Procédés d‘Ablation Laser pour la synthèse de Films minces, Agrégats et Composites Nanostructurés :

de l'élaboration du matériau à son introduction dans des composants électroniques

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Thin films, nanoscale clusters and nanostructured materials

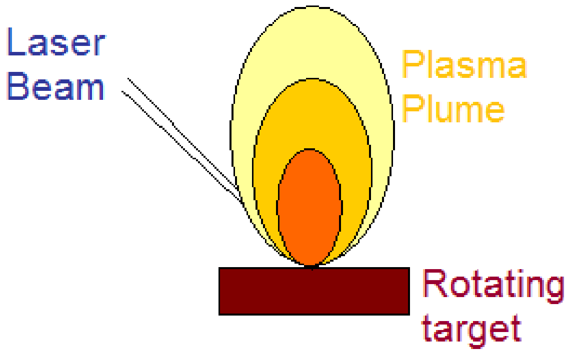
✓ great interest for basic science and applications because of their peculiar physical and chemical properties, different and enhanced from those of isolated atoms and of bulk materials.

✓ applications in electronics, optics, … domains

↳ Development of new integrated performant communication systems

✓ good quality thin-films with tunable properties, new functionalities ("smart" materials)

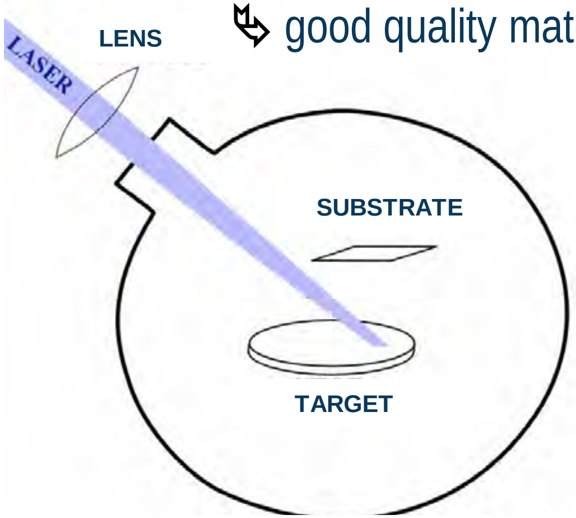
↳ laser ablation processes ⇨ good solutions



Specificities of laser ablation

Well known for thin films deposition ⇨ Pulsed Laser Deposition (PLD)

↳ good quality material ; films with typical thickness < 2 µm



Ultrahigh vaccum cell

👍 Possibility of a complex chemical composition transport from target to substrate

👍 Multi-targets PLD leading to multimaterials deposition (multilayer, doping …)

👎 Surface contamination by condensed particles

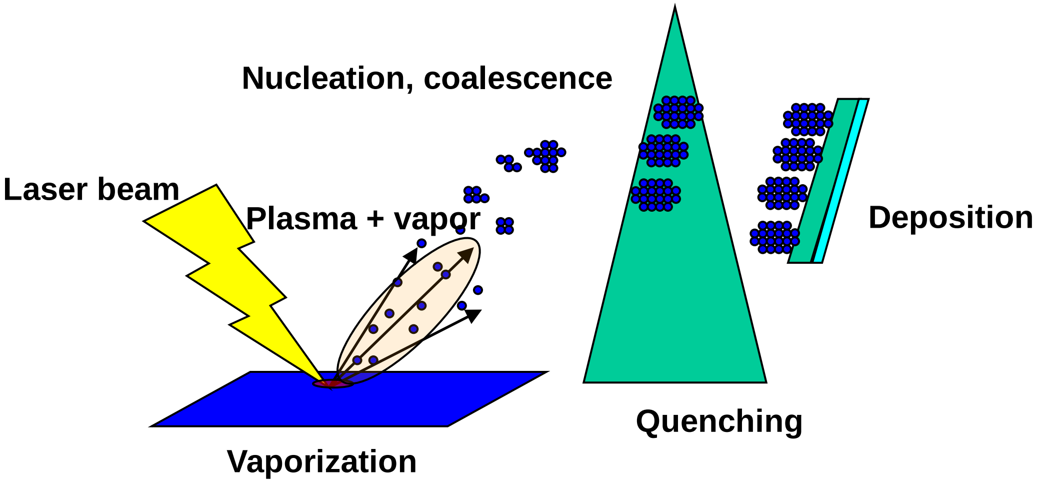
👎 Non-uniformity of deposition on "large" dimensions

☞ *Solutions : judicious PLD parameters, displacement of the substrate with regard to the plasma*

⇨ Growth of in-flight aggregates leading to nanosize clusters

Laser ablation for nanomaterials synthesis:

- If the ablation plume is strongly quenched
  ⇘ synthesis of nanosized particles in the vapor.



- Quenching can be induced by:

  ✓ a cold gas ⇨ Low Energy Cluster Beam Deposition (LECBD)
  ✓ a liquid ⇨ synthesis of colloids by Laser Ablation in Liquid (LAL).

Laser ablation processes:

Elaboration of thin films with optimized properties

Correlation process – material properties

Integration in electronic or optic components

From materials to devices

Exploitation of process potentialities

Doping, Multilayers, nanosize clusters

Innovative new materials

Control of deposition parameters
Studies of ablation mechanisms

Outline

Thin Films

✓ Thin films by PLD for telecom applications

Development of ”smart” material (with phase-transition) for RF system

✓ Doped thin films

Nano materials

✓ Nanostructured thin films by conventionnal PLD

- *AlN*
- *DLC* *(deposited at room temperature)*

✓ Synthesis of clusters and nanostructured thin films by PLD coupled with a free cluster generator (PLD – LECBD)

✓ Synthesis of colloids by Laser Ablation in Liquid

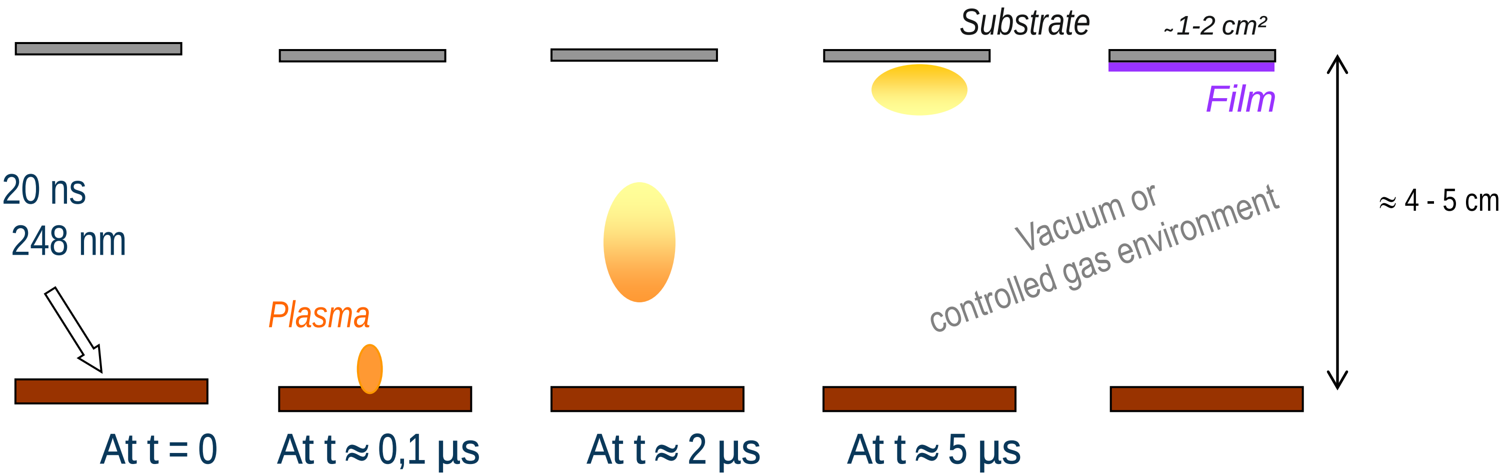
✓ Conclusions and perspectives

Pulsed Laser Deposition (PLD)

Excimer laser KrF :

pulse duration: ~ 20 ns

wavelength: λ = 248 nm



Process control

⇘
- ✓ Laser-matter interaction
- ✓ Ejection of the matter : plasma
- ✓ Transport of species from the target to the substrate
- ✓ Growth of the film

All dependant steps

Parameters :
Target, Substrate
Fluence
Gas, Pressure
Temperature
…

Laser ablation processes:

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From materials to devices

'Smart' material VO_2

Development of PLD ‘smart’ thin films

Development of ”smart” material (for example with phase-transition)

- Mott transition materials as vanadium dioxide VO_2
- Reversible Semiconductor-Metal transition
  - Semi-conductor state : highly resistive, Gap~1 eV at room temperature, Monoclinic phase
  - Metallic state : low-resistivity for temperatures higher than 68°C (~340 K) Tetragonal phase
- Thin film VO_2

Film activation induced :

thermally

electrically (Joule effect or charge injection)

optically - obtain faster transition

down to 100 fs !!

Development of PLD 'smart' thin films

Vanadium dioxide synthesis

Pb : about 15 stable phases for the V-O system ! (V_4O - V_2O_5)

↳ *narrow conditions range to realize VO_2*

PLD parameters

Target: *Vanadium (metallic)*

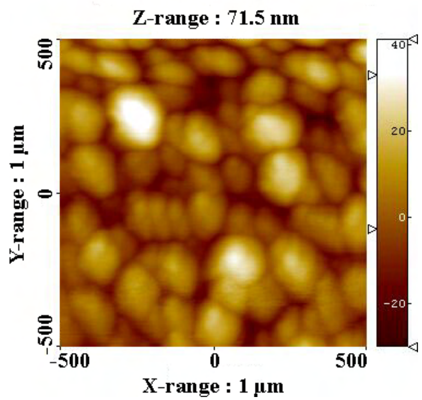
Substrate: *R/ C-cut sapphire, Silicon oxide, Fused silica*

Laser: *KrF, 248 nm, 25 ns at fluence 3.5 J/cm^2*

Temperature: *500 °C* Oxygen pressure during deposition : *2.2×10^{-2} mbar*

No post-annealing of the obtained films

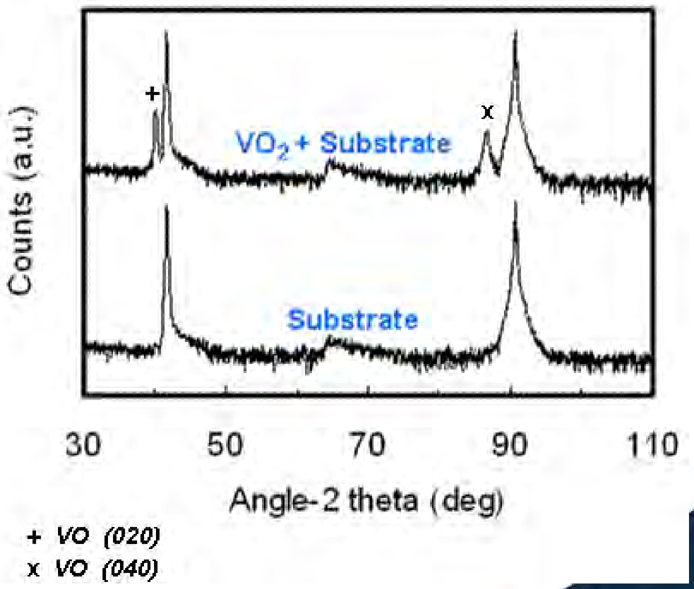
AFM investigations



Typical growth in grain

Only VO_2 monoclinic phase

XRD: (θ, 2θ) at T_{room}

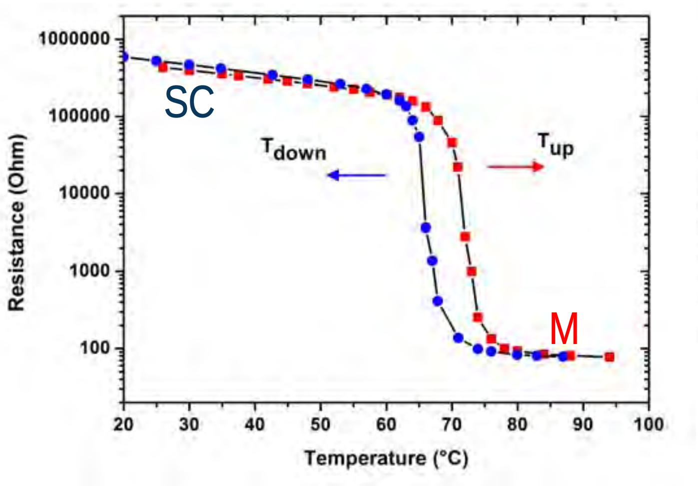


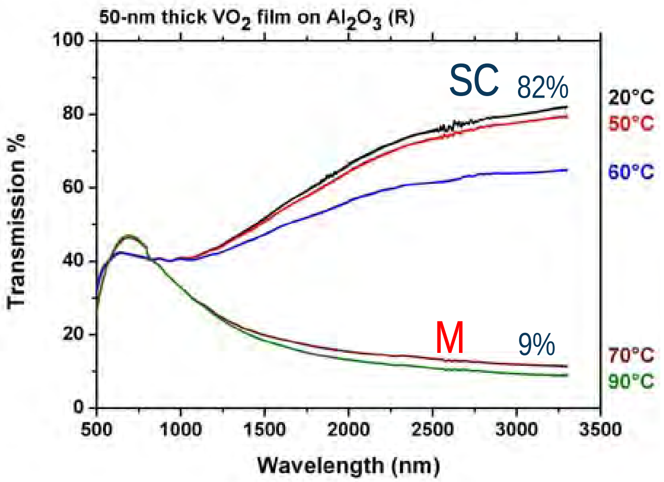
Development of PLD ‘smart’ thin films

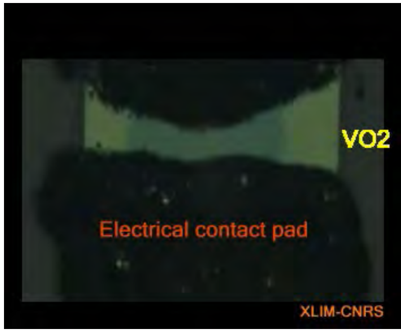
Vanadium dioxide VO_2

✓ Material with Semiconductor – Metal (MIT) transition at 68 °C

- Change in resistivity ~ 10^4 - 10^5
- Change in transmittance ~ 8 - 9







↳ optical and electrical switch

Applied Physics Letters, 2007

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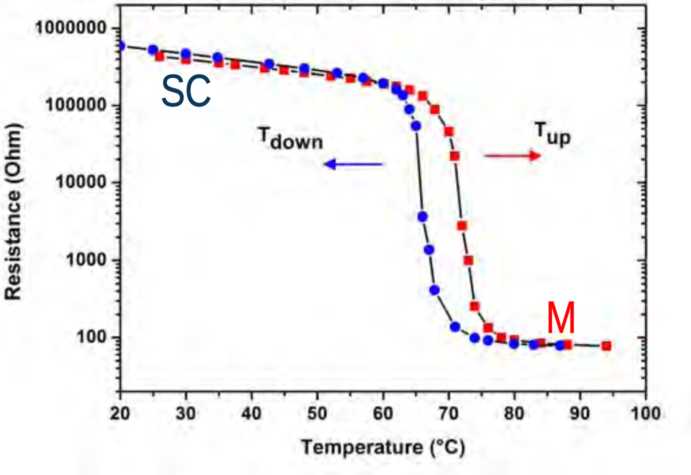

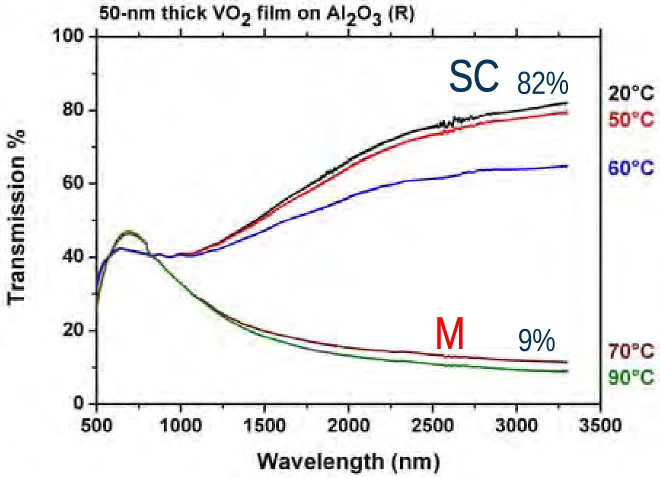

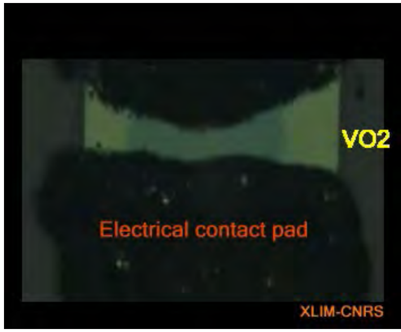

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Applied Physics Letters, 2007

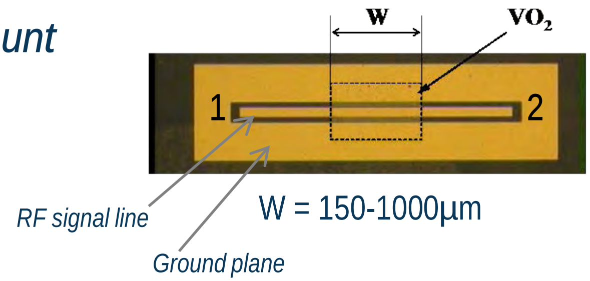
Development of devices with PLD 'smart' thin films

✓ RF switches

On different types of substrates (SiO2/ Si, fused silica, C/ R-cut sapphire)

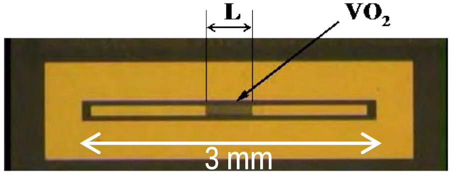
Microwave CoPlanar Waveguide

Shunt

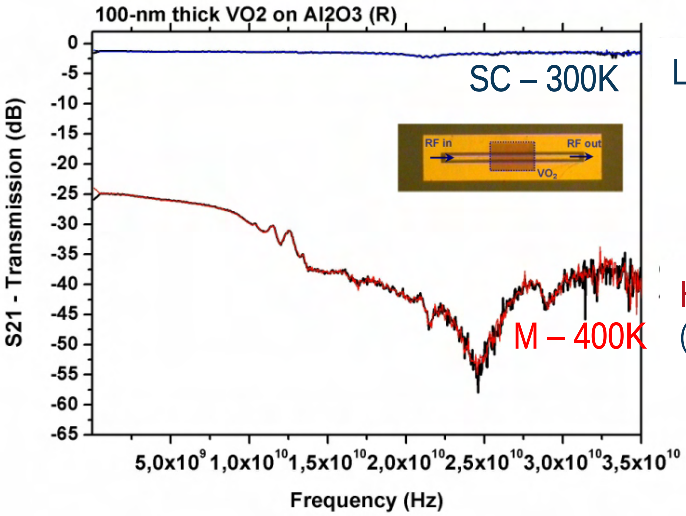


W = 150-1000µm

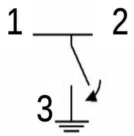
Serial



L = 100-500µm

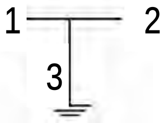


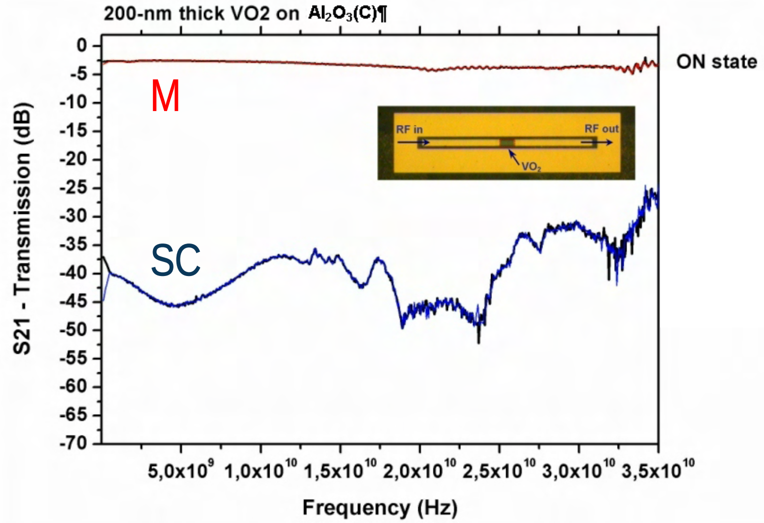
Low losses



High attenuation

(in wide frequency range)





↳ Achievement of shunt and serial RF-switches in wide frequency range

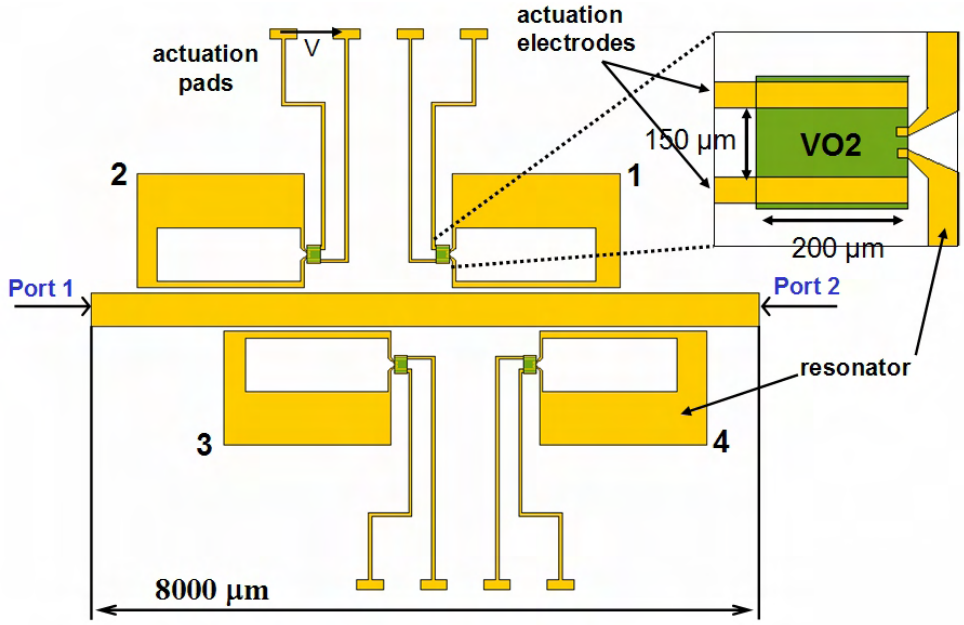
Mat. Res. Soc. Symp. Proc, 2009

Development of devices with PLD ‘smart’ thin films

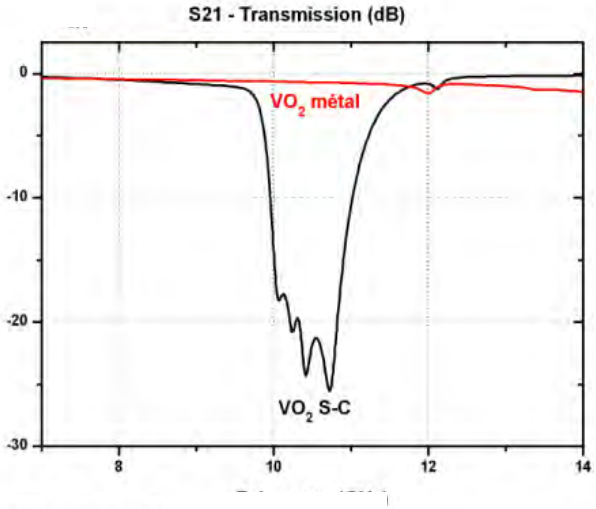
Tunable 4-pole band stop filter based on SC-MT of VO_2 thin films

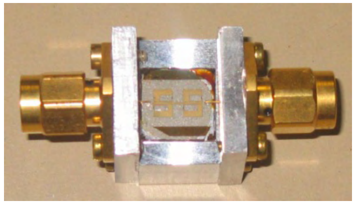
- Microstrip transmission line coupled with 4 U-shaped resonators

✓ Electrically activated : “discrete tunable band-stop filter”



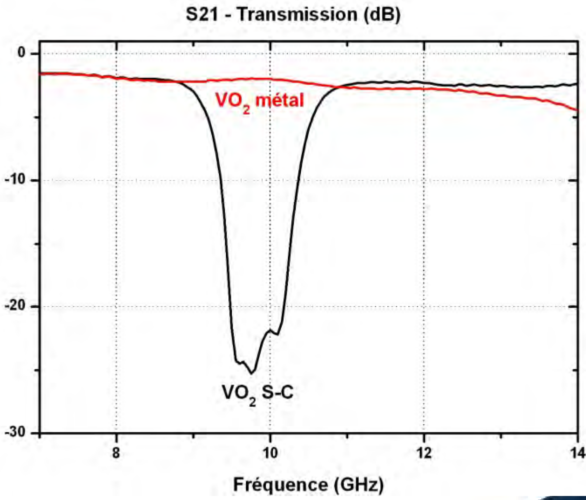
Simulation





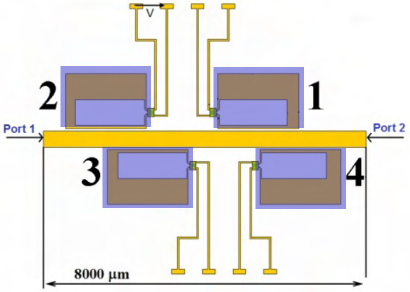
Measures

Electrical activation



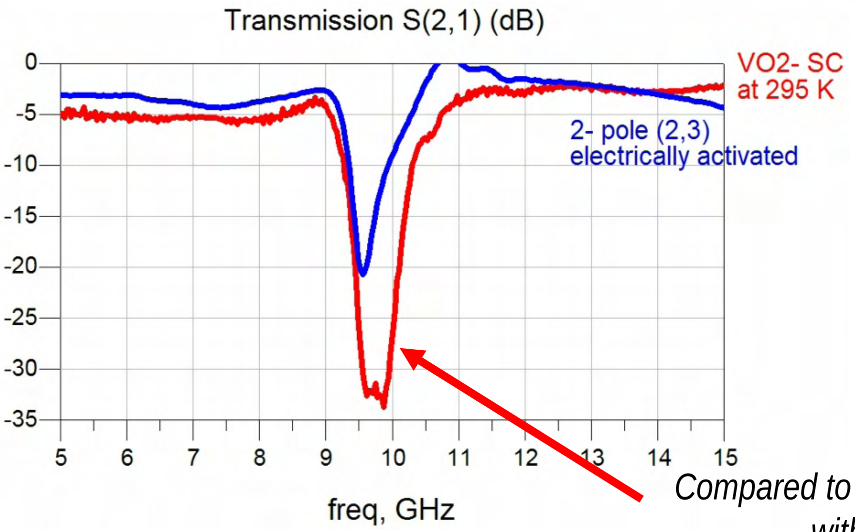
4-pole band stop filter: Tunability

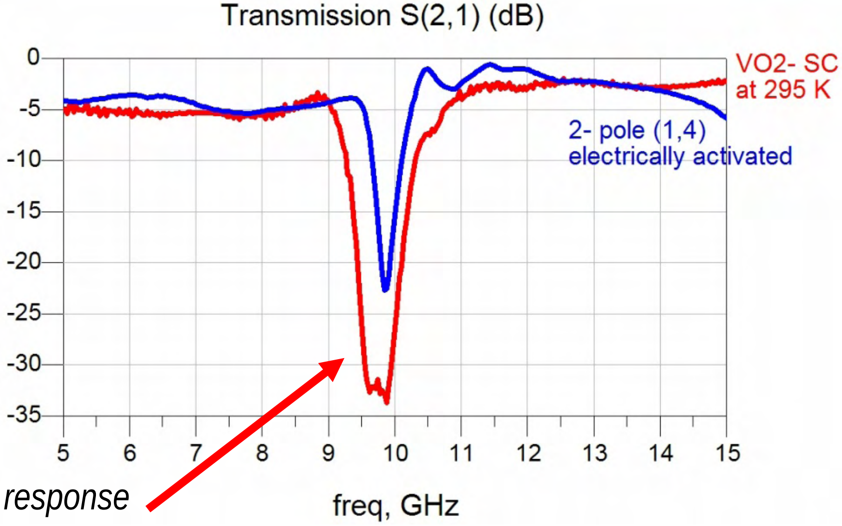
Measured response of the 4 pole band stop filter



Resonators 2 and 3 activated

Resonators 1 and 4 activated





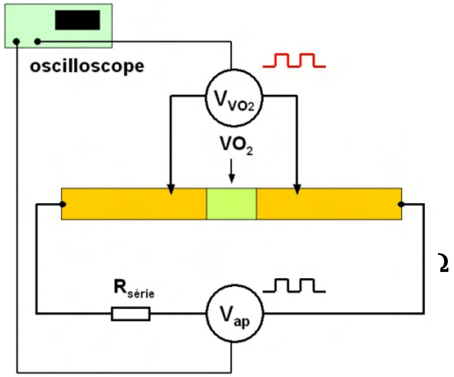
Compared to the measured response without activation

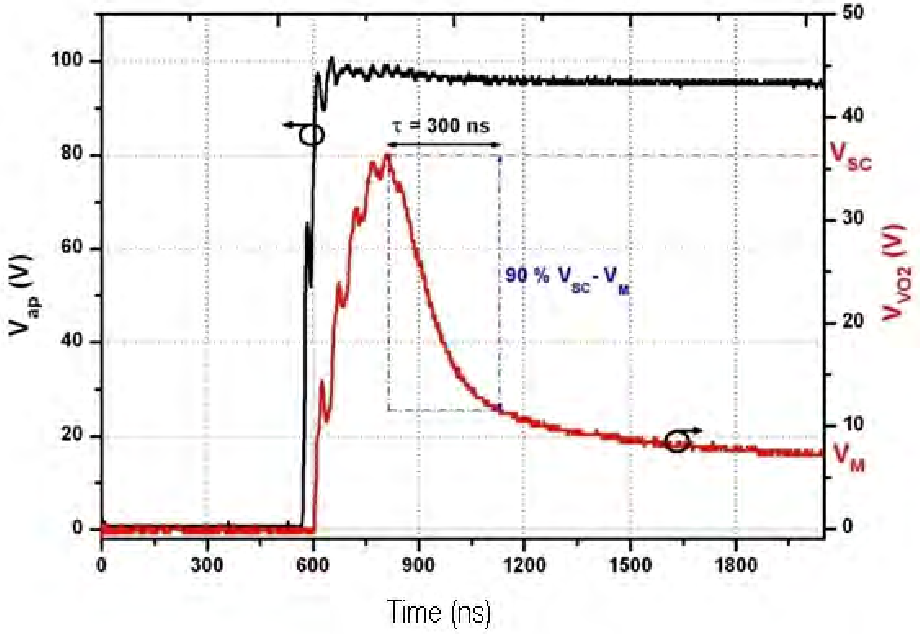
Electrical activation of 2, 3 (1, 4) resonators leads to a displacement of the central frequency of the filter to lower (higher) frequencies

↳ **Tunability demonstrated**

What about the switching time ?

2 terminal device





↳ Commutation time : 300 ns

Comparison to others RF switches

	advantages	drawbracks
➢ semi-conductors	Switching time (1-100 ns) Reliability (10^{12} cycles) Cost (0.5-8 €)	Insertion losses (0.3-2.5 dB) Band (< 20 GHz) Consumption (0.05-100 mW)
➢ MEMS	Insertion losses (0,05-0,2 dB) Parasite capacity (1-10 fF) Large band (DC-120 GHz) Reliability (10^{12} cycles)	Cost (8-20 €) Encapsulation necessary
➢ Switch VO_2	large band (DC to 35 GHz) Simple fabrication (2 levels) Switching time (~ 300 ns)	*consumption (> 50 mW)* *(activation by current)* *sensibles to temperature*

Outline

Thin Films

- ✓ Thin films by PLD for telecom applications
  Development of ”smart” material (with phase-transition) for RF system
- ✓ Doped thin films

Nano materials

- ✓ Nanostructured thin films by conventionnal PLD
  - AlN
  - DLC (deposited at room temperature)
- ✓ Synthesis of clusters and nanostructured thin films by PLD coupled with a free cluster generator (PLD – LECBD)
- ✓ Synthesis of colloids by Laser Ablation in Liquid
- ✓ Conclusions and perspectives

Development of ‘doped’ thin films

✓ Specificity of PLD :

Mean ‘thickness’ per laser pulse 0.01 – 1 Å

↳ Control the deposition at an atomic layer level
by monitoring the number of laser pulses

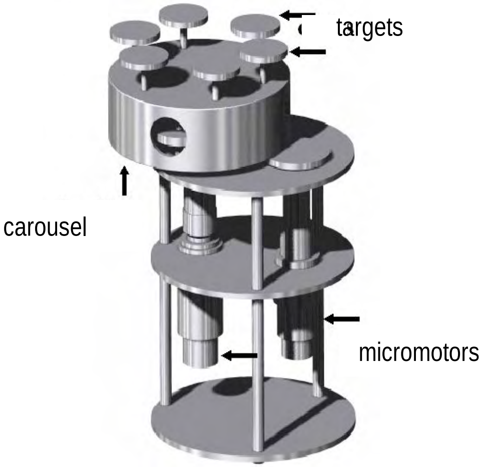
↳ Novel materials

⇨ **multiple target carousel**

⇙ ⇘

- Combinatorial Approach

- Doping

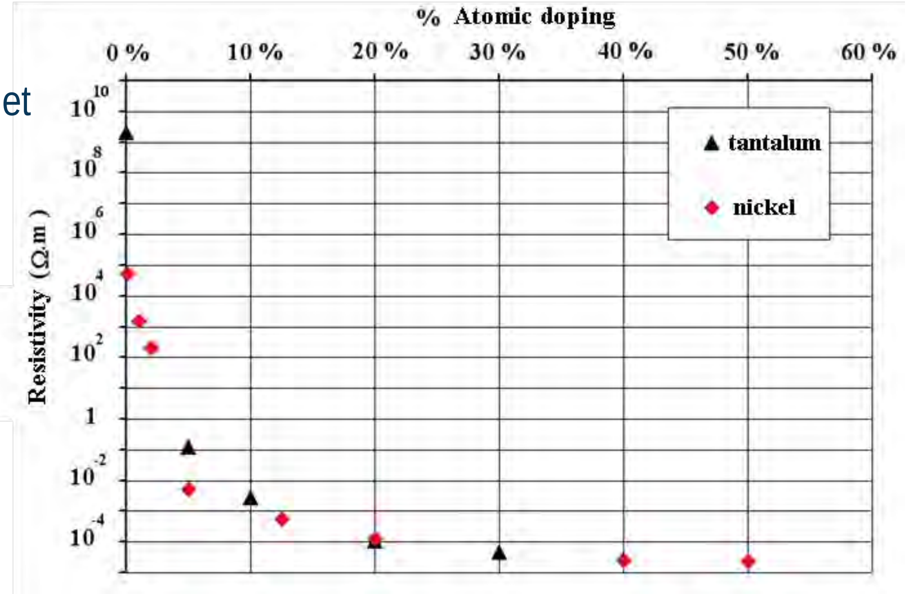


Development of ‘doped’ thin films

At room temperature

✓ Metal doped carbon PLD thin films

loop: n shots on carbon target, 1 shot on metal target



Strong change in the resistivity

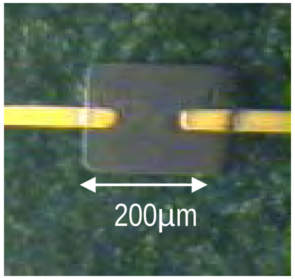
↳ ’control’ of resistivity

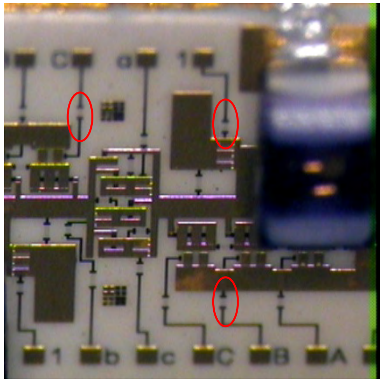
8 - 13 orders in magnitude

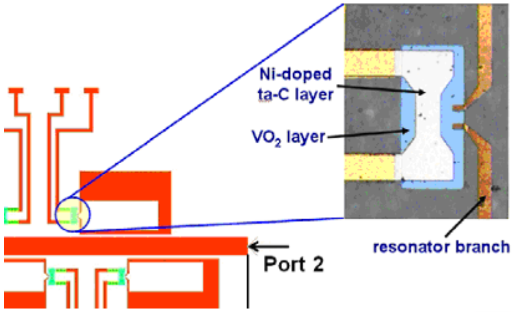
⇩

- fabrication of ‘calibrated’ resistances
  - to annihilate the signal losses through the biasing lines of MEMS

- heating micro-resistances (VO_2 transition)





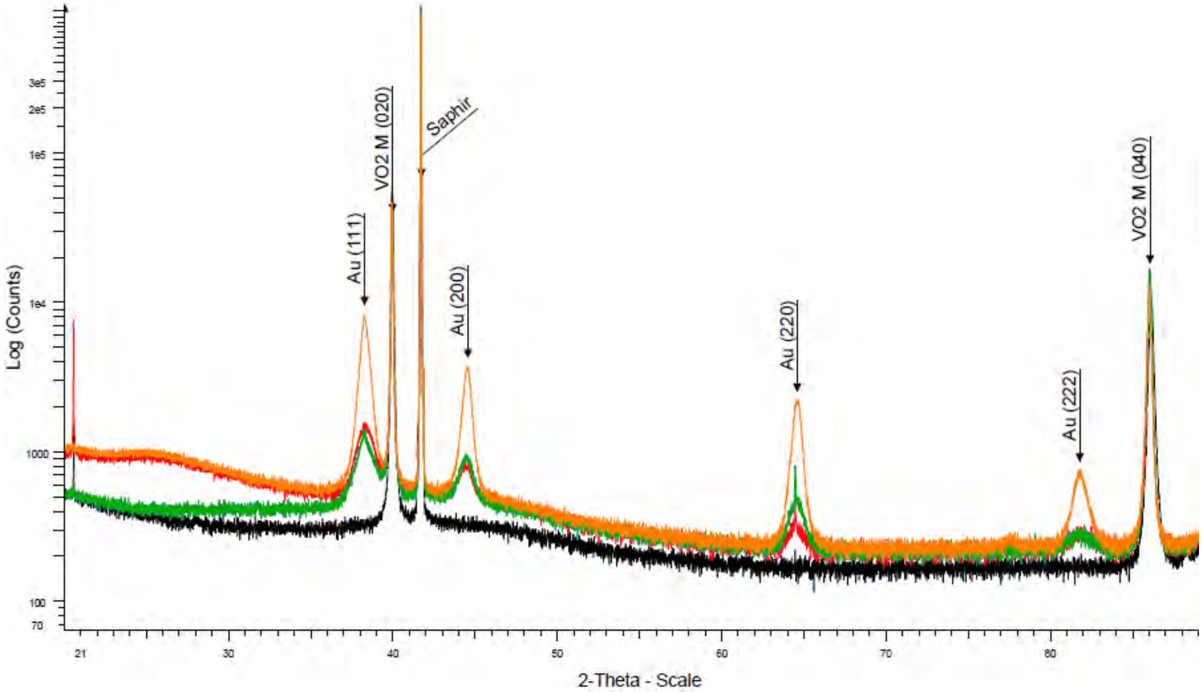


Development of ‘doped’ thin films

✓ Gold-doped VO_2 PLD thin films

loop: n shots on Vanadium target, 1 to 5 shots on gold target

Deposition at 600°C



XRD: (θ, 2θ)

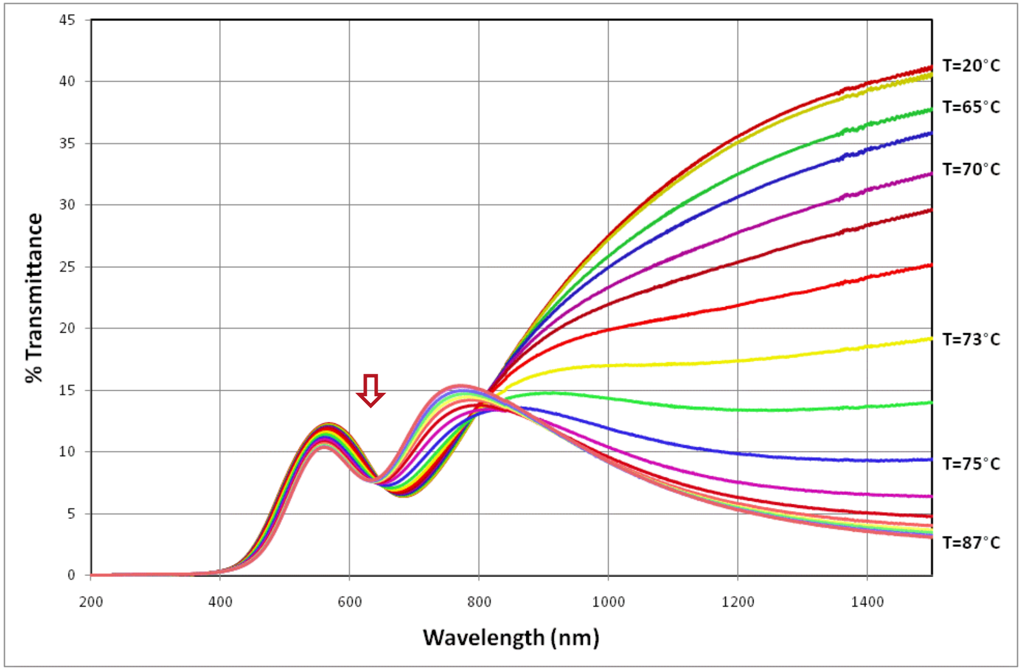
↳ Crystallization of Au and VO_2

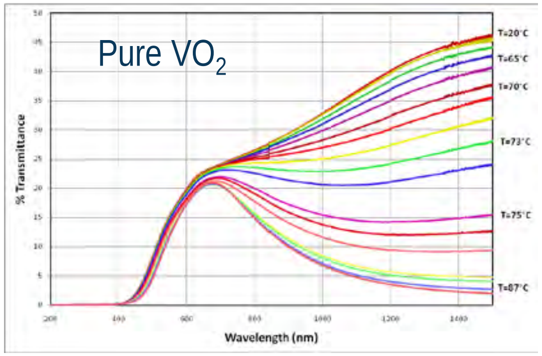
‘Doped’ thin films

Deposition at 600°C

- ✓ Gold-doped VO_2 PLD thin films
  loop: n shots on Vanadium target, 1 shot on gold target

↳ Gold nanoparticles (SPR)





↳ Surface Plasmon Resonance tunability of Au-NP in VO_2 matrix
(blueshift of SPR during SC-M transition of VO_2)

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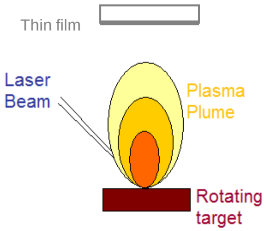
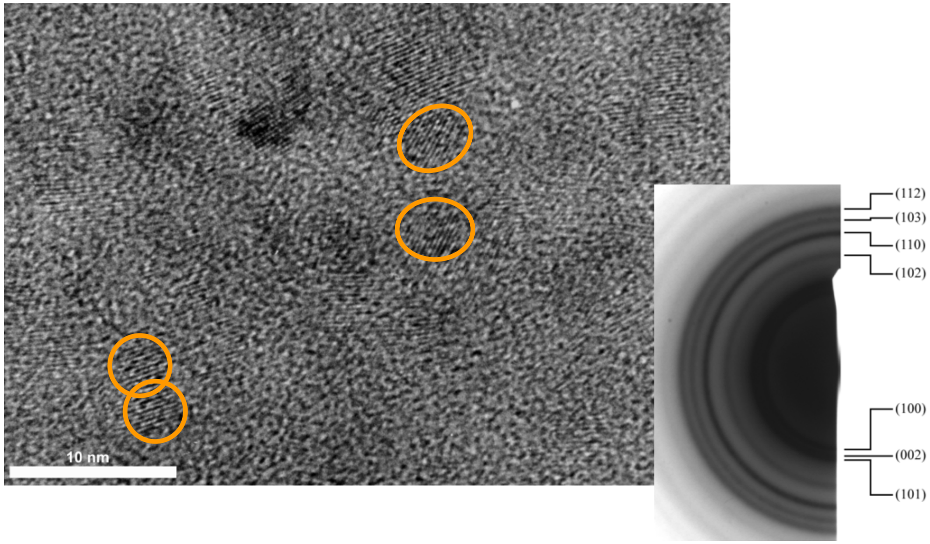
✓ Conclusions and perspectives

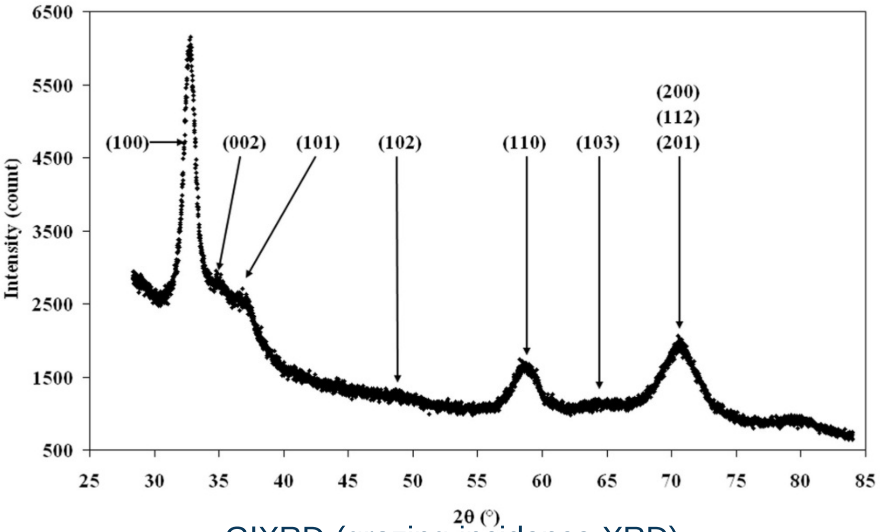
Nanostructeured materials by conventionnal PLD



- Aluminum Nitride (AlN) thin films at room temperature

  Piezoelectric material for Film Bulk Acoustic Resonator applications





HR TEM image and SAED

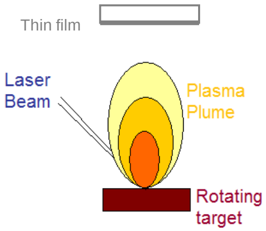
GIXRD (grazing incidence XRD)

of ns PLD AlN film deposited at room temperature, pressure 0.1 Pa N_2 fluence 6J.cm^{-2}

Nanocomposite thin film :

- ✓ AlN nanoparticles ≈7 nm in size, embedded in amorphous matrix
- ✓ hcp crystallized AlN nanoparticles
- ✓ piezoelectric response : d_{33} = 2 - 3.5 pm.V^{-1} / 5-7 pm.V^{-1} (bulk)

Nanostructeured materials by conventionnal PLD



- Diamond like Carbon thin films

PLD at room temperature of carbon target

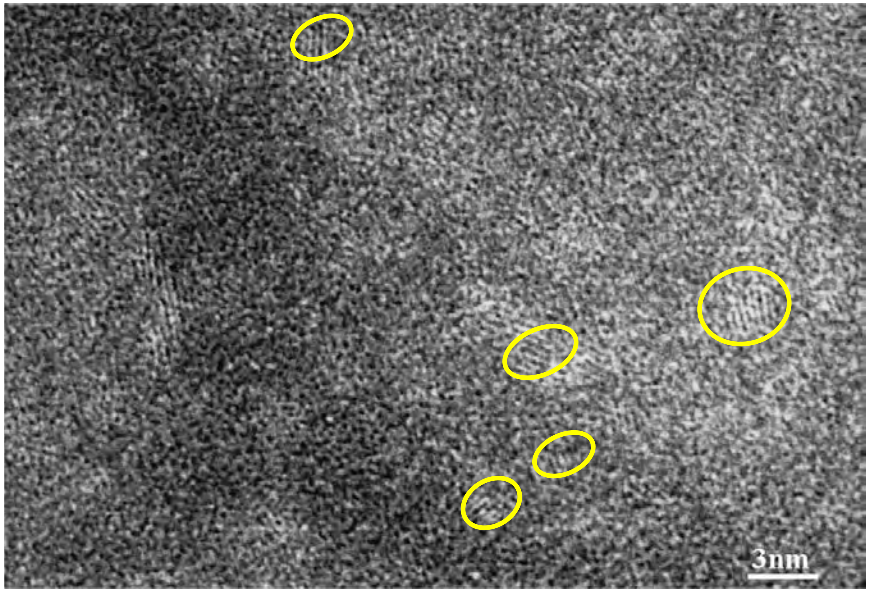
- ✓ ta-C with high sp^3 bonding proportion (80%)
- ✓ sp^2 clusters in sp^3 matrix
- ✓ Properties:

Hardness : 50 - 60 GPa / 100 GPa diamond
Young Modulus : 500 – 600 GPa / 1000 GPa diamond

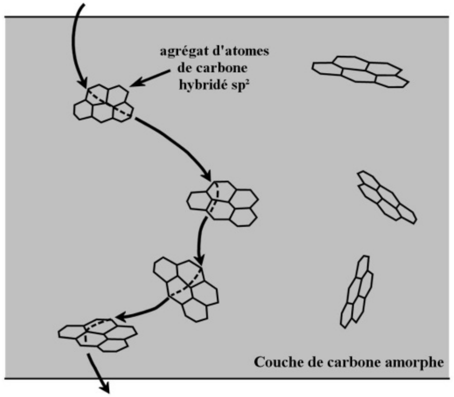
Dielectric constant : $\varepsilon = 5.7 \pm 0.2$ / 5,67 diamond

Electrical conduction mechanism :

Variable Range Hopping between sp^2 clusters



HR TEM image of ns PLD ta-C film deposited at room temperature



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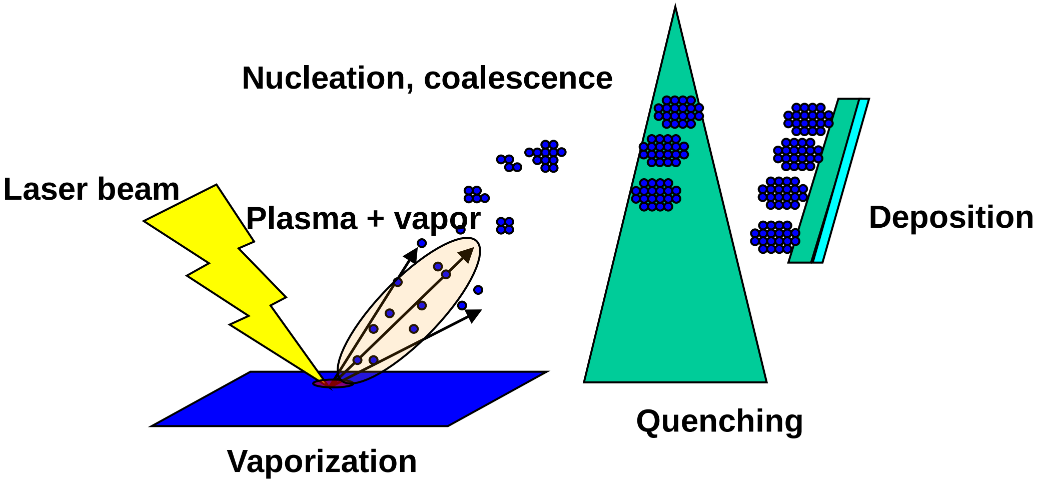
Exploiting the potentialities of laser ablation process
Synthesis of nanosized particles

✓ Quenching induced by a cold gas

  ⇨ Low Energy Cluster Beam Deposition (LECBD)



Homogenous Nucleation in vapor phase

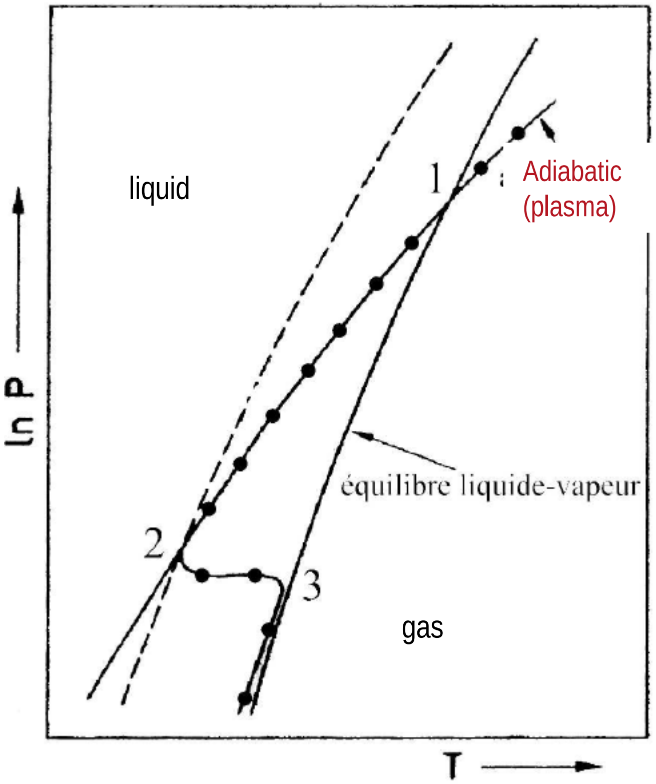
✓ Thermodynamic approach

$$S = P / Ps$$

P : partial pressure
Ps : vapor pressure at *Ts*, temperature of gas/condensed phase interface

P/Ps < 1 : vaporization from the condensed phase
P/Ps > 1 : condensation from the gas

Nucleation required Supersaturation
S = P / Ps   > 1



1 : supersaturation
2 : nucleation and increase of T (2-3)

✓ **Laser ablation** : adiabatic expansion of the vapor
- in vacuum : no supersaturation
- in gas (high pressure, high thermal conductibility): He

and

✓ stop the cluster growth
↳ expansion of mixture of gas and clusters

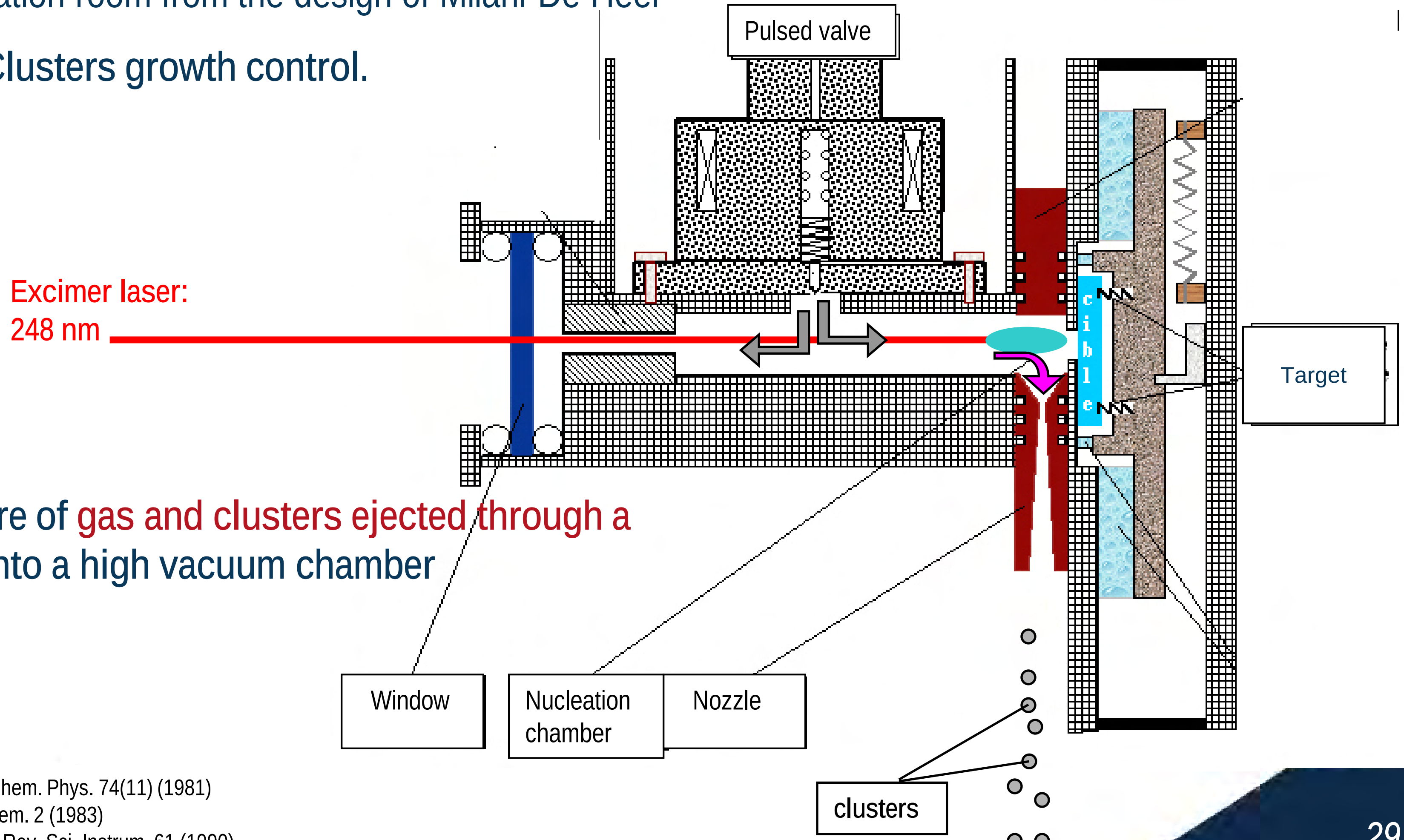
↳ specific set up

Principle of Cluster Generator

- Synthesis of nanoclusters

Target vaporization with a KrF laser
Gas injected by a pulsed valve (Smalley[1,2] device).
Nucleation room from the design of Milani-De Heer[3]

↳ Clusters growth control.



↳mixture of gas and clusters ejected through a nozzle into a high vacuum chamber

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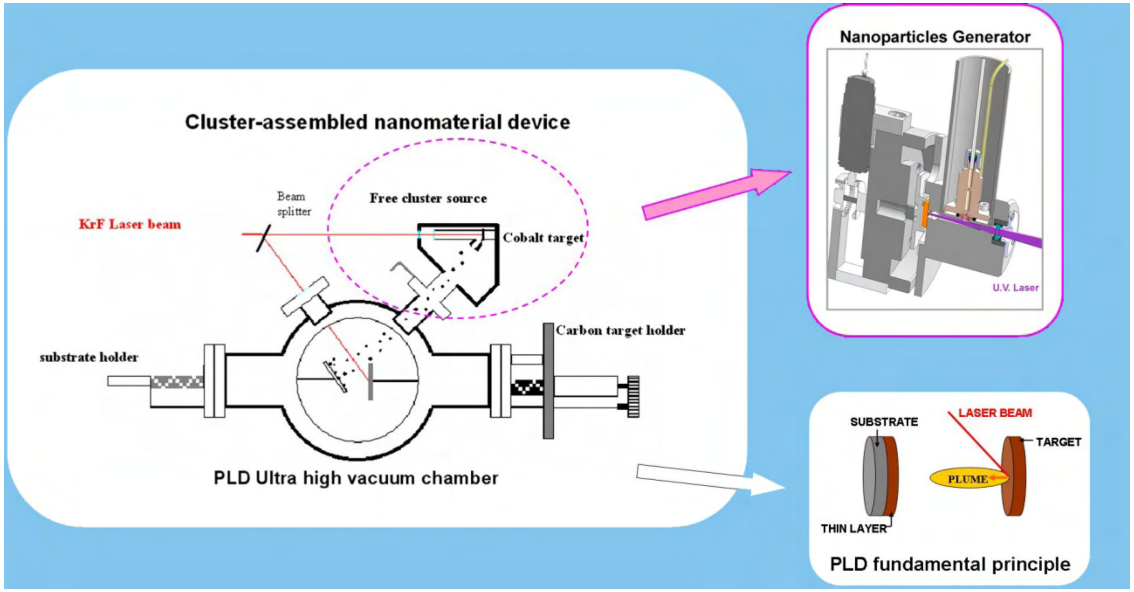
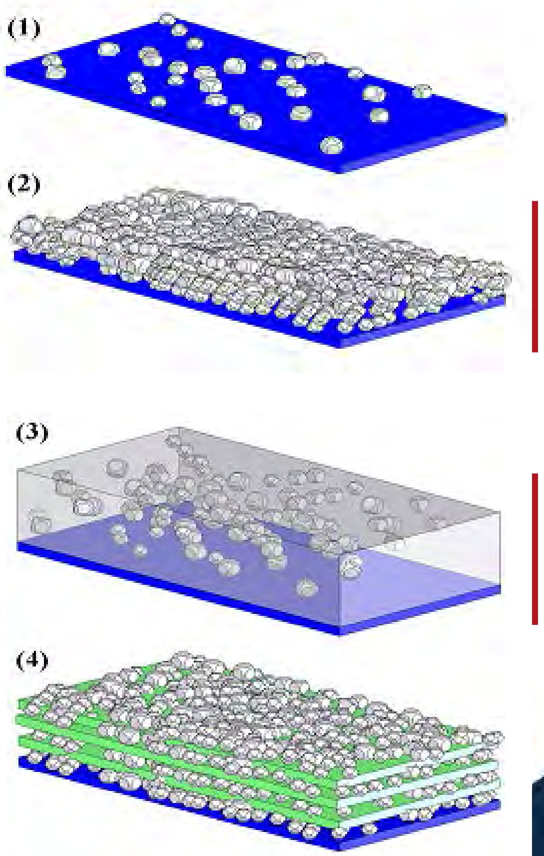
[1] R.E. Smalley et al., J. Chem. Phys. 74(11) (1981)
[2] R.E. Smalley, Laser Chem. 2 (1983)
[3] P. Milani, W.A. deHeer, Rev. Sci. Instrum. 61 (1990)

Overview of the PLD-LECBD set-up

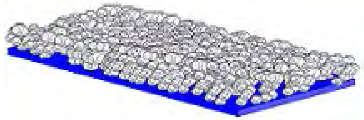
Conventional PLD set-up coupled with a free cluster generator





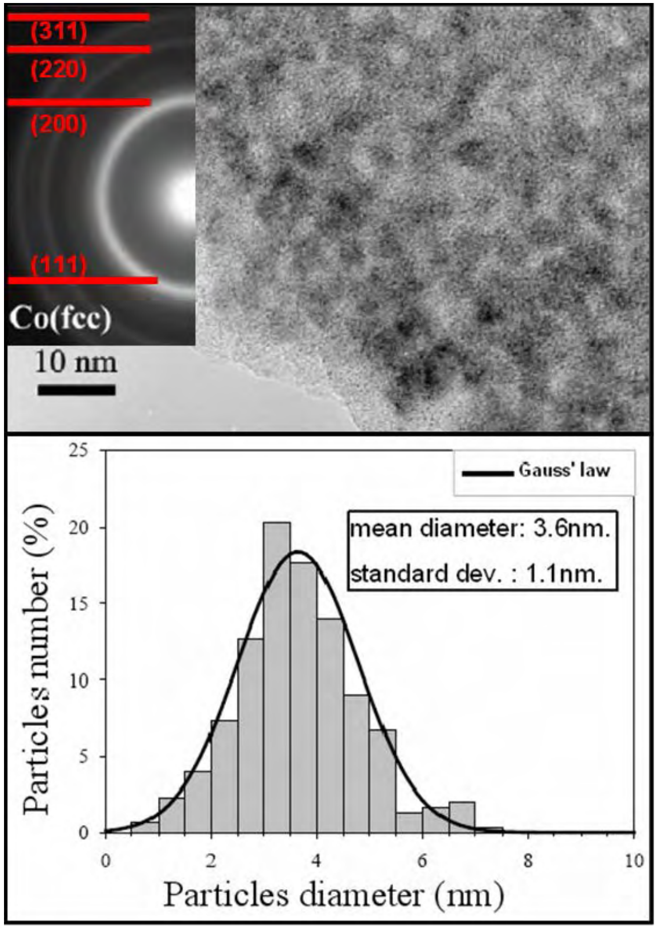
Stacking of ‘Nanoclusters’ by LECBD

Co nanoclusters by LECBD



- TEM characterization

  20 nm-stack on a Copper grid

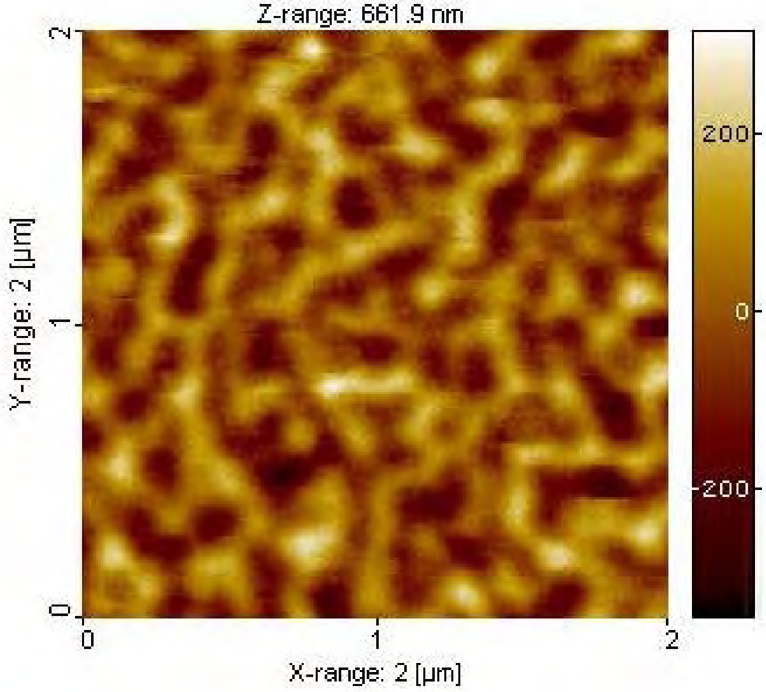


- Individualized quasi-spherical clusters.
- Monodisperse size

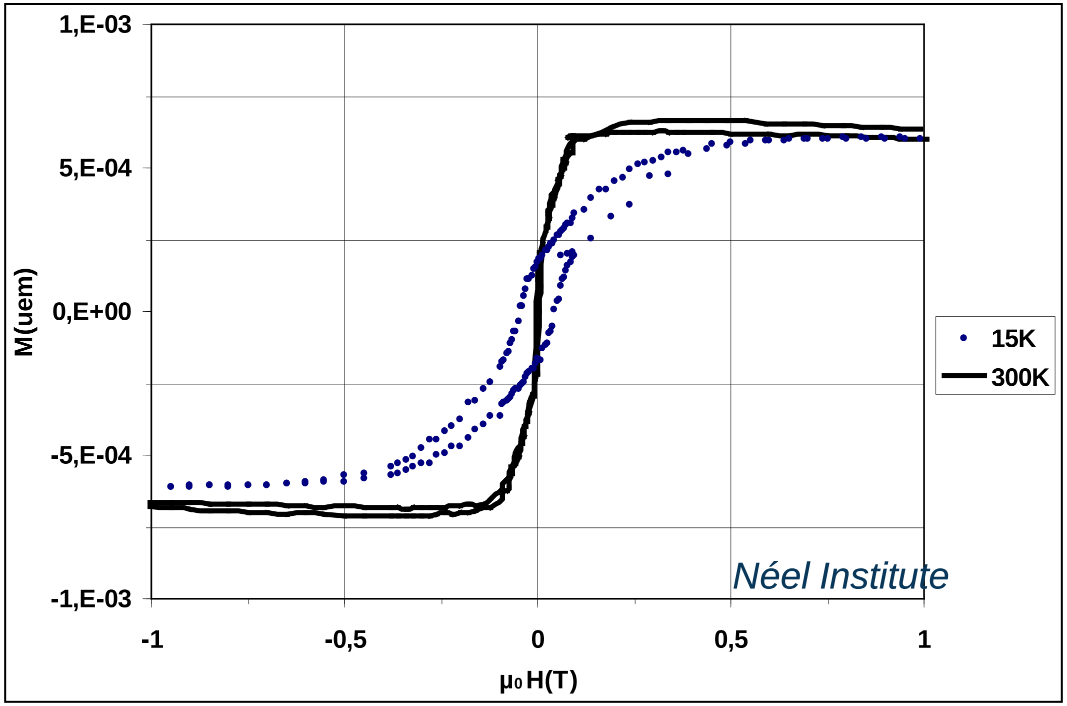
3.6 nm average size
Co fcc clusters

Co nanoclusters stacked by LECBD: magnetic properties

- Magnetic force microscopy



- Vibrating Sample Magnetometry



- Multi magnetic domains assembling.
- Magnetic domains > nanoparticles size

- **Ferromagnetic behavior** while a single cluster is superparamagnetic

⇨ Clusters magnetic coupling.

Crystalline entity ≈ 3.6 nm, magnetic entity ≈ 9.2 nm

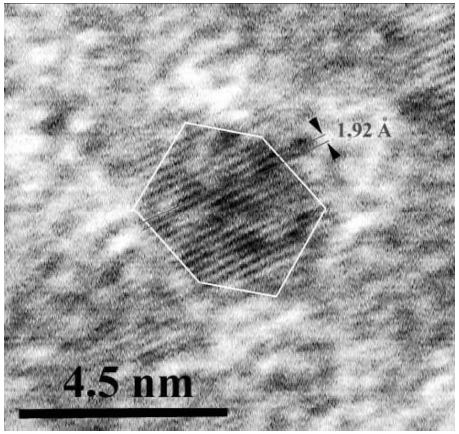
Collaboration : D. Givord,
Institut Néel, Grenoble, France

J. Appl. Phys., 2006

Co nanoclusters by LECBD

Correlation experiment - simulation

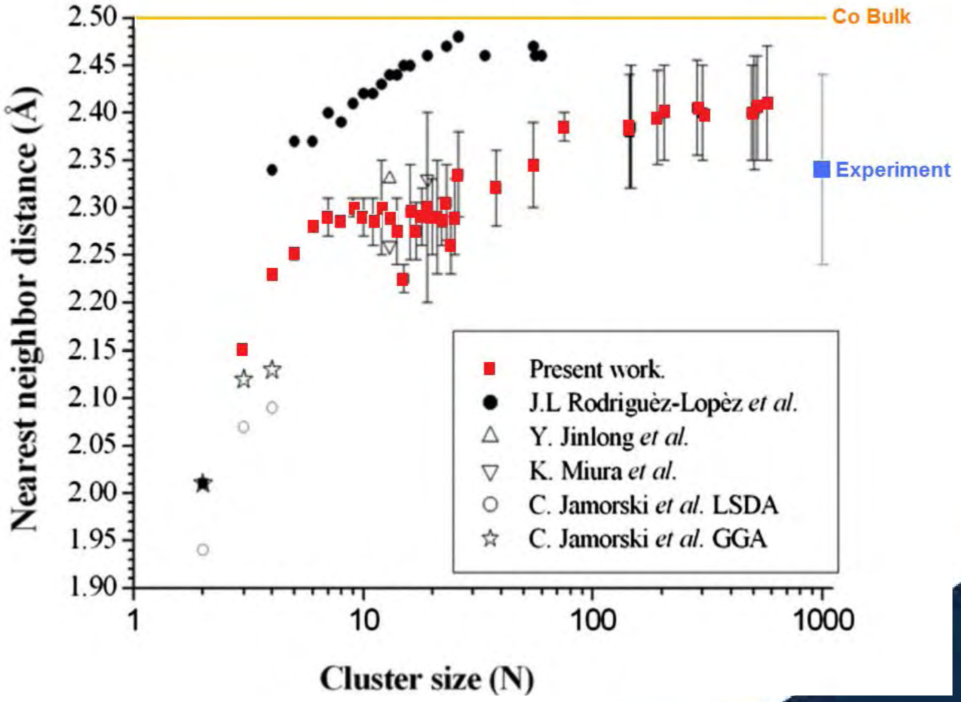
HRTEM of a isolated aggregate



- Size ~ 3 nm, fcc(111) planes
- Interplanar Distance : 1.92 Å ± 5%

2.05 Å between (111) planes of bulk fcc Co

↳ contraction of lattice parameter



Simulation by Molecular Dynamics

- Interatomic and interplanar distances calculated from the average nearest-neighbor distance of each atom in the cluster

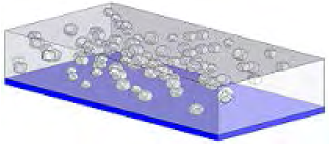
↳ good agreement

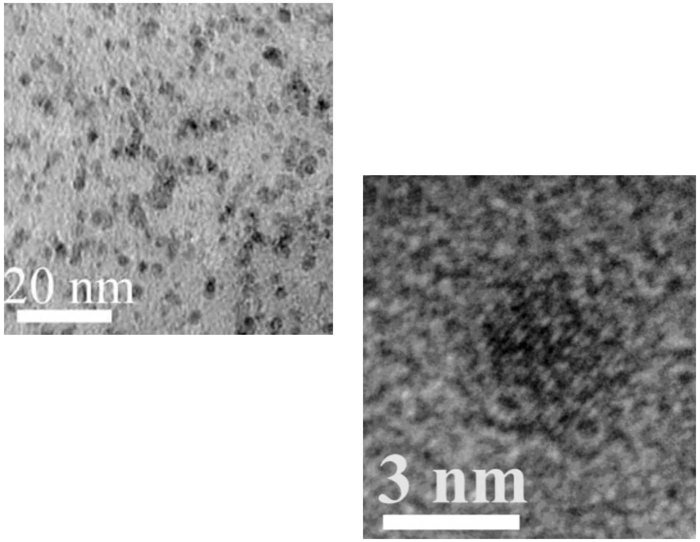
Collaboration : R. Ferrando
Univ. Gênes (Italie)

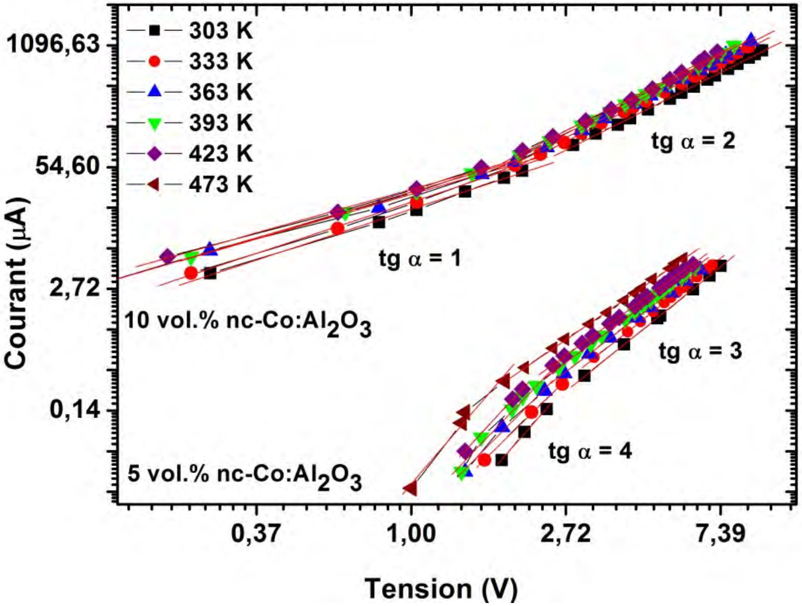
Phys Rev B, 2008

Nano-composites: nanoclusters by LECBD in PLD matrix

Co nanoclusters embedded in Al_2O_3 matrix by LECBD/PLD







Highly dispersed spherical clusters in the amorphous Al_2O_3 matrix(thickness 200 nm)

- Mean cluster size: 2.3 nm
- Electronic diffraction: in flight structure kept: Co fcc well crystallised clusters.

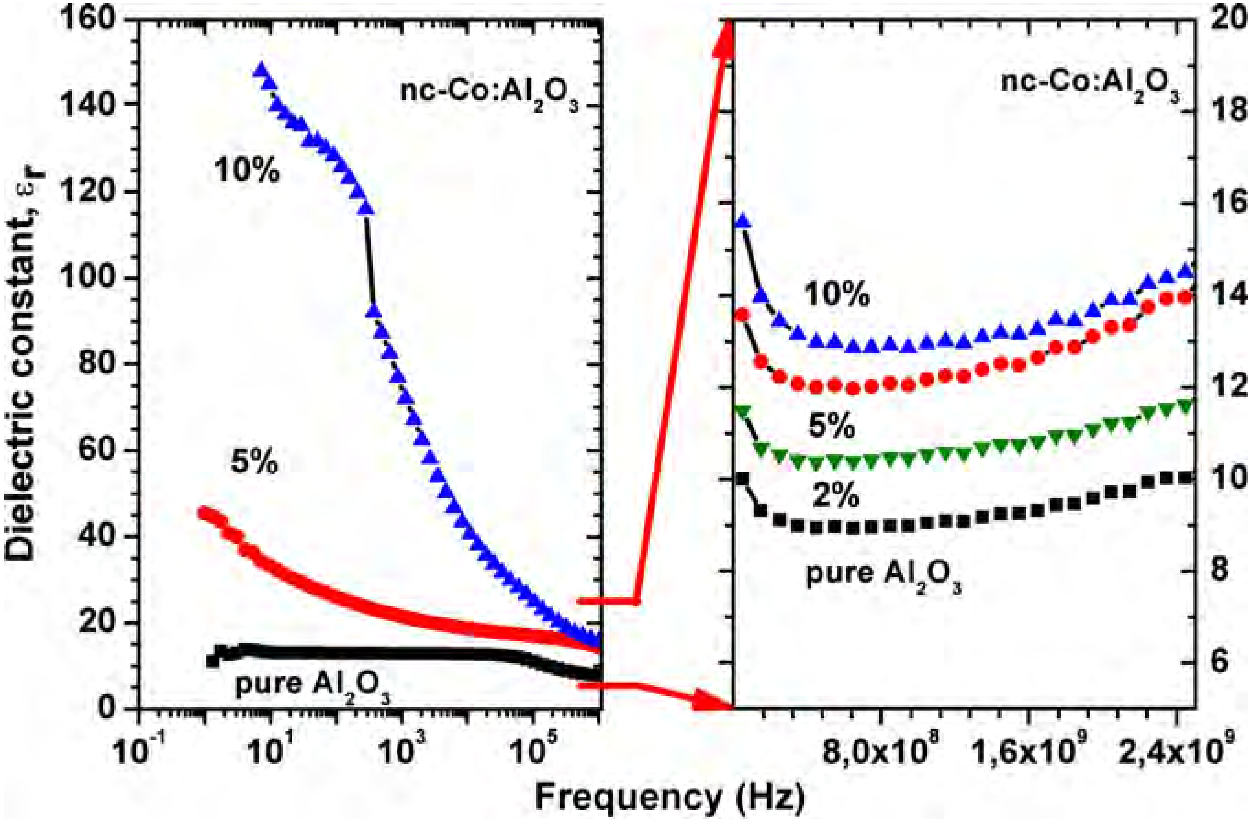
Conduction mechanisms (non ohmic) described by

Trap-Charge-Limited Space-Charge-Limited Conductivity (I=V^n)

Nano-composites : nanoclusters by LECBD in PLD matrix

Electrical characterizations

- Permittivity: Evolution of ε_r with doping.

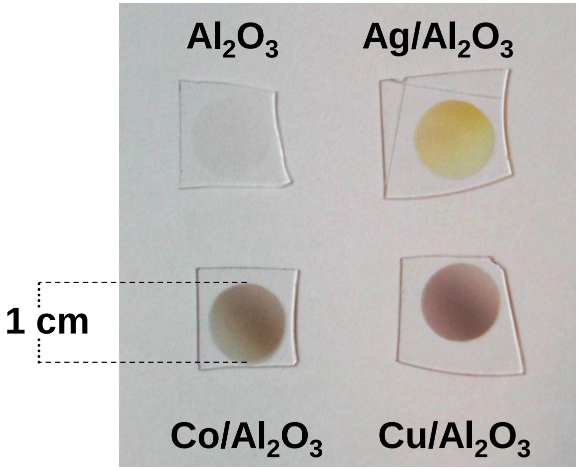


Increase of doping ⇨ increase of relative permittivity ε_r

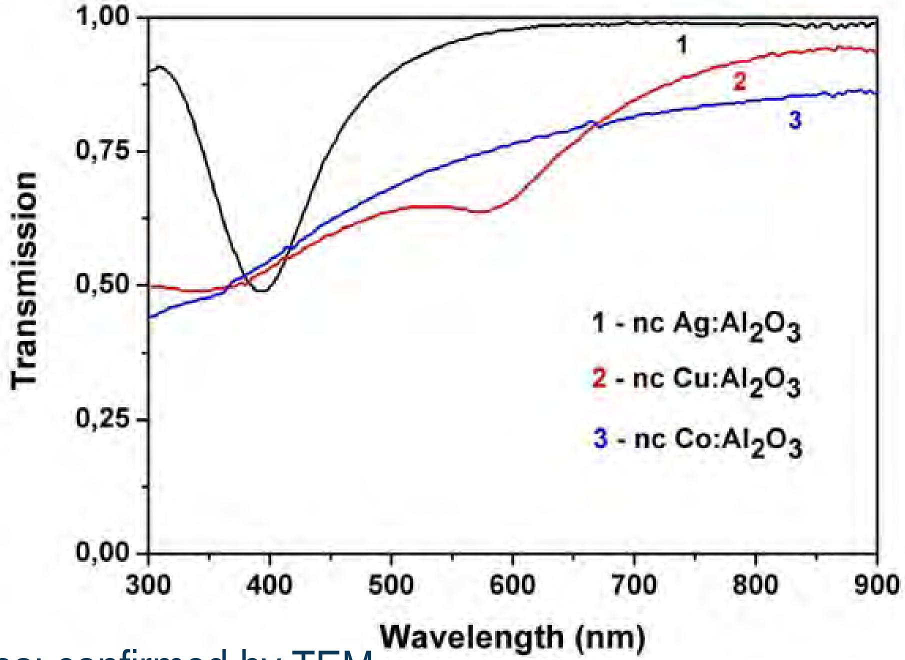
Nano-composites : nanoclusters by LECBD in PLD matrix

Co, Cu, Ag nanoclusters in Al_2O_3
Optical characterizations

- Absorbance → Surface Plasmon Resonance (SPR)



5% doping



- SPR extinction peaks:

↳ Metallic behavior of Ag and Cu clusters ⇨ no oxides: confirmed by TEM.

↳ Size:

- Silver: 394 nm (3.1 eV), 4.5 nm optical diameter (TDLDA modeling)
- Copper: 572 nm (2.2 eV), 2.6 nm optical diameter (Doyle approach)
- Cobalt: extinction in U.V

Outline

Thin Films

- ✓ Thin films by PLD for telecom applications

  Development of ”smart” material (with phase-transition) for RF system

- ✓ Doped thin films

Nano materials

- ✓ Nanostructured thin films by conventionnal PLD
  - *AlN*
  - *DLC* *(deposited at room temperature)*

- ✓ Synthesis of clusters and nanostructured thin films by PLD coupled with a free cluster generator (PLD – LECBD)

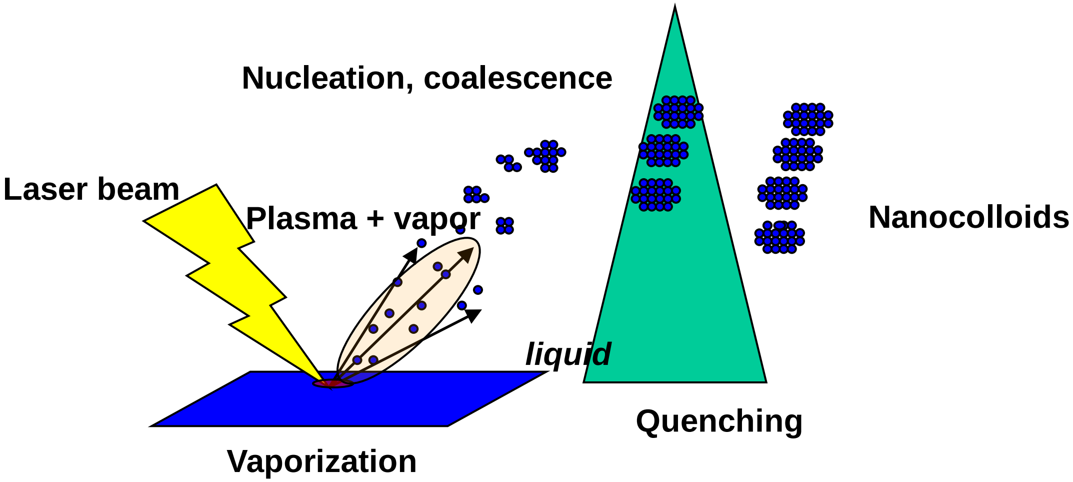
- ✓ Synthesis of colloids by Laser Ablation in Liquid

- ✓ Conclusions and perspectives

Exploiting the potentialities of laser ablation process
Synthesis of nanosized particles

✓ Quenching induced by a liquid

⇨ Synthesis of nanocolloids by **Laser Ablation in Liquid** (LAL)



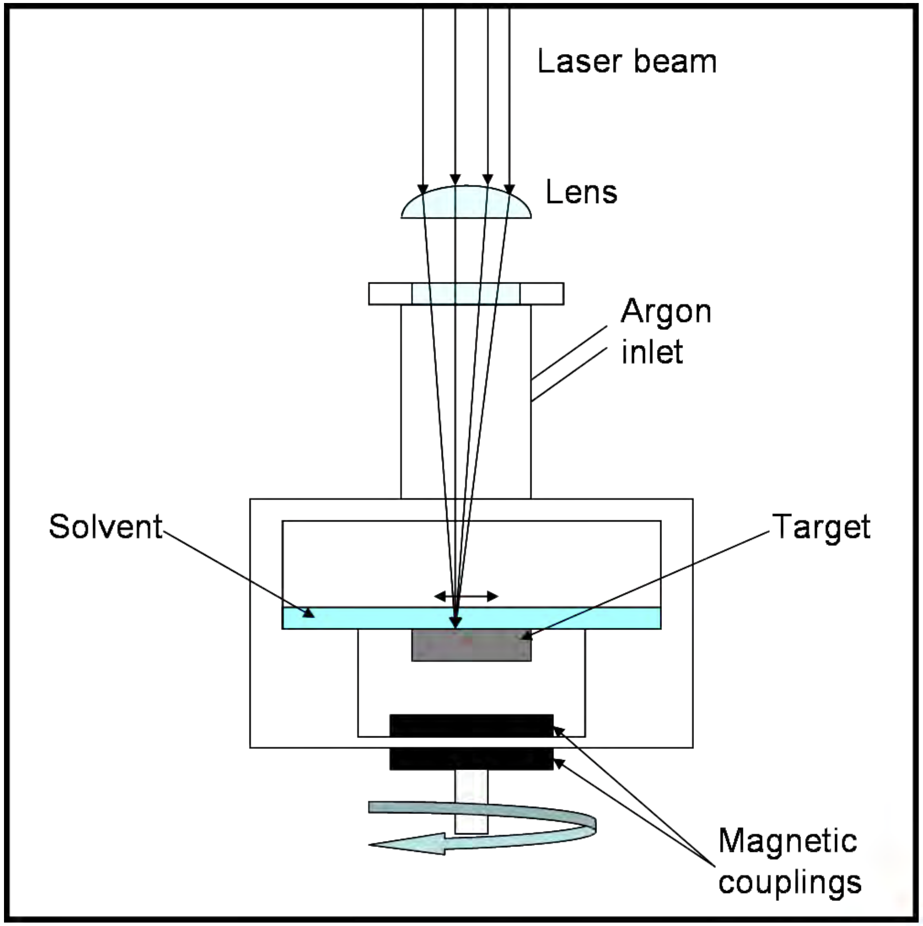
Nano-colloids by Laser ablation in Liquid

✓ Principle

- Ablation of target in liquid
- ‘quenching’ of the plasma plume

↳ growth of nano-clusters

at room temperature and atmospheric pressure

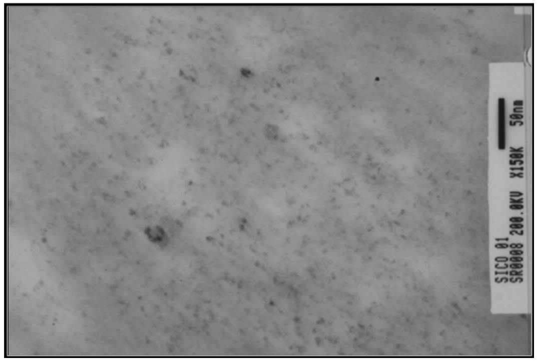


↳ Experimental set up:

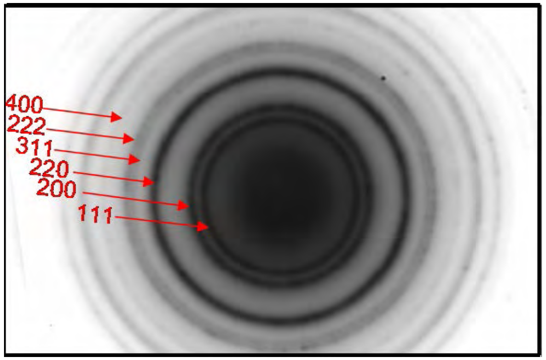
- Nd:YAG laser at 2ω, 532 nm, pulse duration: 7 ns, 10Hz,
- fluence: 1.5 - 6J/cm^2
- Cobalt target ablation under 5 mm of ethanol or water.

Co nanocolloids by LAL

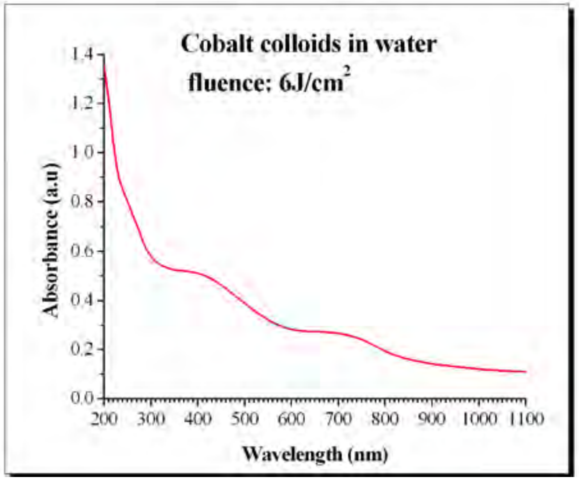
LAL in water



TEM



SAED



Absorbance

- Homogeneous particles : 2 - 4 nm.
- Randomly spread

  ⇘ non magnetic behavior

- Crystallized Nanoclusters:

  ⇘ CoO fcc

- Shoulders at 350 et 650 nm

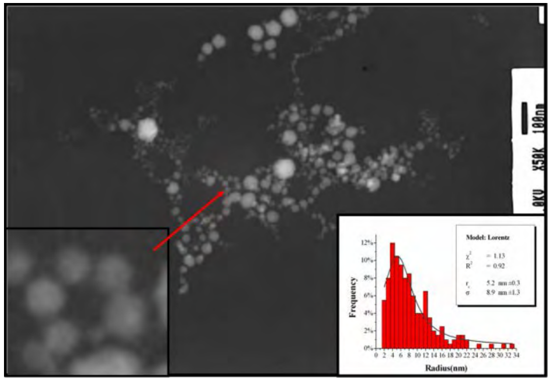
  ⇘ oxidation CoO

⇩

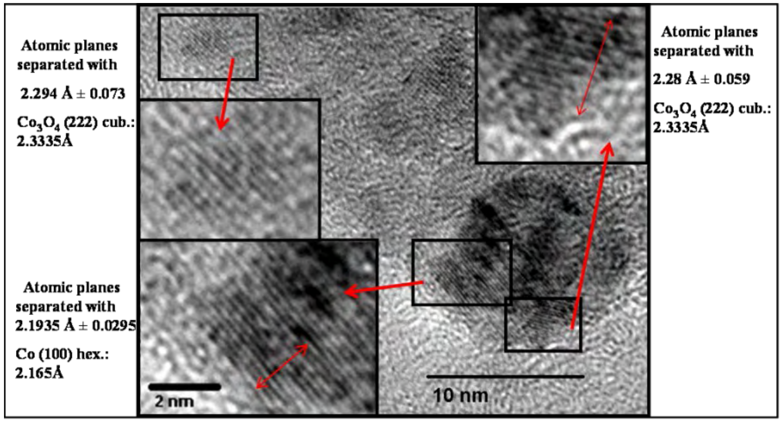
CoO fcc, non magnetic

Co nanocolloids by LAL

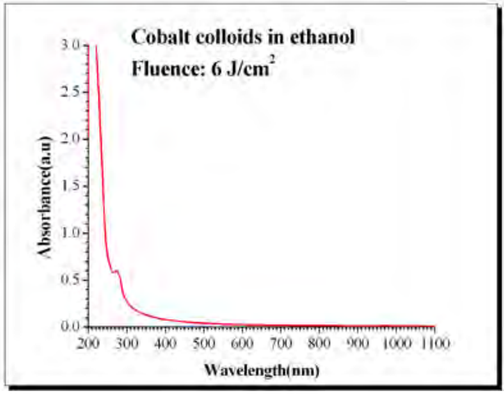
LAL in ethanol



TEM



HRTEM



Absorbance

- Spherical particles: 2 - 60 nm
- Pentagonal or necklace like organization

  ⇘ magnetic behavior

- Diffraction pattern blurred: high size dispersion or/and several structures.
- Direct interatomic distances measurement with HRTEM:

  ⇘ Co hcp (100) and Co_3O_4 fcc (222)

- Shoulder at 280 nm

  ⇘ oxidation Co_3O_4

⇩

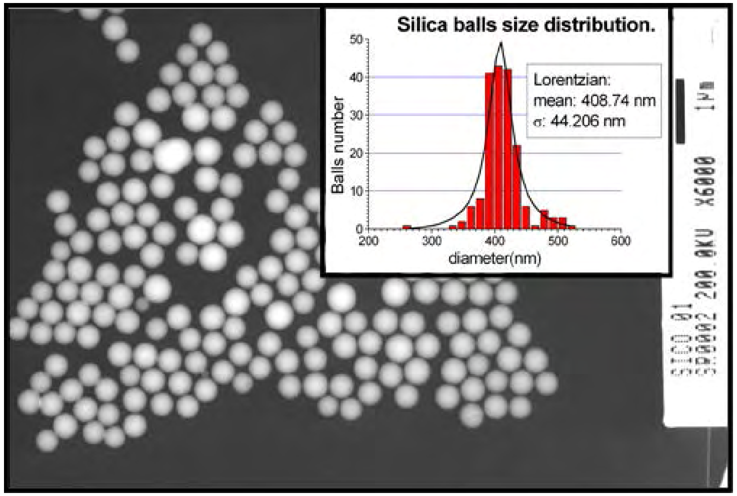
Co and Co_3O_4 magnetic

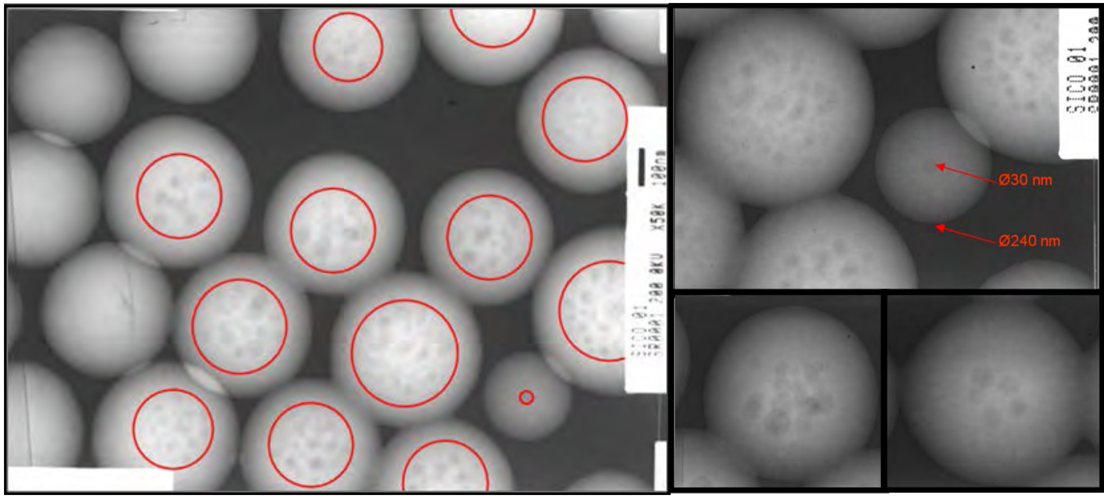
High influence of the quencher liquid over the characteristics of the clusters

LAL: Silica coating

- Co colloids synthesized by LAL in ethanol coated with Silica by a Stöber method:

Alkyl-silicates (TEOS) hydrolysis → silicic acid condensation in water/ethanol solution
+ ammoniac as morphologic catalyst.





- Silica balls homogeneous:

diameter ≈ 400 nm

- Self organized.

- Balls core: 1 to 20 nanoparticles,

few without core and monoparticular due to **lack of dispersion in the suspension.**

- Core nanoparticles agglomerated in necklaces or in geometrical forms (pentagon)

↳ magnetic behavior

Conclusion

✓ Potentialities of laser ablation

- Introduction of “new” materials in RF devices

✓ Laser ablation processes for nanostructure synthesis:

- LECBD/PLD for nanoclusters stacks and nanoclusters-embedded thin films with interesting optical and electrical properties
- LAL

→ Applications in opto and micro electronics.

On going work

✓ Development of association of more complex materials with different functionnalities :

- Multilayers
- Nanocomposites by LECBD for RF and optic components
- Nanopowders by Laser Ablation in Liquid for ceramic processes (stereolithography, ink-print…)

✓ Properties at nanometric size of smart nanostructured composites

Thank you for your attention !