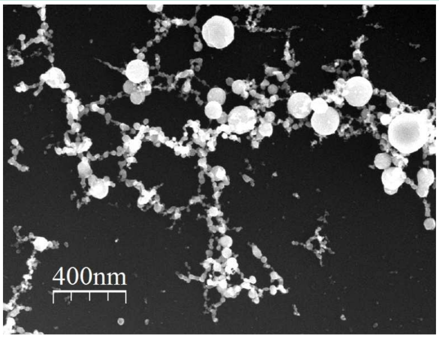
Fractal TiO_2 nanostructures by femtosecond non-thermal laser ablation in air



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i-LAMP

National Enterprise for nanoScience and nanoTechnology

NEST

i-LAMP Interdisciplinary Laboratories for Advanced Material Physics

NANOSCIENCE
Synthesis of nanostructures
Scanning probe microscopies

ELPHOS
Non linear photoemission
Time resolved fs spectroscopy

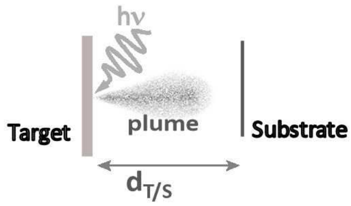
SURFACE SPECTROSCOPY
XPS
Thin films

ULYSSES
Scanning time-resolved spectroscopy
Non linear optics

QUANTUM
Simulations and modelling of complex systems

- 3 associate professors
- 4 researchers
- 3 tenure track researchers
- 7 PhD students
- undergraduate students

Ablation process



Nanosecond pulse

Femtosecond pulse

3 steps
- Pulse Absorption
- Lattice heating
- Plume emission

Pulse Absorption + Lattice heating: 10 ps

Plume emission: > 20 ps

Pulse absorption + Lattice heating

- Electron excitation into CB
- Thermal equilibrium with lattice ≈ 5-10 ps.

The pulse brings the material to a high P and T state before material emission

Marco Vitiello, Ph.D. Thesis, Università di Napoli "Federico II", 2005

Nanostructured material synthesis methods

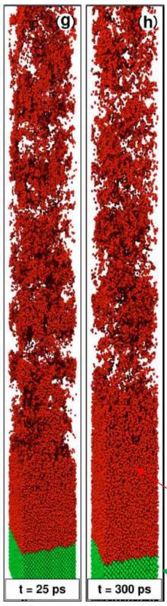
- wet chemistry
- self assemby on templated substrates
- CVD
- Pulsed laser deposition

Critial issues

- Simple process
- Control over size and stoichiometry
- Cost of materials
- Industrial scalability
- Range of applicability

MD simulation [1]

Ablation process: theory



Si(100)
Δt = 500 fs
F = 0.495 Jcm^{-2}

$\rho \approx \rho_0$

T ≈ 16000 K

P ≈ 28 GPa

Liquid

Solid

Fragmentation

Expulsion mechanisms [2]

Laser Fluence

Low

- Spallation
- Phase Explosion
- Fragmentation
- Vaporization

High

Expelled Material

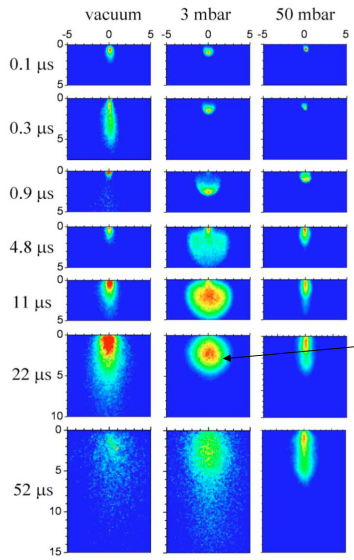
V ≈ 800 ms^{-1} [1]

NP, atoms, ions [2]

[1] P. Lorazo, L. J. Lewis and M. Meunier, Phys. Rev. B 73, 2006

[2] Marco Vitiello, Ph.D. Thesis, Università di Napoli "Federico II", 2005

Ablation process: pressure



Fast, intensified-CCD photography

300 fs, 527 nm
F = 0,6 Jcm^{-2}
Target: Fe
Ar pressure

Atoms and ion up to 2 mm away from target

NP up to 5 mm

high Plume density in the center

The plume expansion is limited by the interaction with the gas

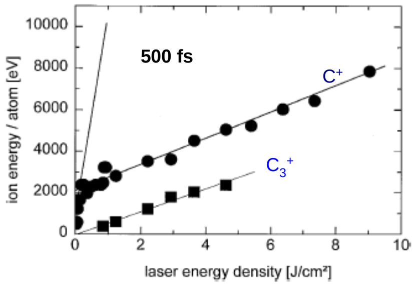
↓

Ambient pressure: shorter expansion

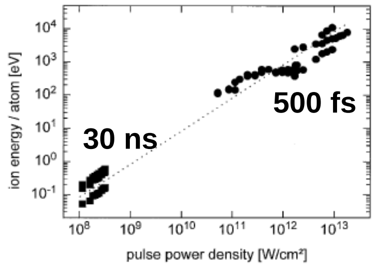
Amoruso et al, Applied Physics Letters 92, 041503 (2008)

Ablation process: laser parameters

248 nm
HOPG
Vacuum



KE is proportional to
Laser Fluence



KE proportional to
Laser Pulse Duration

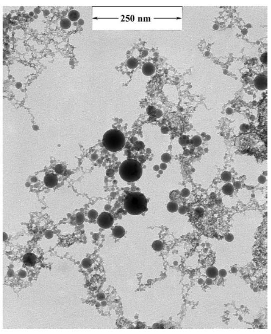
Koster, Mann, Applied Surface Science 109/110 (1997), 428-432

Ablation: results of deposition

ns

Water

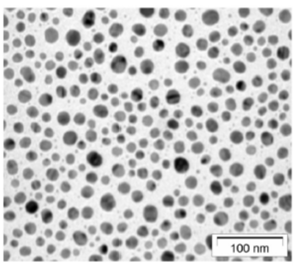
TiO_2, rutile, 50 Jcm^{-2} [1]



Fractals?

Vacuum

Ag, 10 ns, 0,64 Jcm^{-2} [2]

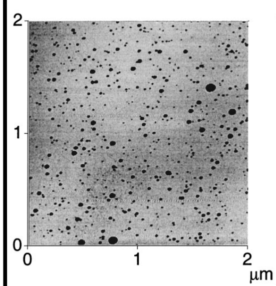


nanoparticles

fs

Vacuum

Ag, 120 fs, 0,5 Jcm^{-2} [3]

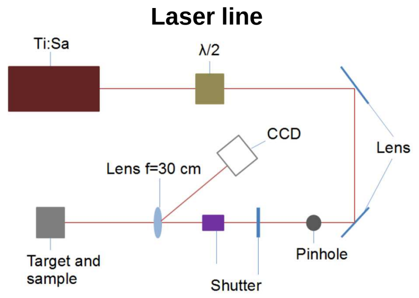


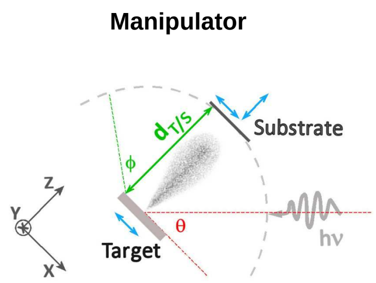
nanoparticles

fs pulses in air? unexplored!

[1] J. Appl. Phys. 106, 054306 (2009)
[2] J.C. Alonso et al. / Applied Surface Science 255 (2009) 4933–4937
[3] Appl. Phys. Lett., Vol. 84, No. 22, 31 May 2004

fs Ablation: experimental setup





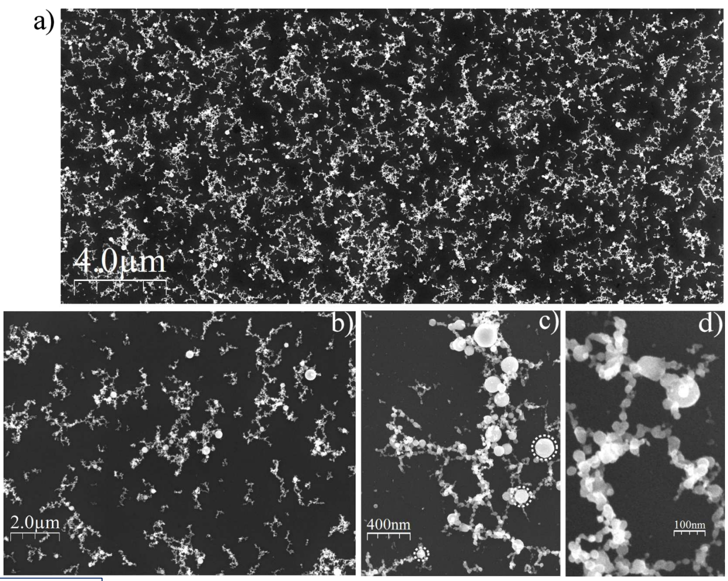
- Pulse: 120 fs @800 nm
- Fluence: 4 - 9,6 Jcm^{-2}
- 150 pulse each deposition
- $\theta = 45°$
- $\phi = 0°$

Characterization

SEM
RAMAN
XPS
AFM

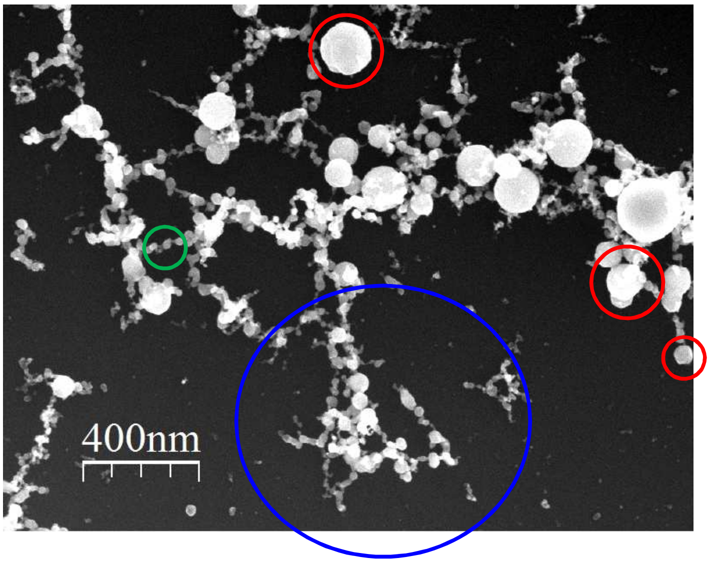
fs Ablation

- Target: Ti
- substrate: Si
- RT
- P = 1 atm
- SEM



Complex structures

fs Ablation

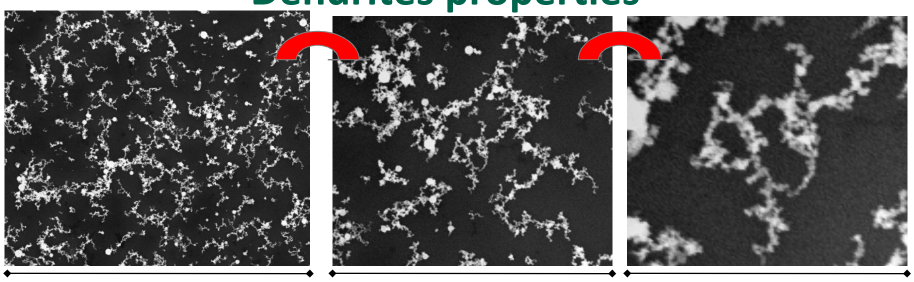


Polygonal NP

very small NP

Dendrites composed of NP

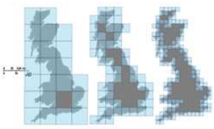
Dendrites properties



10 µm | 3 µm | 700 nm

Self-similarity : same shape on different scales

How to measure the irregularity of a structure?



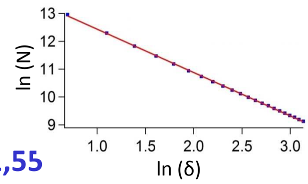
Box counting

N = # of boxes to cover object

δ = box size

$$D \approx -\frac{\log N(\delta)}{\log \delta}$$

Hausdorff-Besicovich dimension



D = 1,55

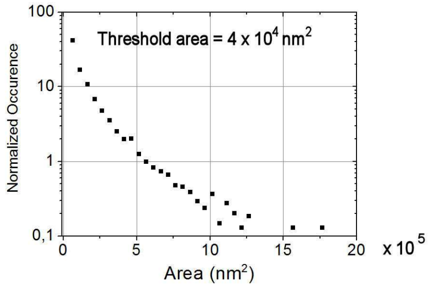
FRACTALS

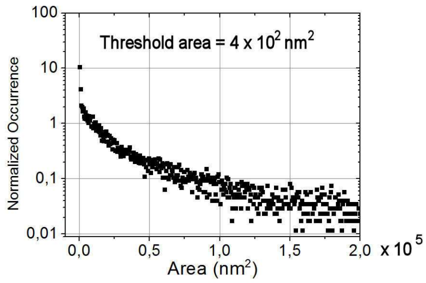
D calculated on at least hundreds of structures

Fractals and NP characterization

Look for preferential sizes etc

Area of the nanostructures



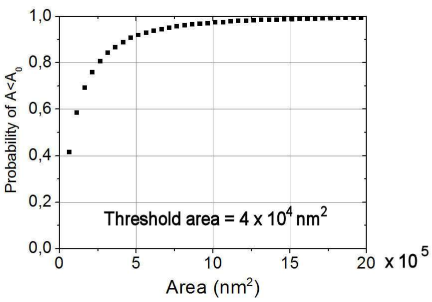


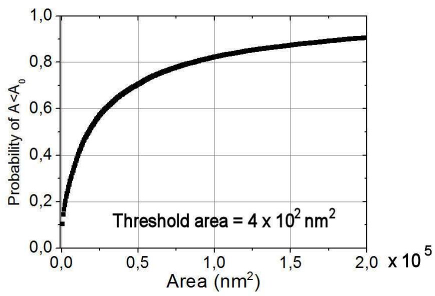
Statistic calculated on over 5000 nanostructures

but still noisy on higher values due to limited occurrences

Fractals and NP characterization

Cumulative distribution function (CDF)

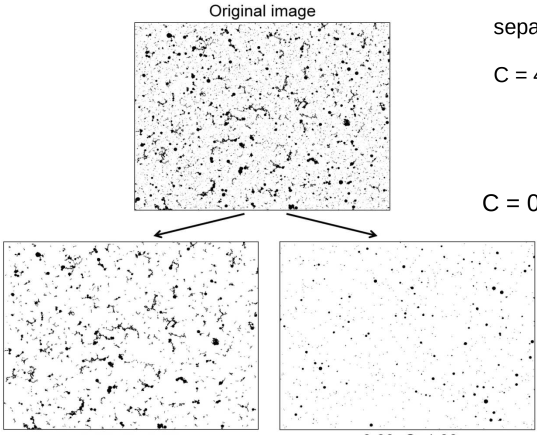




Probability of finding an area $A < A_0$

Better comparison for different synthesis parameter

Fractals and NP characterization

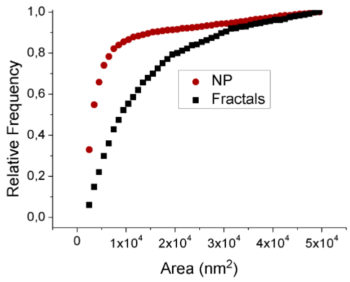


separate NP and fractals through circularity

$C = 4\pi \text{ Area} / \text{perimeter}^2$

C = 0 line

C = 1 circle

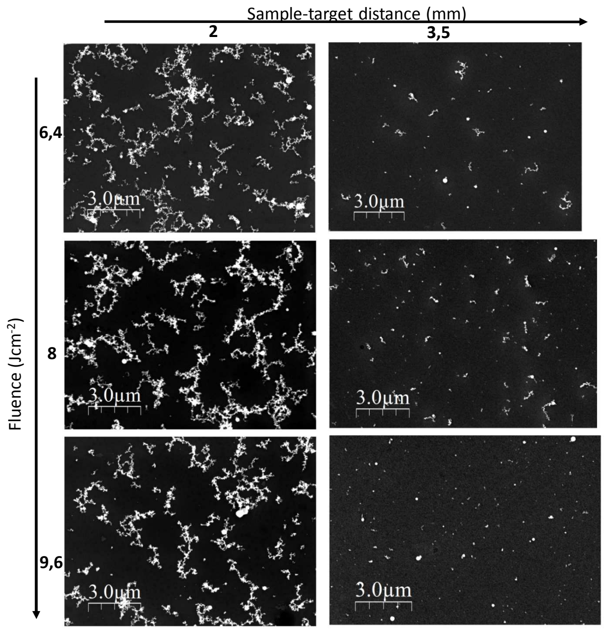


Larger NP with diameter above 50 nm

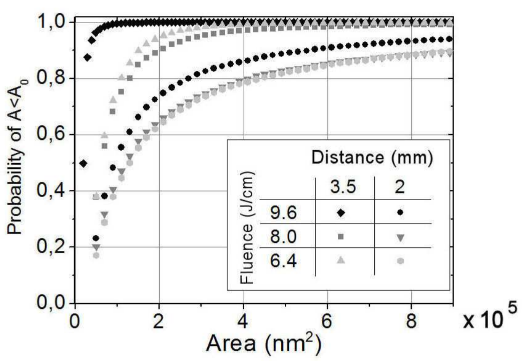
≈ 80% NP diameter < 70 nm

Most of NP are below 20 nm

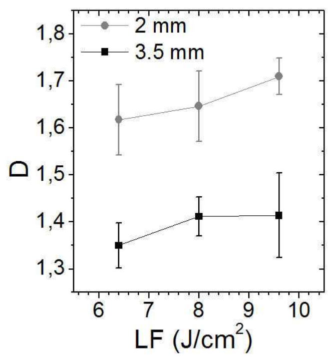
Fractals vs synthesis parameters



Fractals vs synthesis parameters



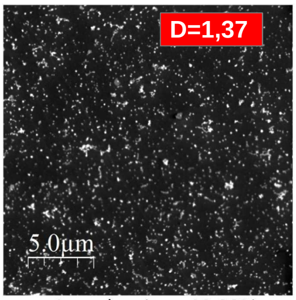
Hausdorff-Besicovich dimension



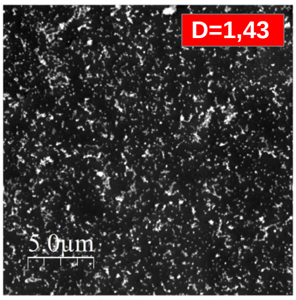
Increasing fluence = decreasing area
Shorter distance = larger fractals

D depends on synthesis

Fractals vs density

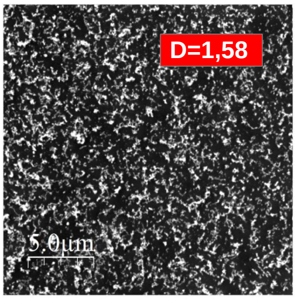


Area density = 10,23%

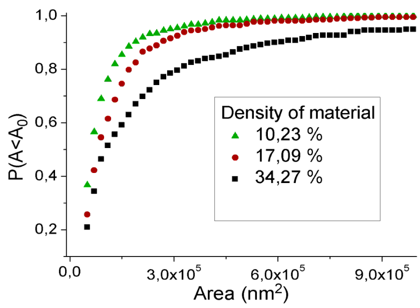


Area density = 17,09%

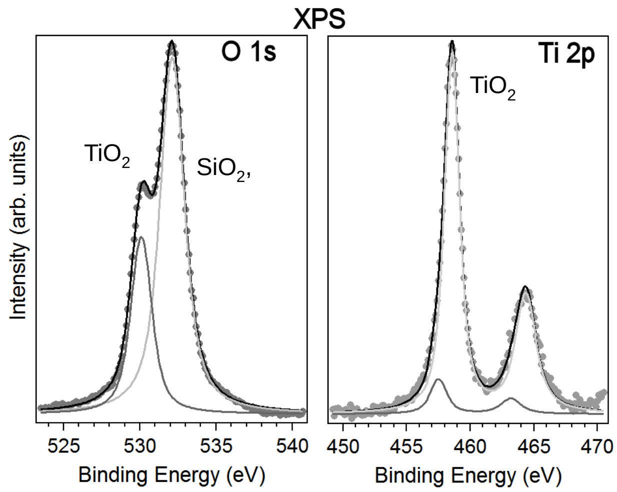
fractal area and D increase with density



Area density = 34,27%



Fractals: chemical state



TiO_2 = 530.1 eV
SiO_2 = 532.1 eV

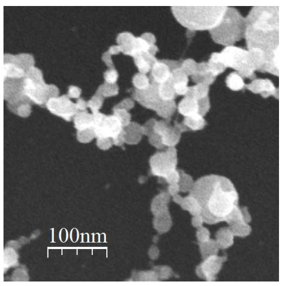
TiO_2 = 458.8 eV

E_B = 457.3 eV

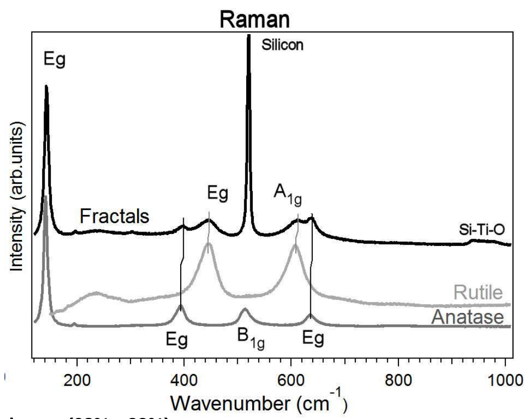
Metallic Ti or O vacancies at the NP surface

Fractals are mainly TiO_2

Fractals: crystalline structure



Polygonal shaped NP: crystals

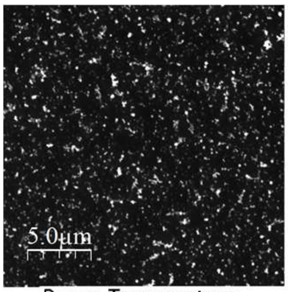


- **Coexistence of Anatase and Rutile phases (68% - 32%)**
- **Sharp lines, i.e. good crystals**

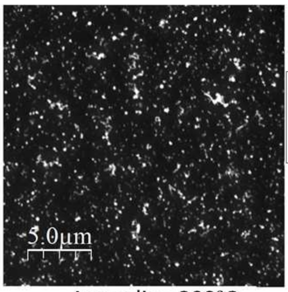
- **Blueshift of the Raman peaks**
  - ~~**Oxygen vacancies**~~
  - **different NP sizes**

Fractals are anatase and rutile TiO_2

Fractals vs temperature



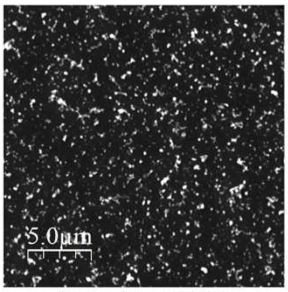
Room Temperature



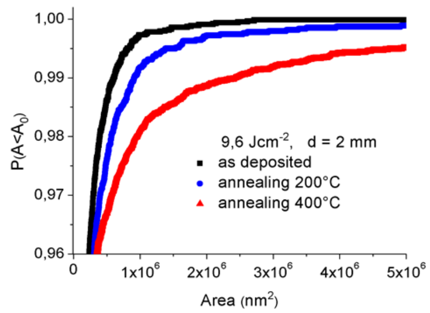
Annealing 200°C

Fractal area increases with temperature

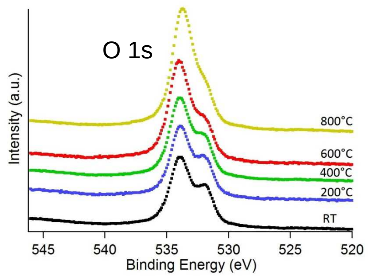
Higher mobility
further aggregation

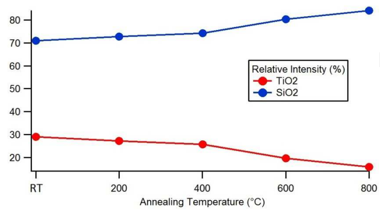


Annealing 400°C

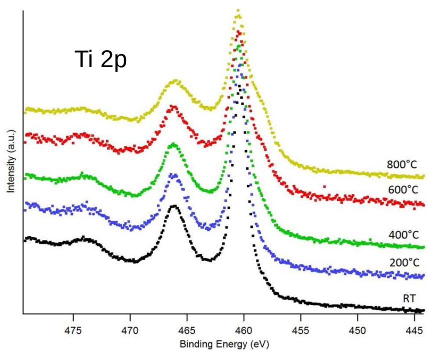


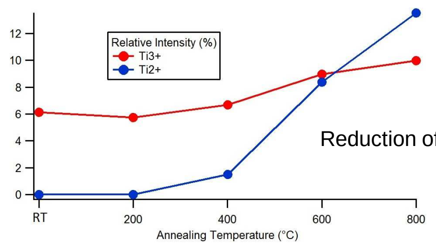
Fractals vs temperature





Decrease of TiO_2



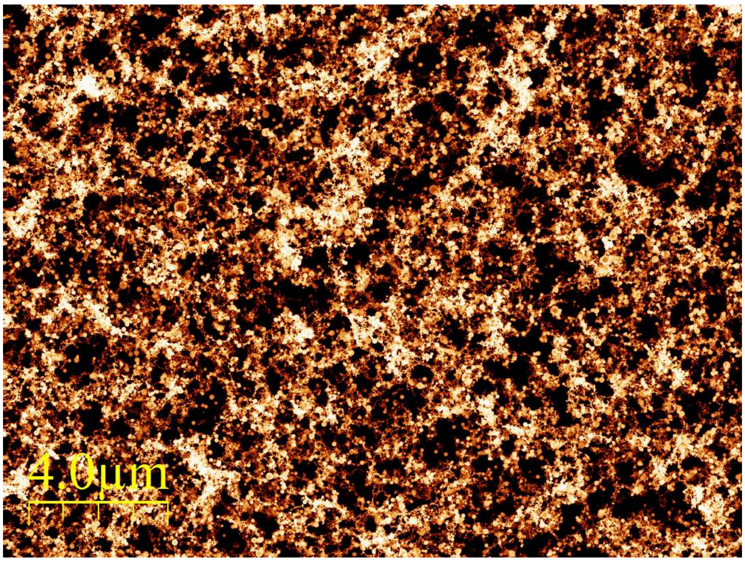


Reduction of TiO_2

Total TiO_2 intensity decrease = 10 % @ 800

Stable structures

High coverage: extremely porous material



Conclusions

- Synthesis of TiO_2 fractal nanostructures at ambient pressure and RT by non thermal fs-PLD
- Fractals are composed by aggregates of nanoparticles (NP) (∅ < 20 nm). Larger NP have ∅ > 50 nm.
- Fractals and NP are crystalline: anatase (68%) or rutile (32%)
- Complexity and Fractal Area changes with LF and geometrical parameter
- Fractals and NP are TiO_2
- No oxygen vacancies at the surface
- It is possible to tune the size and complexity of nanostructures synthesized by fs-PLD

Next

- Different ablated material: Au
- Different substrates: HOPG, Quartz
- Role of substrate and pressure in fractal formation

Acknowledgments

- Emanuele Cavaliere
- Gabriele Ferrini

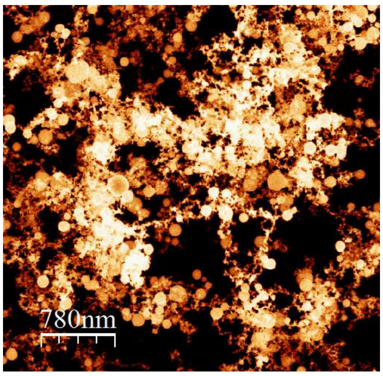
- Pasqualantonio Pingue

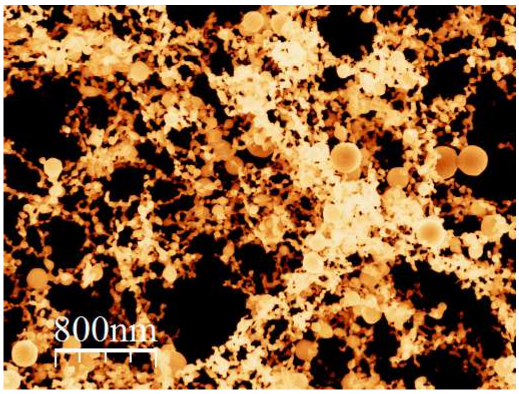
- Gian Andrea Rizzi
- Gaetano Granozzi

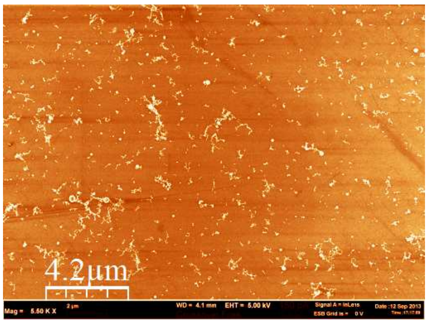
fondazione cariplo

Controlled nanostructures by low-cost non-thermal laser ablation on metals at atmospheric pressure

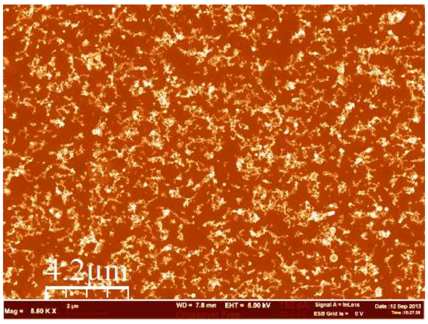
High coverage



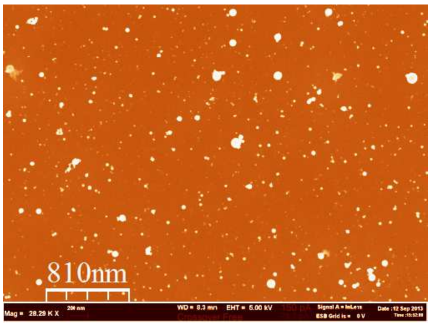




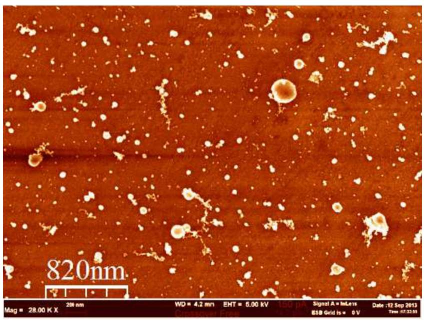
Ti/Quartz



Ti/HOPG



Au/Si

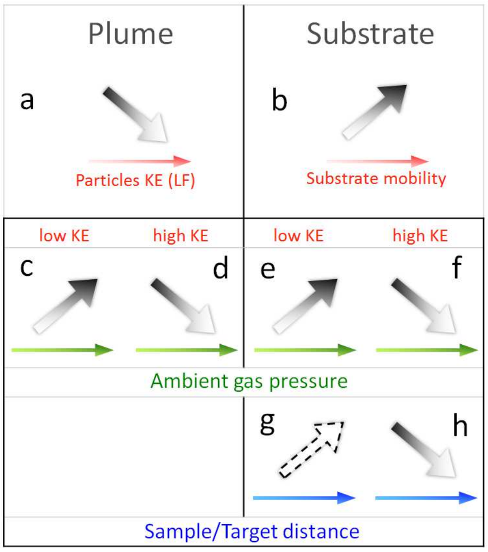


Au/Quartz

General Trends

NP aggregation processes

NP aggregation processes



Project status

O1: Development of innovative LA deposition procedures	Status on Ti	To do	In progress
1a) Production of supported NanoStructures	Photon incidence angle, fluence, number of pulses	Pressure, precision in position, Graphite, quartz Start with Au	Manipulator and chamber design
NP controlled dimensions, size distribution and eventually ordering on the surface	Fractals in plume center NP on sides Size depends on fluence	Ordering	
NTF nanometer-thick films extending over macroscopic areas with roughness at the atomic scale	not yet obtained	Find the parameters to obtain NTF	It should depend on pressure and fluence

Project status

O2: Characterization of the physical properties (morphology, chemical composition, catalytic activity) and study of the formation mechanism of the deposited nanostructured systems	Status on Ti	To do	In progress
NP controlled dimensions, size distribution and eventually ordering on the surface	Fractals in plume center NP on sides Size depends on fluence	Ordering	
Stability for different substrates	Silicon only	Deposit on graphite, quartz	
physical behavior of the grown nanostructures, their stability and interaction with the substrate (silicon, graphite, and quartz		measurement of the catalytic and photocatalytic activity trough Thermal Programmed Desorption (TPD), Thermal Programmed Reaction (TPR) and novel photoreductive process which uses hydroxyethyl (HEC), glycerol and the redox dye resazurin	