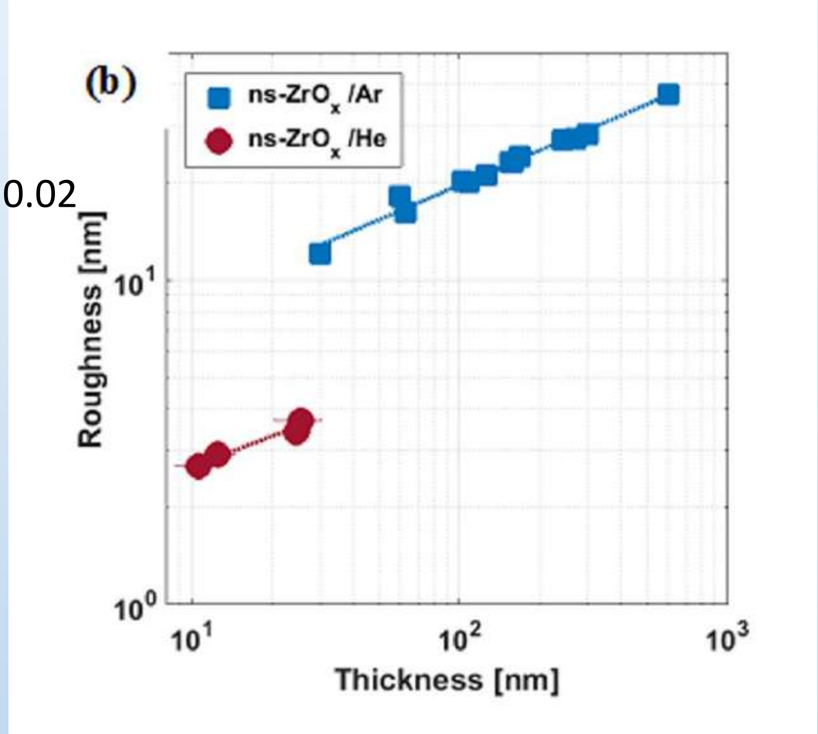

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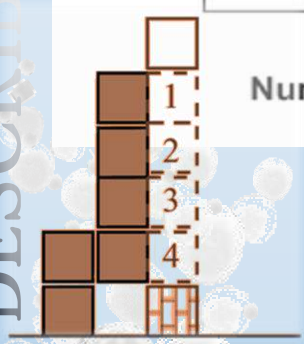

Sticking probability ≠1

A.G. Konstandopoulos, Powder Technol. 109, 262 (2000)

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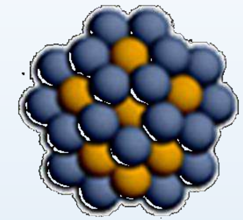

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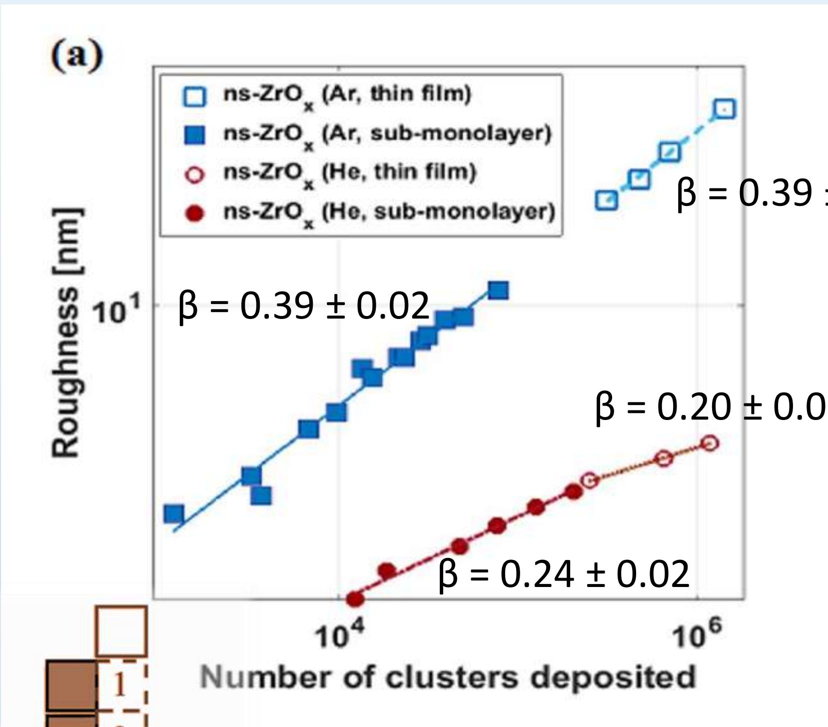

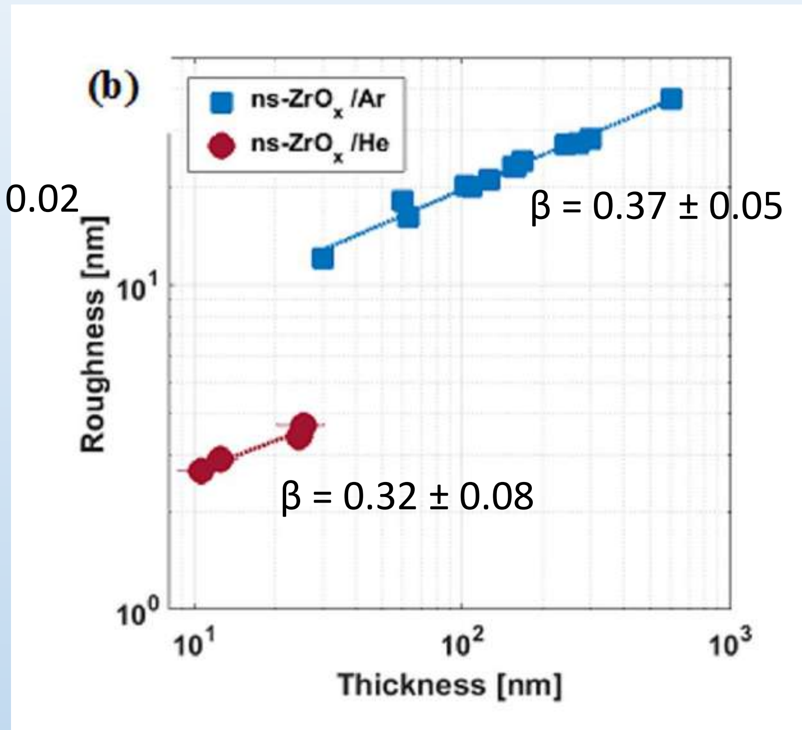

CONTROL

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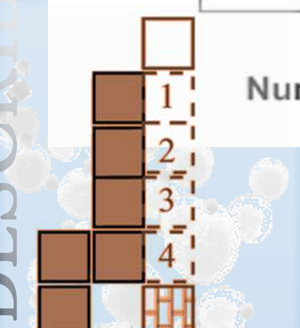

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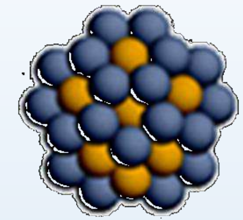

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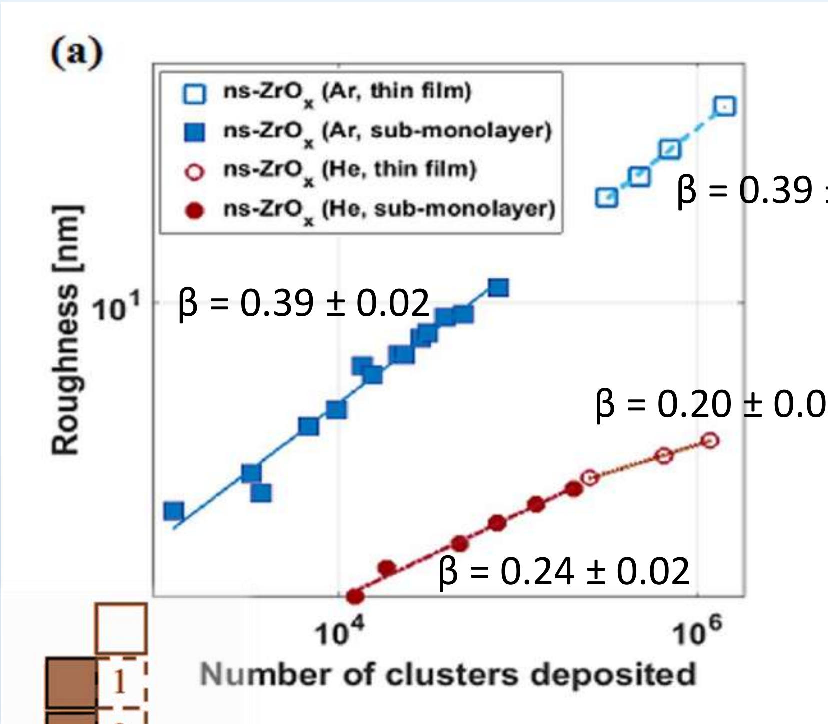

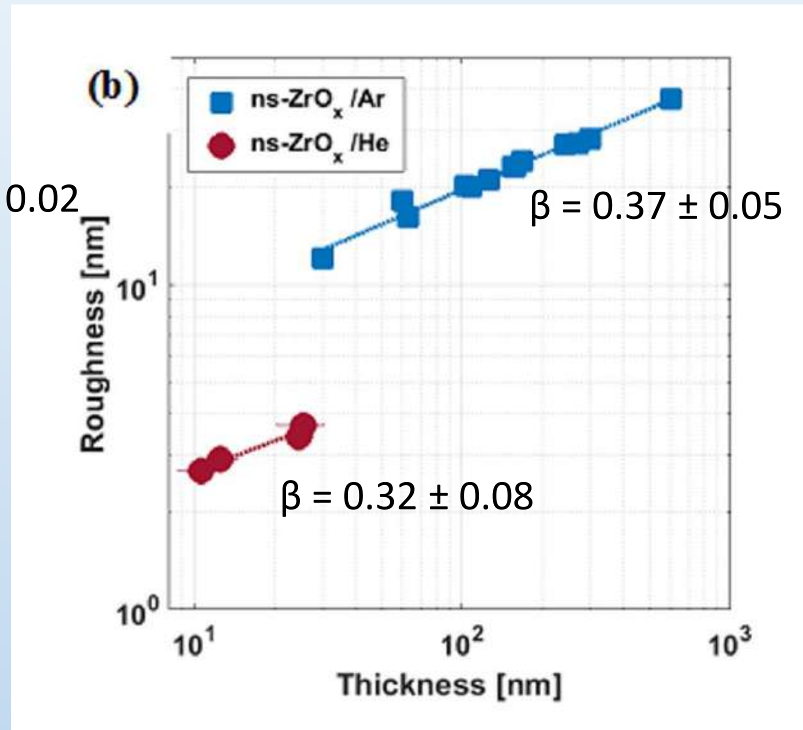

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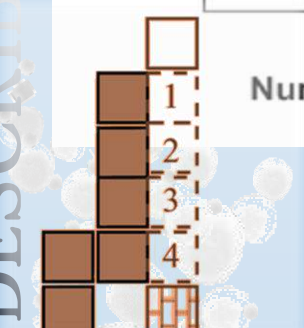

BALLISTIC DEPOSITION in 2+1 MODEL!

Sticking probability ≠1

Barabási, A.-L. & Stanley, H. E. *Fractal Concepts in Surface Growth*. (Cambridge University Press, 1995)

A.G. Konstandopoulos, Powder Technol. **109**, 262 (2000)

ENGINEER

SURFACE GROWTH ON SPHERICAL GEOMETRY

CONTROL

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ENGINEER

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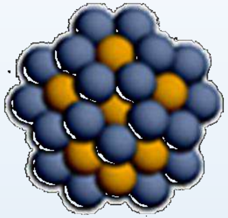

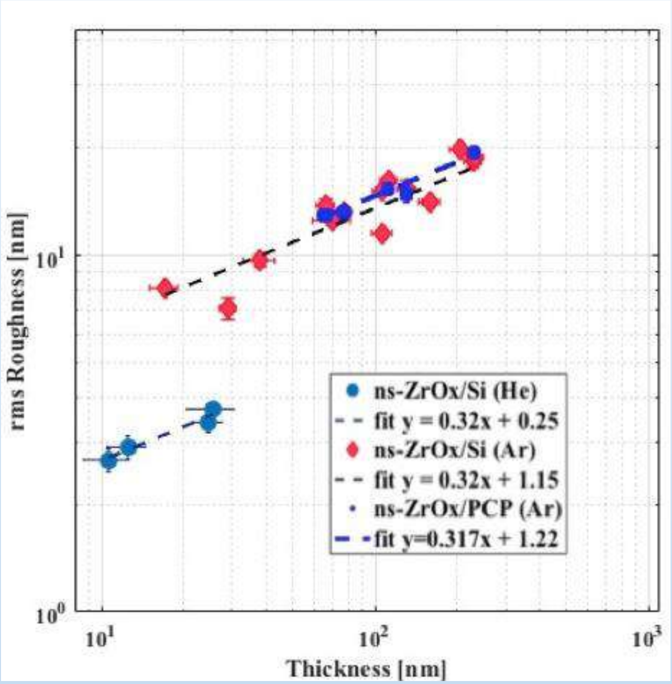

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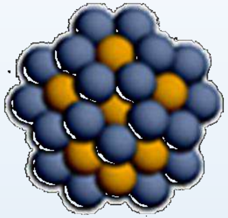

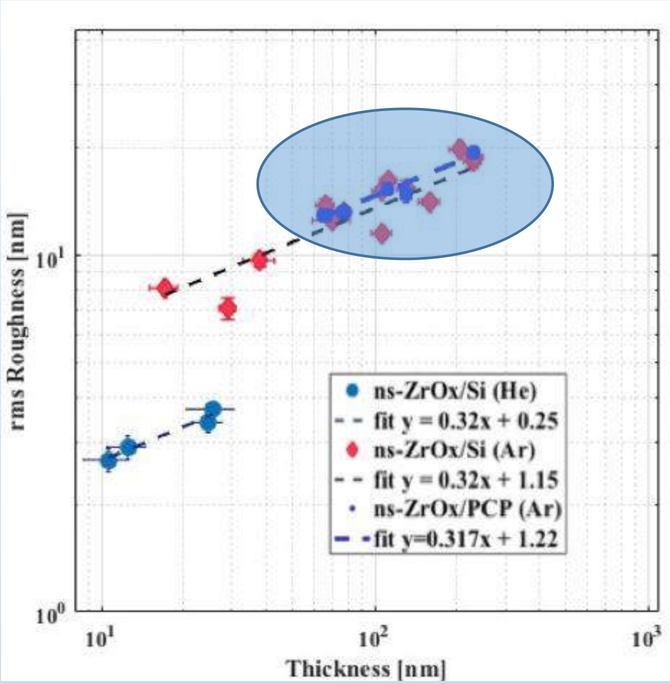

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SURFACE GROWTH ON SPHERICAL GEOMETRY


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A 1939 defense of basic research resonates today p. 806
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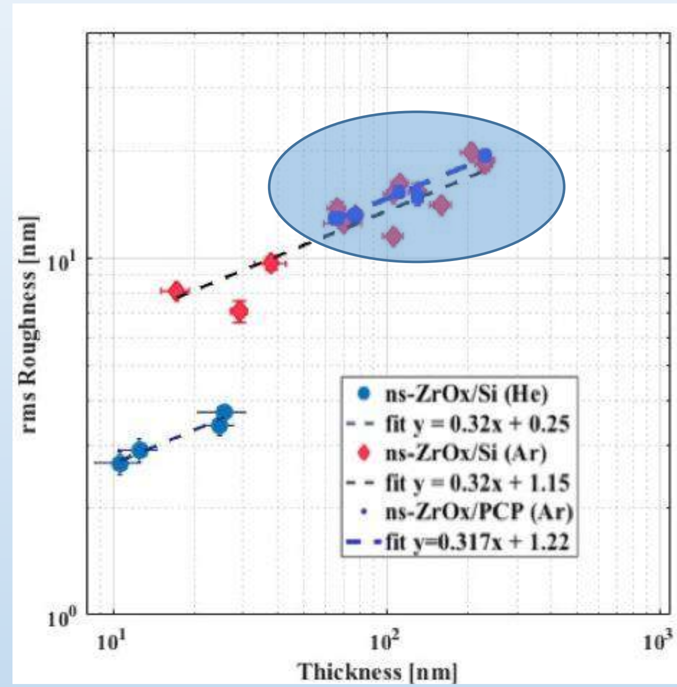
F. Borghi, M. Chighizola, L. Marfori



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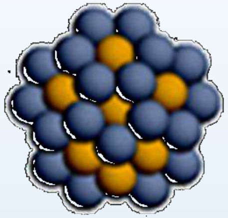
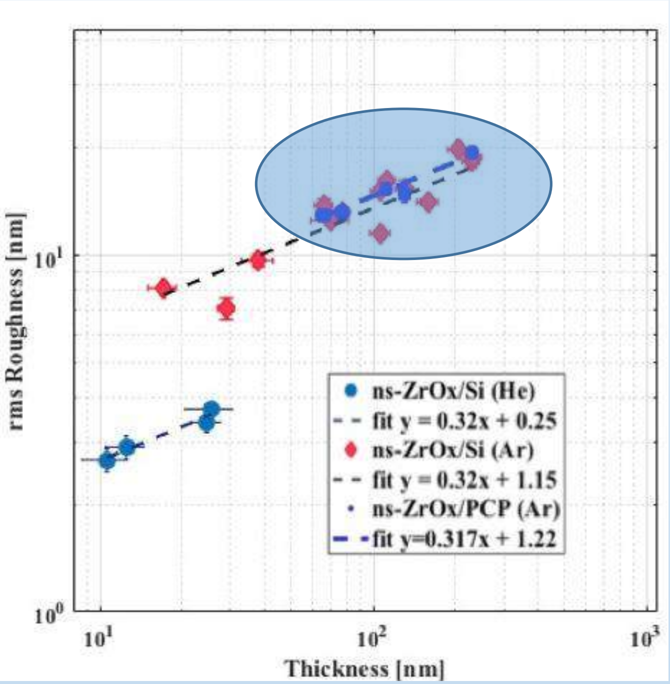
SURFACE GROWTH ON SPHERICAL GEOMETRY





F. Borghi, M. Chighizola, L. Marfori

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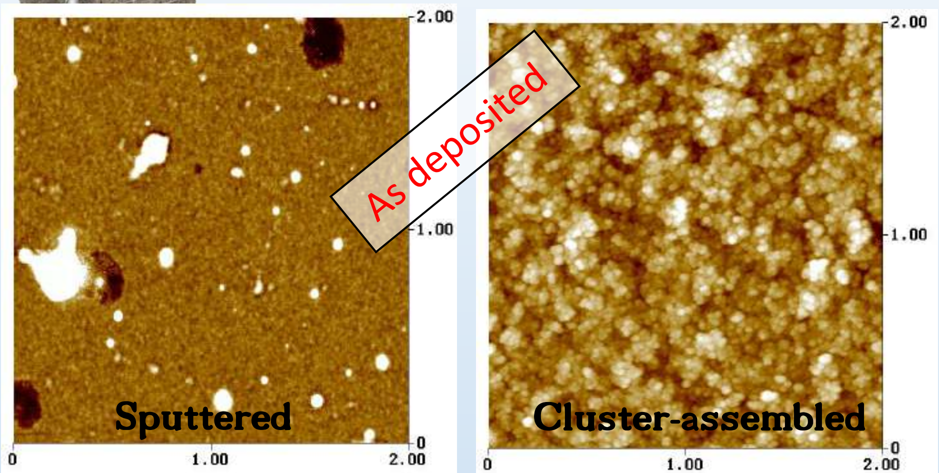
SURFACE GROWTH WITH ANNEALING

Ns-TiOx



Rq=1 nm

Rq =20 nm

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SURFACE GROWTH WITH ANNEALING

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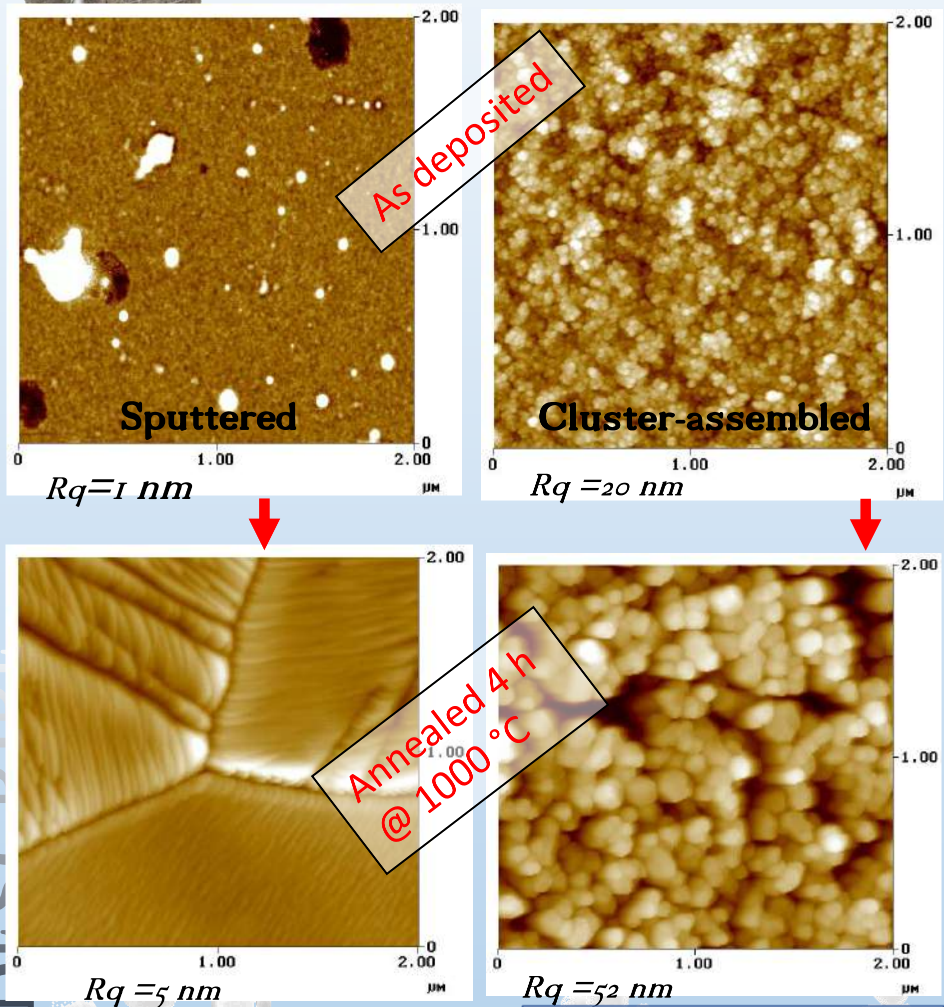

C. Lenardi & A. Podestà

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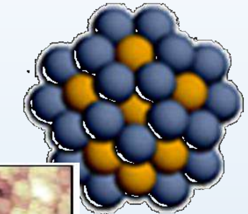
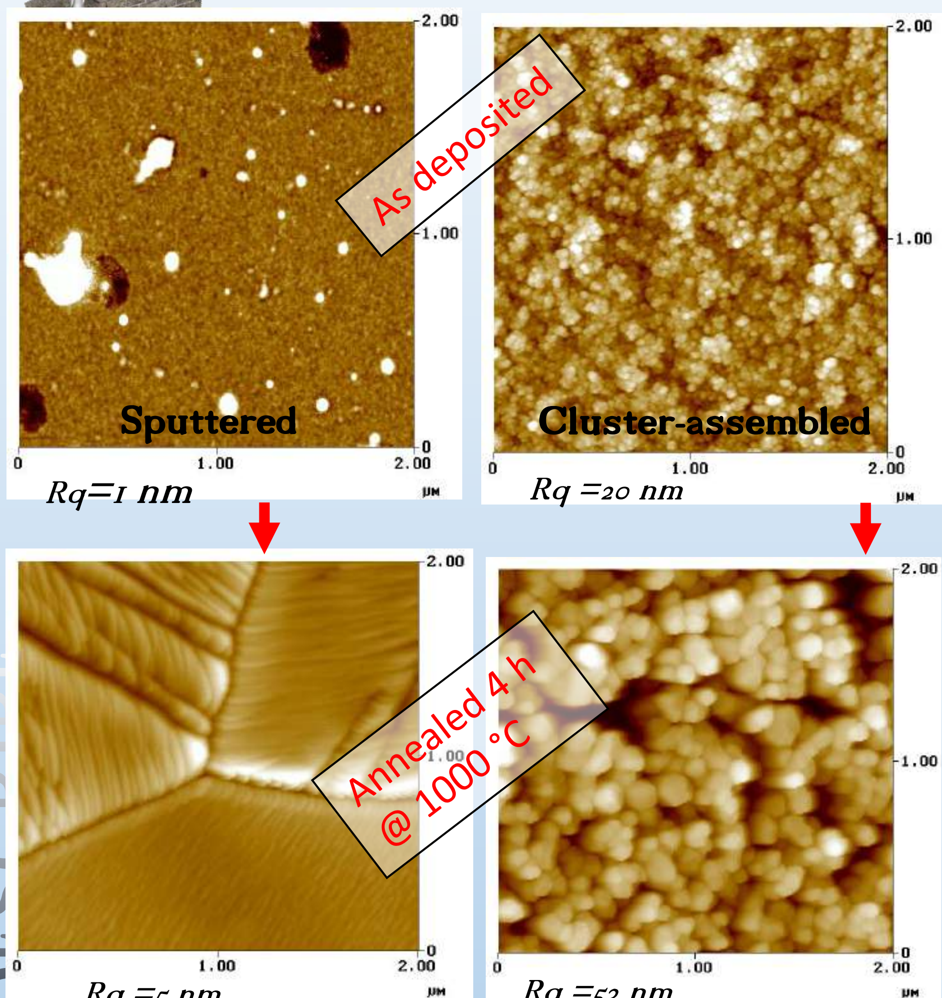
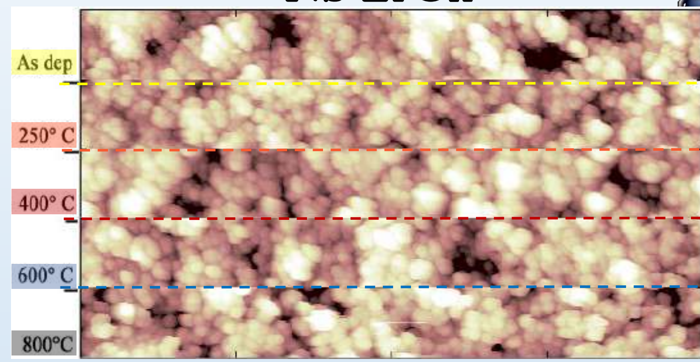
SURFACE GROWTH WITH ANNEALING







2μm x 1μm x 0.01μm

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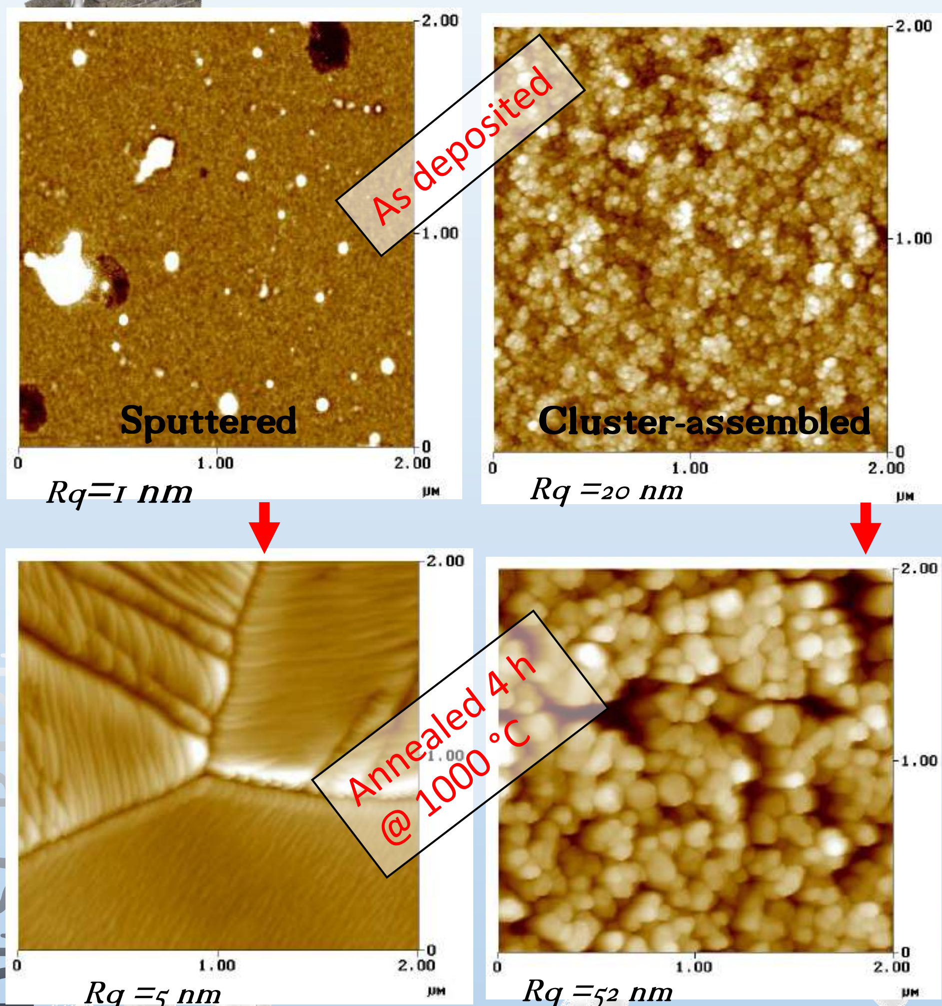
SURFACE GROWTH WITH ANNEALING

Ns-TiOx



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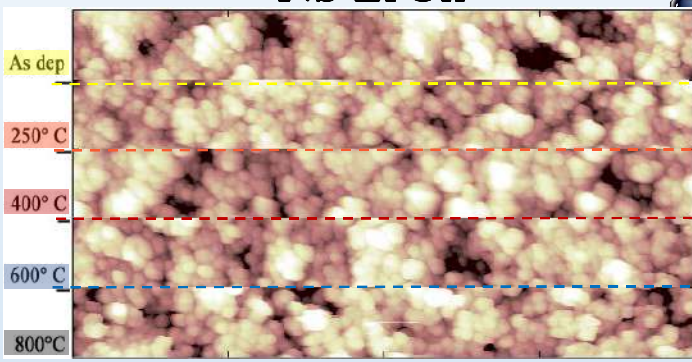
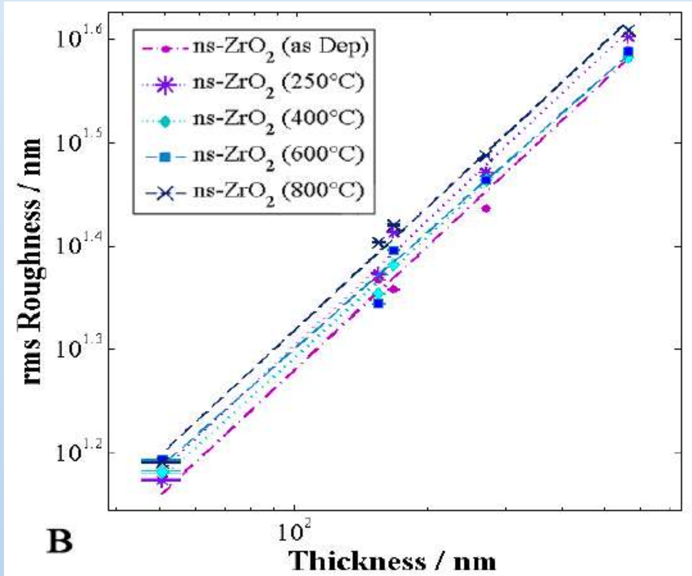
Ns-ZrOx



2µm x 1µm x 0.01µm



F. Borghi, et al. Journal of Applied Physics (2016)

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CONCLUSIONS

✓ Growth dynamics in sub-monolayer regime determines different morphological properties of the cluster-assembled thin film

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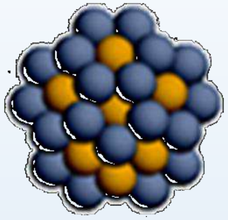
CONCLUSIONS



- ✓ Growth dynamics in sub-monolayer regime determines different morphological properties of the cluster-assembled thin film
- ✓ The morphological properties of cluster-assembled samples in thin-film regime evolve according to a ballistic deposition model (2+1), irrespective of the incident cluster dimensions

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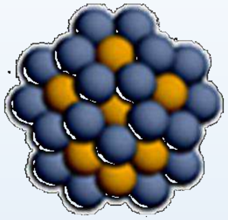
CONCLUSIONS



- ✓ Growth dynamics in sub-monolayer regime determines different morphological properties of the cluster-assembled thin film
- ✓ The morphological properties of cluster-assembled samples in thin-film regime evolve according to a ballistic deposition model (2+1), irrespective of the incident cluster dimensions
- ✓ Thin films preserve their morphological properties and their history even after a quite severe annealing process

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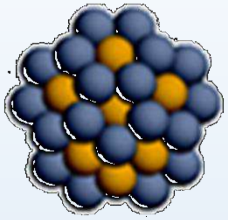
CONCLUSIONS



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- ✓ The morphological properties of cluster-assembled samples in thin-film regime evolve according to a ballistic deposition model (2+1), irrespective of the incident cluster dimensions
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MAIN RESULT

We can describe and control the growth of nanostructured thin films in order to tune the functional properties of the interface by changing its morphology

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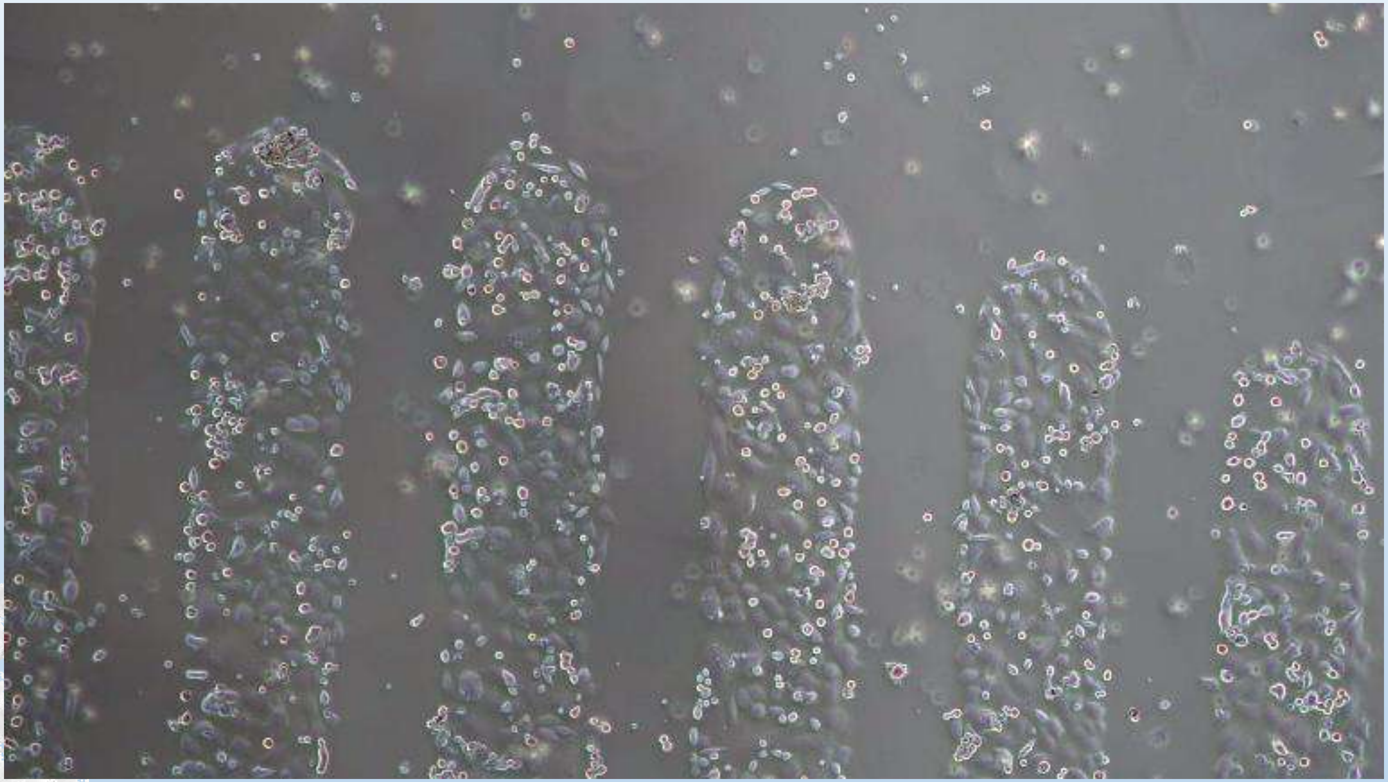
PERSPECTIVE

Novel nanostructured scaffolds to investigate signalling in reconstructed neuronal networks



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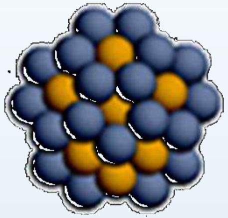
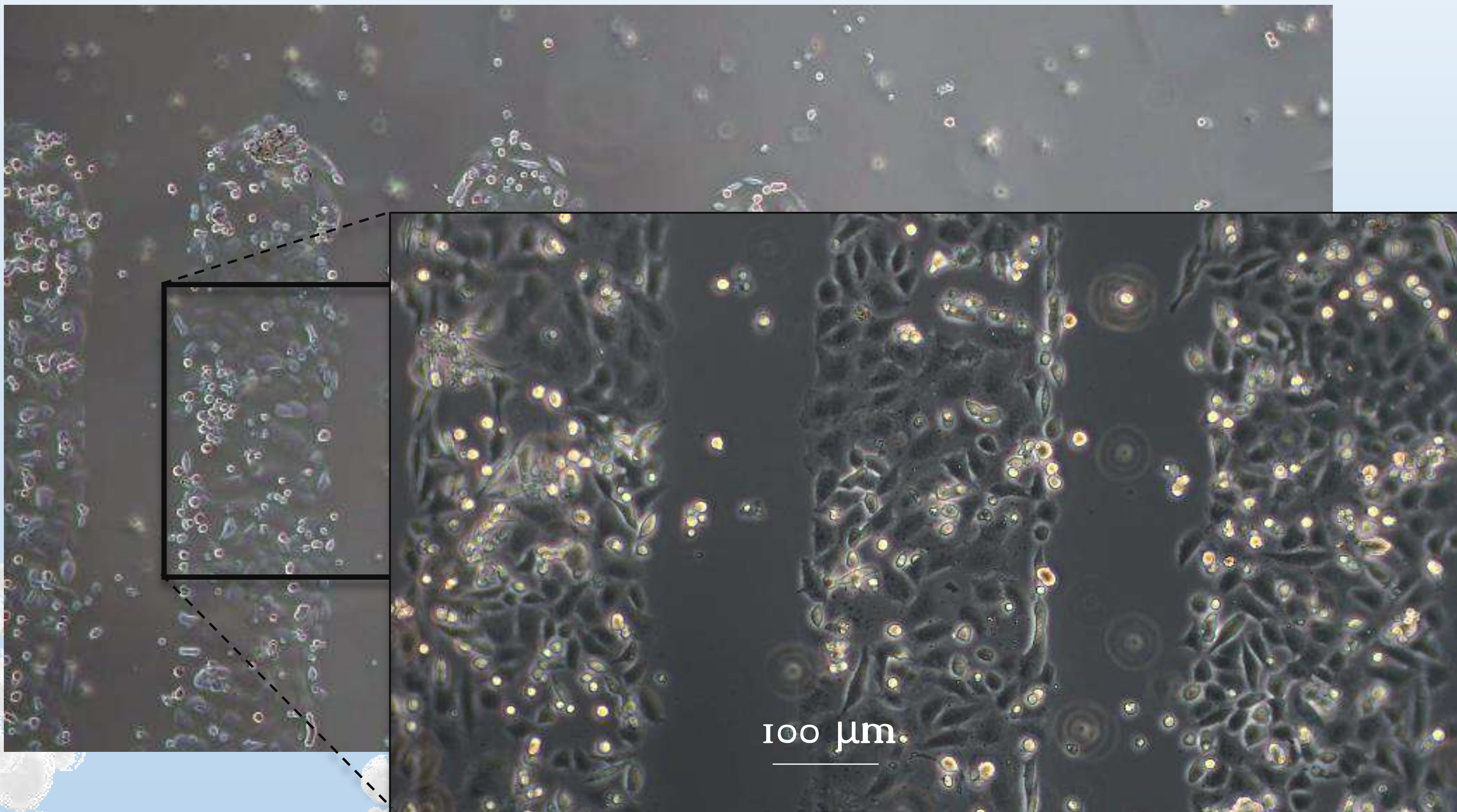


Novel nanostructured scaffolds to investigate signalling in reconstructed neuronal networks



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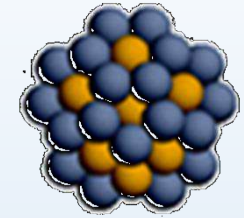

PERSPECTIVE

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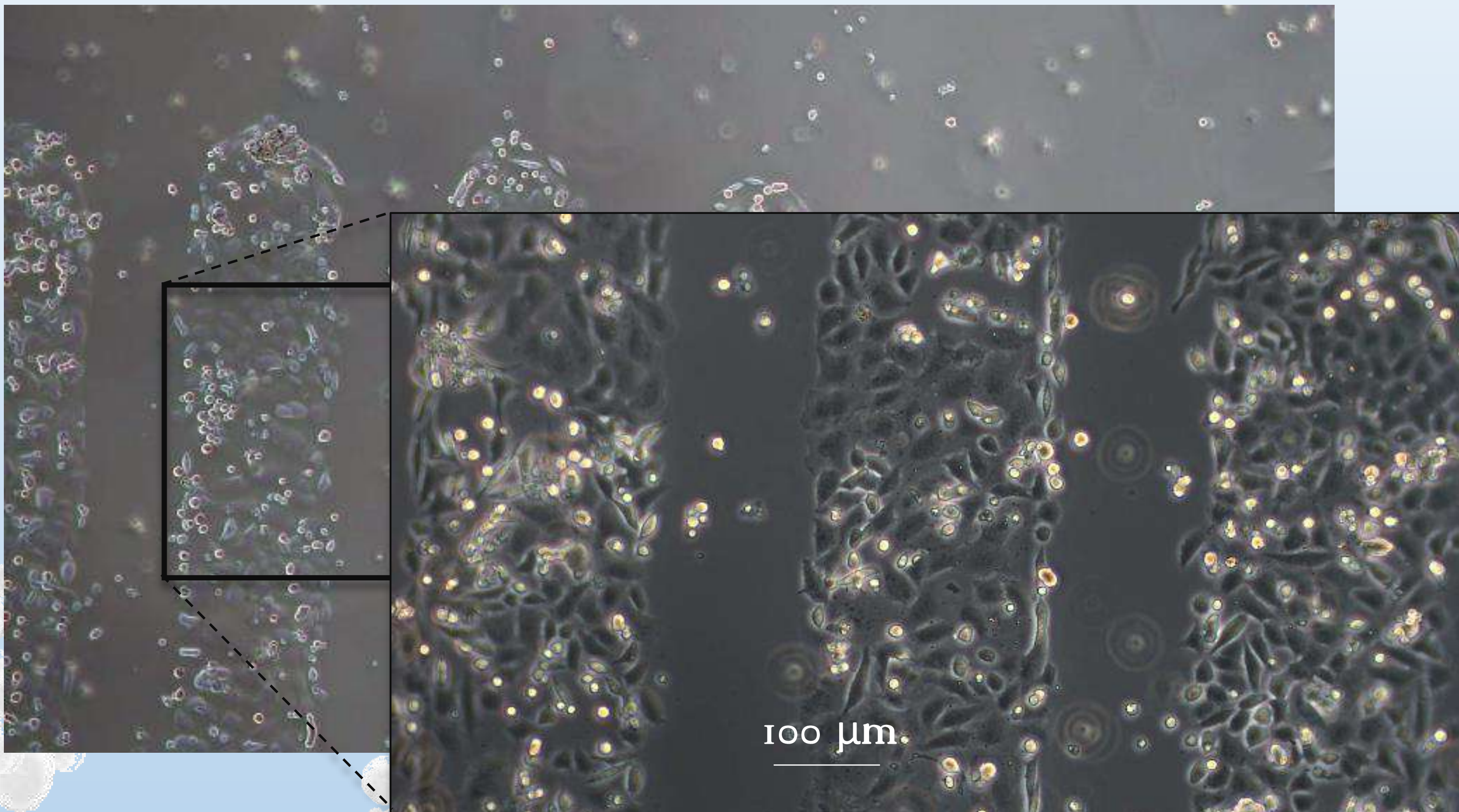

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Control on morphological properties → functional ones

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THANK YOU FOR YOUR ATTENTION!