Roma, September 21st -25th , 2015

Ablazione laser con impulsi ultracorti: dal "direct surface processing" alla deposizione di film nanostrutturati

Laser Ablation with ultrashort pulses: from "direct surface processing" to deposition of nanostructured film

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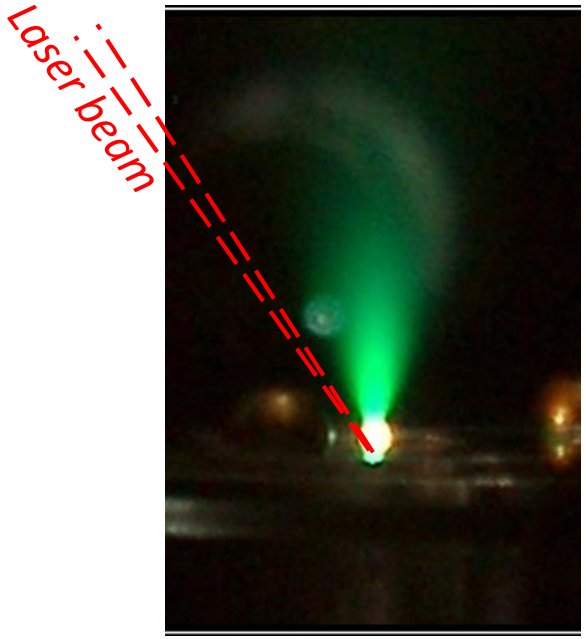
Laser Ablation with ultrashort pulses: from “direct surface processing” to deposition of nanostructured film

Outline

- ✓ Background and Motivations
- ✓ Overview of the basic mechanisms
- ✓ Generation of NPs and main features
- ✓ Deposition of NPs-assembled films
- ✓ Direct fs laser surface structuring
- ✓Summary & Acknowledgements



BACKGROUND AND MOTIVATIONS

Laser ablation with ultrashort pulses

fs laser pulses on a metal/semiconductor

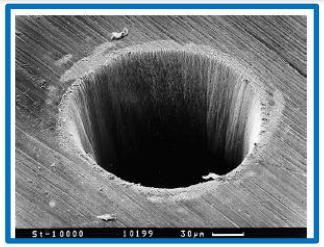
non-equilibrium state of matter and subsequent relaxation

① Quenching of peculiar states of surface
[*direct laser surface processing*]

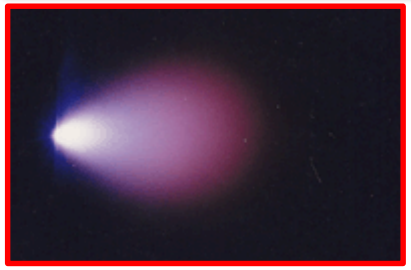
② Transient hot plasma
[*ions, atoms and nanoparticles (main part)*]

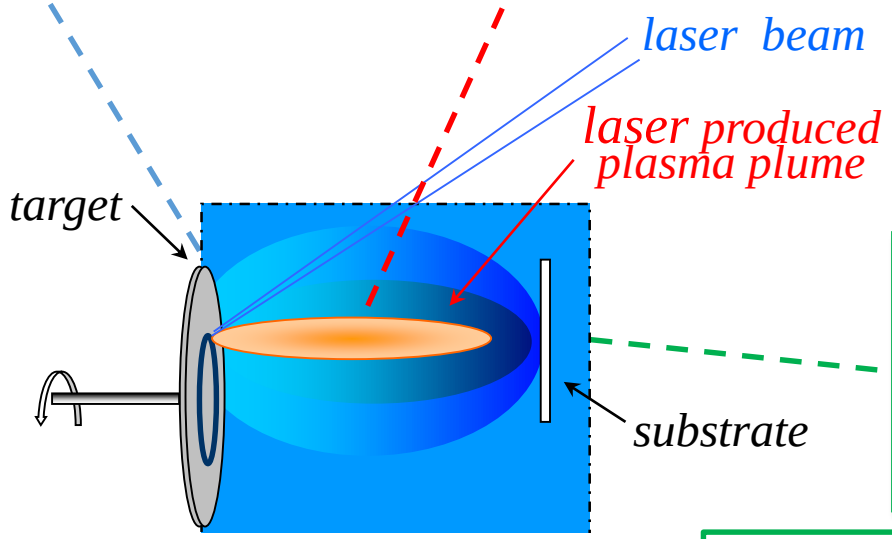
③ Collection of nanoparticles on substrates
[*fabrication of nanoparticle-assembled films*]

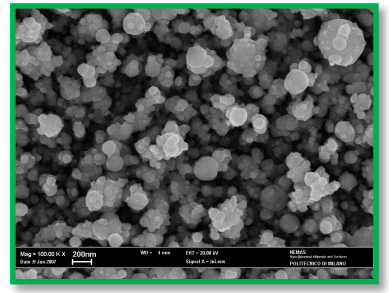
① *Surface processing*



② *Transient Plasma*





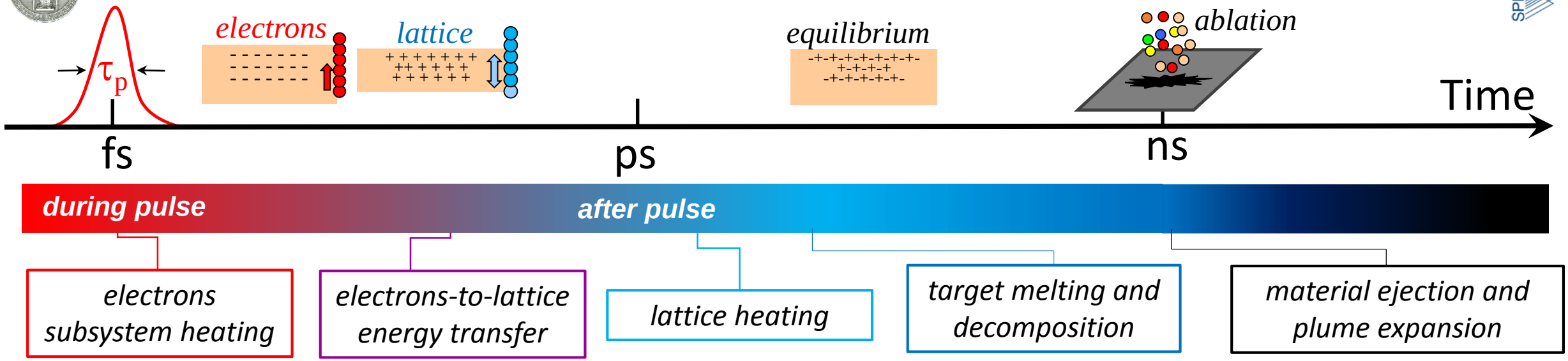


③ *NPs & NPs-assembled films*

Other fields of application

- *LIBS for material analysis*
- *Ion beam generation*
- *EUV light generation*
- *μ-thruster for satellites*
- *3D structuring (dielectrics)*
- *Templates for cell growth*
- . . . . . .
- . . . . . .

OVERVIEW OF THE BASIC MECHANISMS



. . . at later time

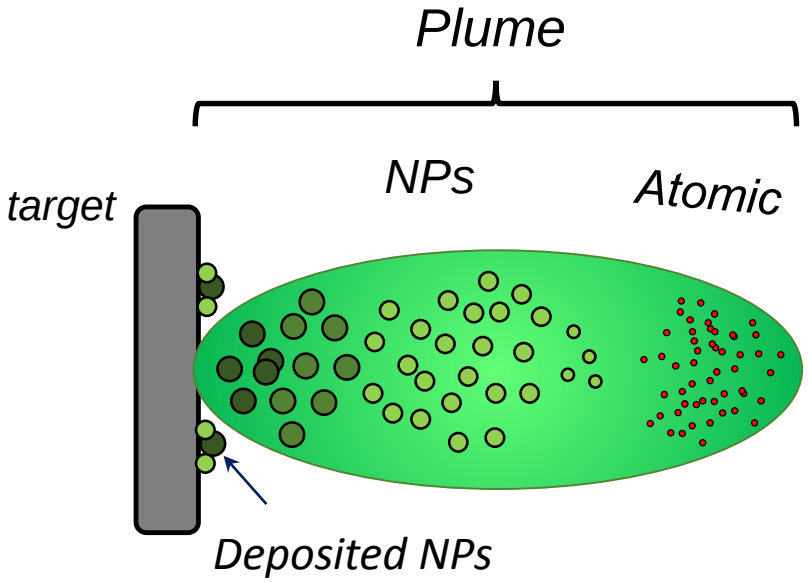
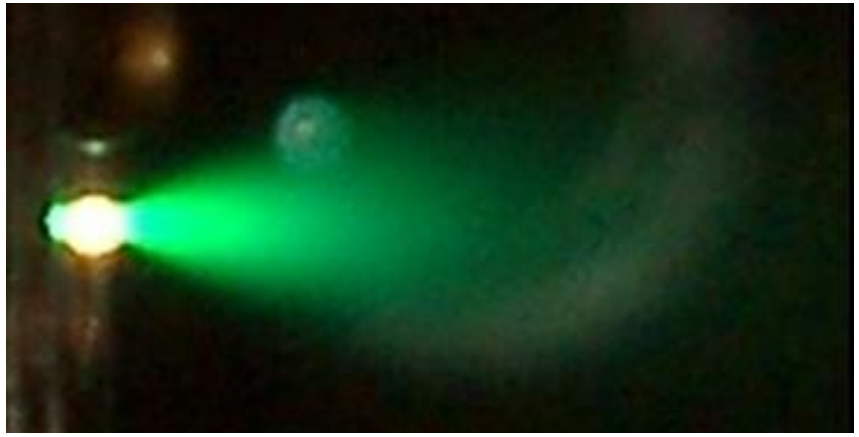
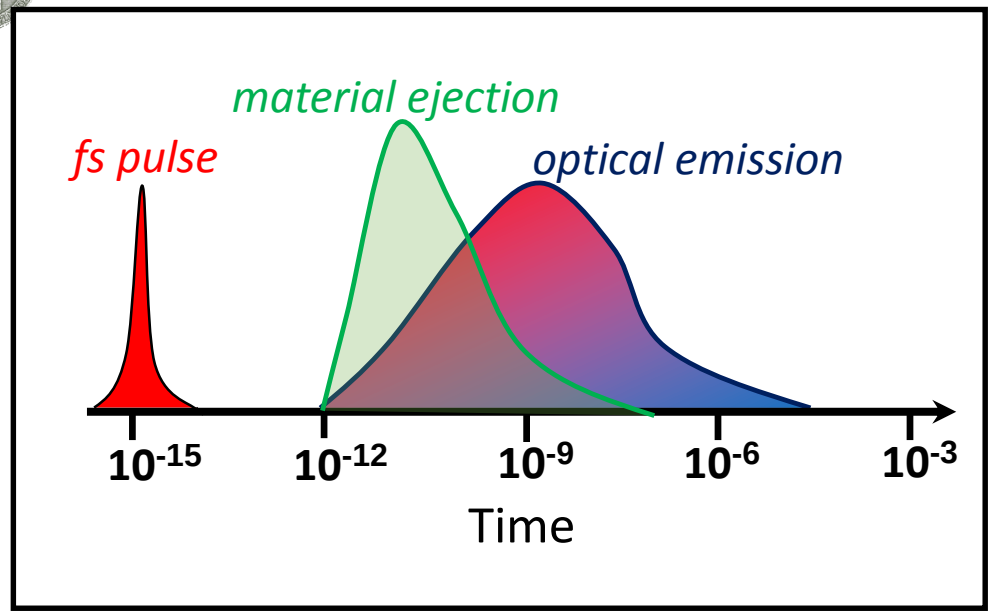
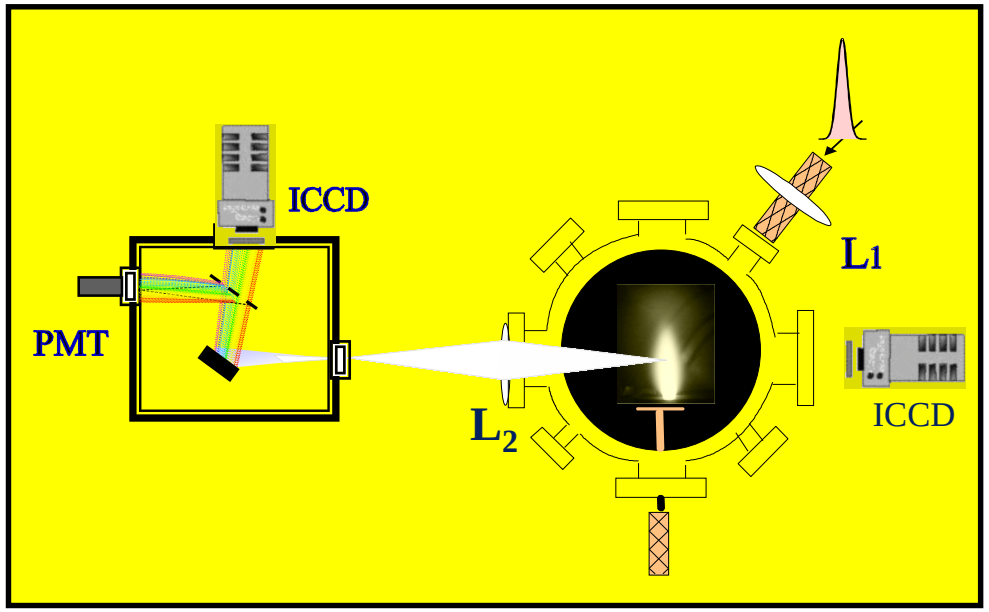


Photo of a silver fs ablation plume



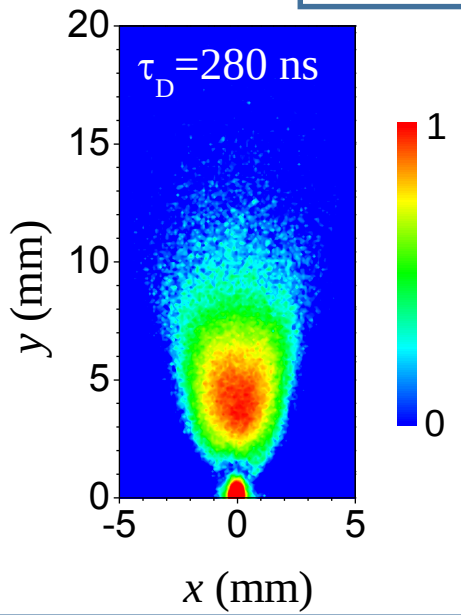
The plume of ablated material

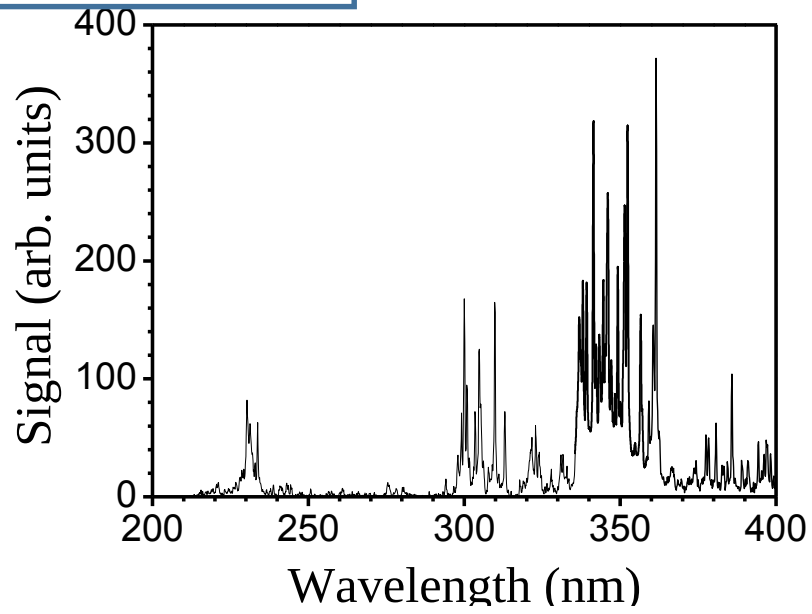




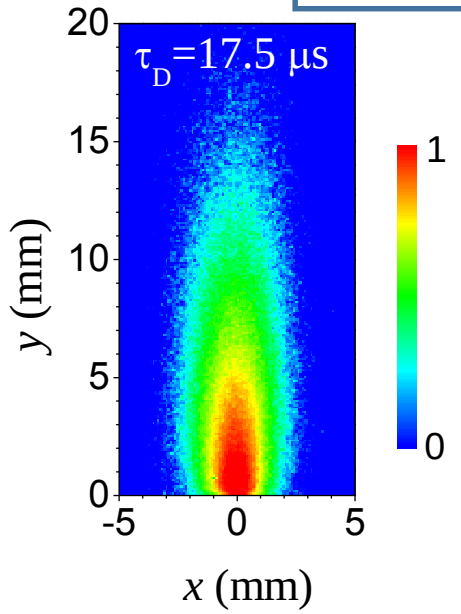
Amoruso et al., J. Appl. Phys. **84**, 4502 (2004)

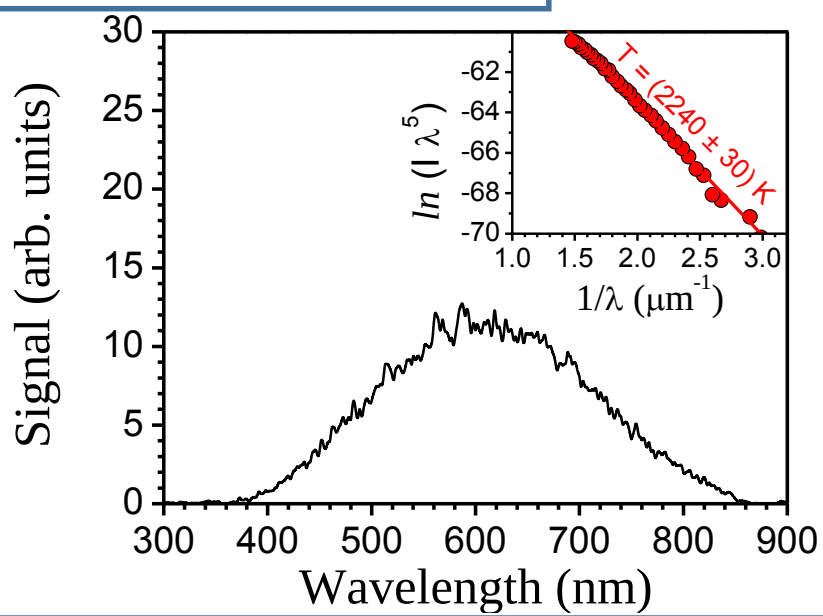
Atomic plume emission





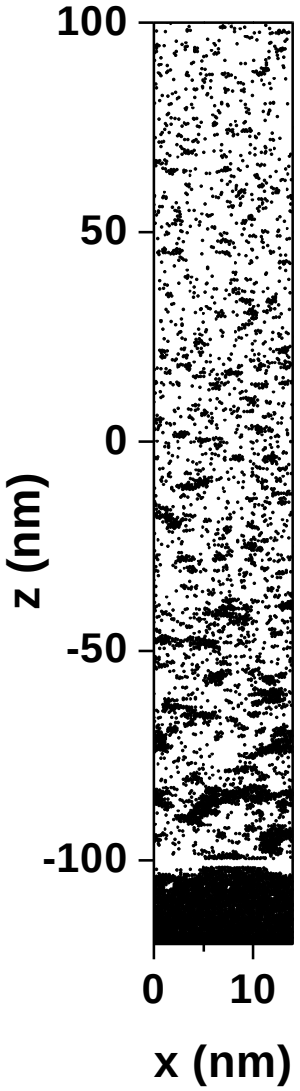
Nanoparticles plume emission



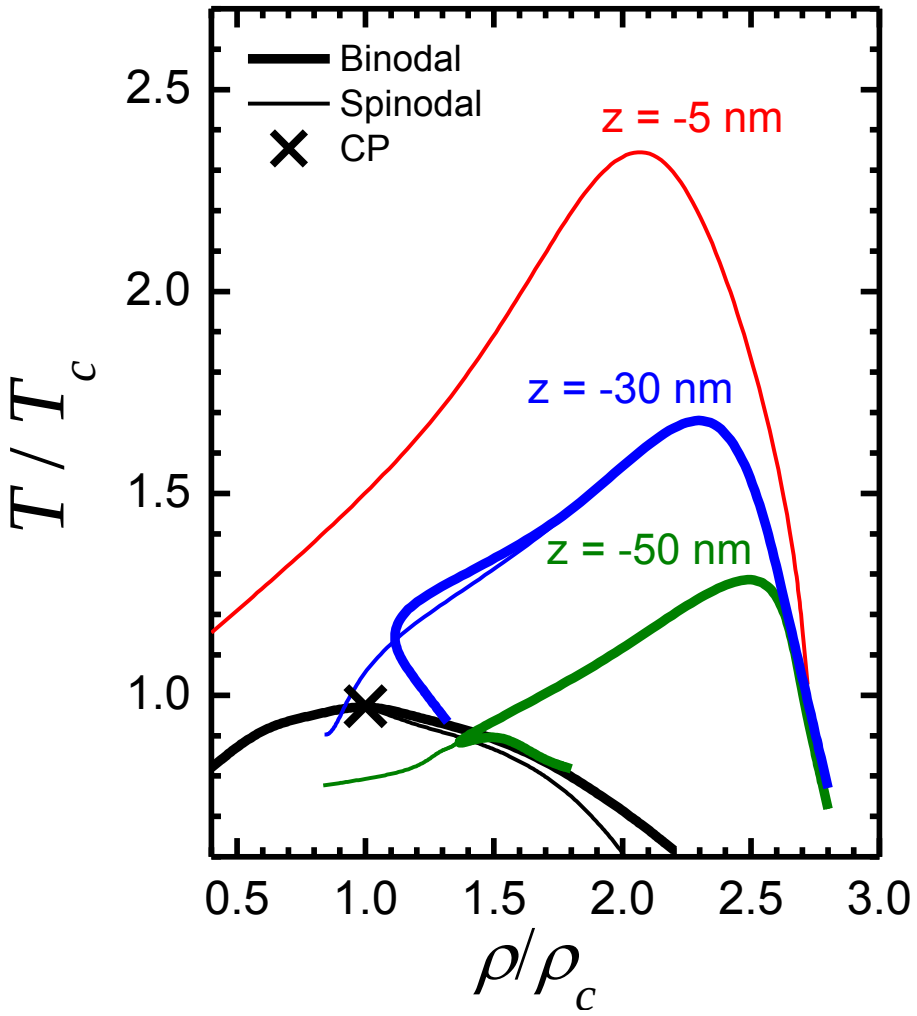


Material decomposition – MD-TTM simulations

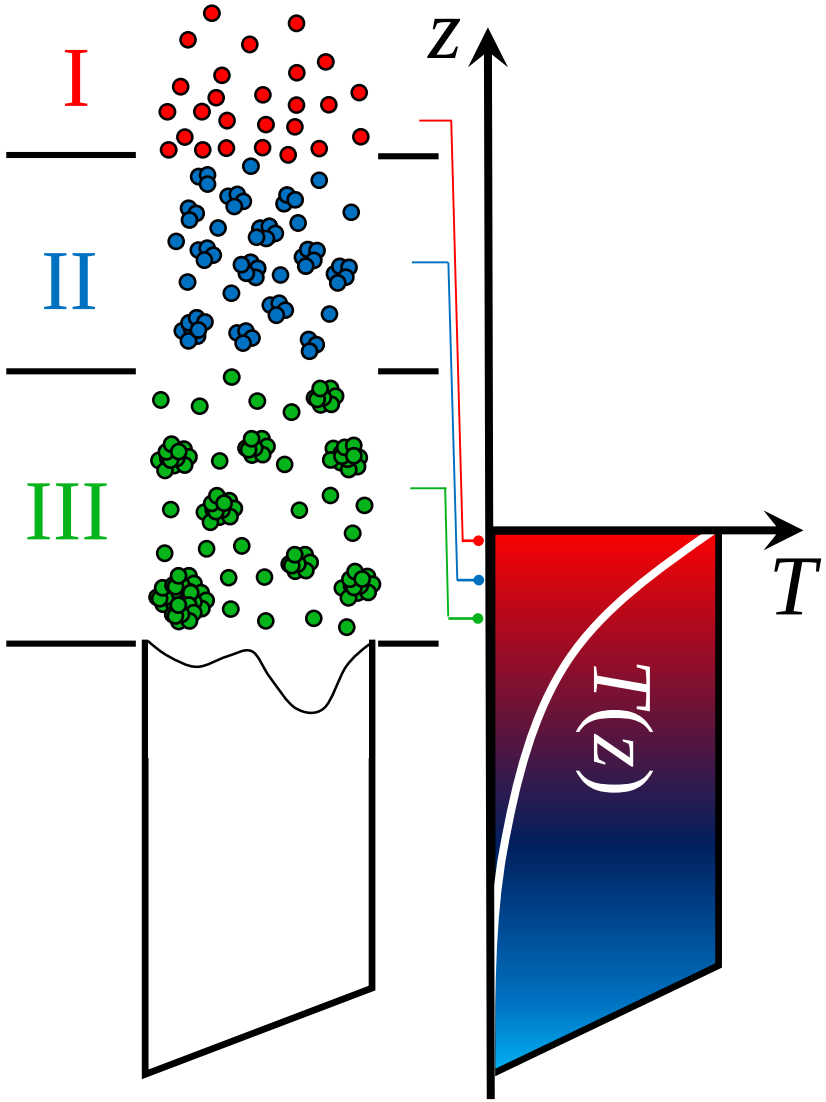
Amoruso et al., J. Phys. D **40**, 331 (2007)



MD snapshot



Trajectory in phase diagram



Sketch of the process

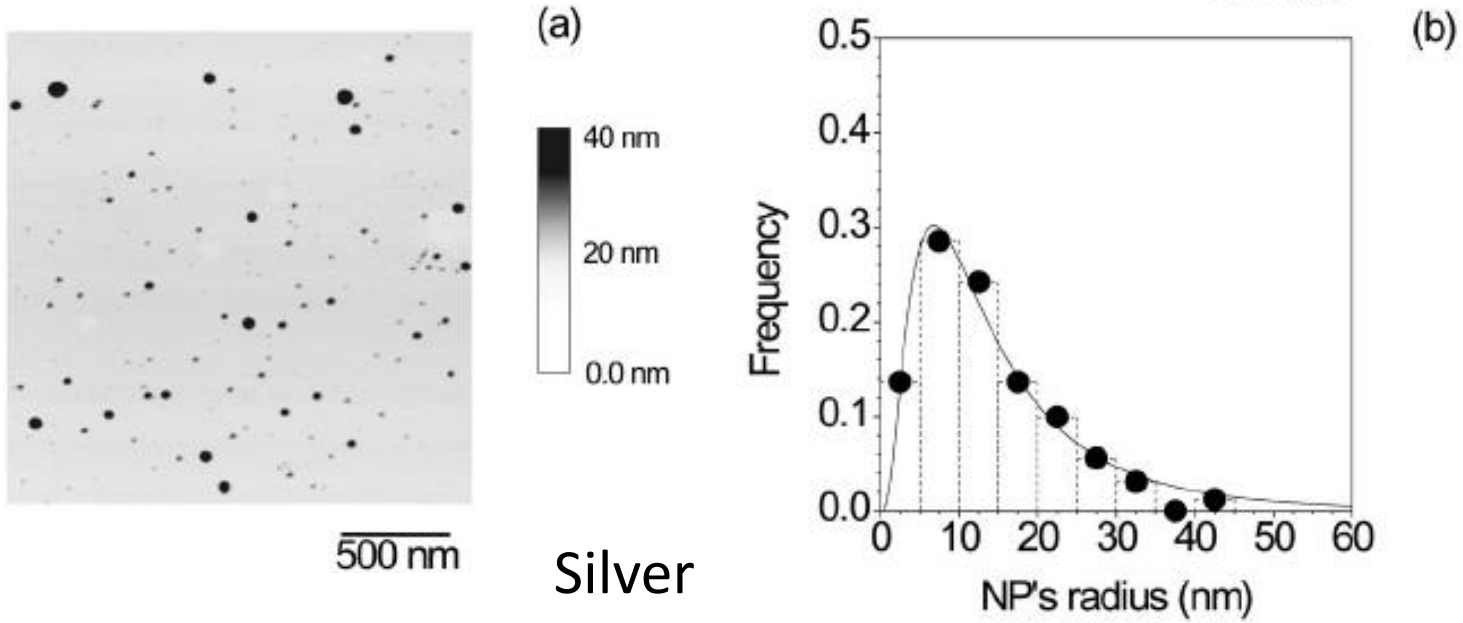
GENERATION OF NPS AND MAIN FEATURES

NPs of any material (metal, semiconductor, elemental/multicomponent)

PHYSICAL REVIEW B **71**, 033406 (2005)

Femtosecond laser pulse irradiation of solid targets as a general route to nanoparticle formation in a vacuum

S. Amoruso, G. Ausanio, R. Bruzzese, M. Vitiello, and X. Wang
Coherentia - INFM and Dipartimento di Scienze Fisiche, Univerità di Napoli Federico II, Complesso Universitario di Monte S. Angelo, Via Cintia, I-80126 Napoli (Italy)
(Received 29 June 2004; published 21 January 2005)



(a) AFM image of a dispersed Ag NPs; (b) Size distribution of Ag NPs in-plane radius.

List of materials

Al, Ag, Au, Cu, Pd,…
Ni, Co, Fe, Mn, …

—

Si, Ge, …

—

NiFe, CoCu, SmCo, AlN, …

—

CdS, ZnS, TiO_2, ZnO, VO_2,…

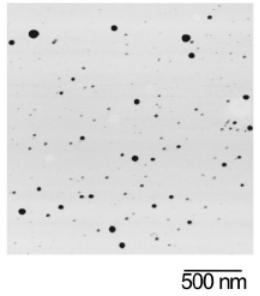
—

LSMO, TbDyFe, …

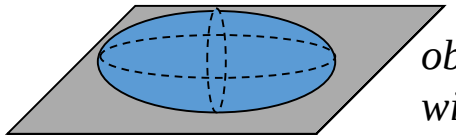
—

!? What is next ?!

NPs shape and size properties



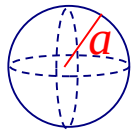
NP shape at AFM



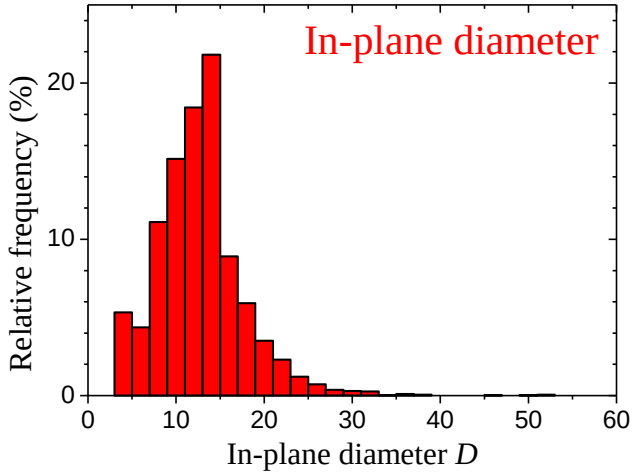
oblate ellipsoid with volume V

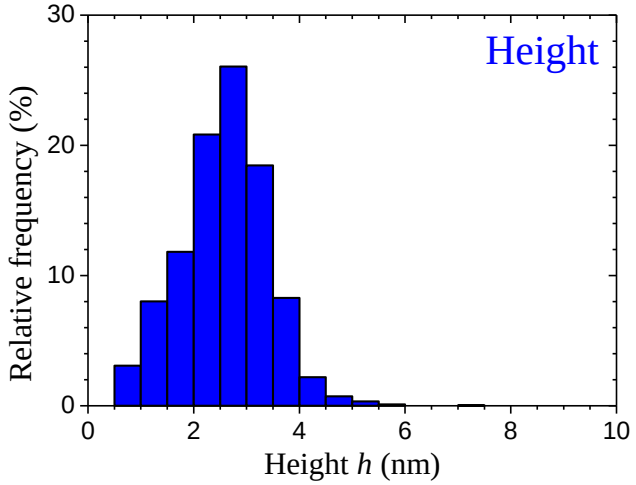
substrate

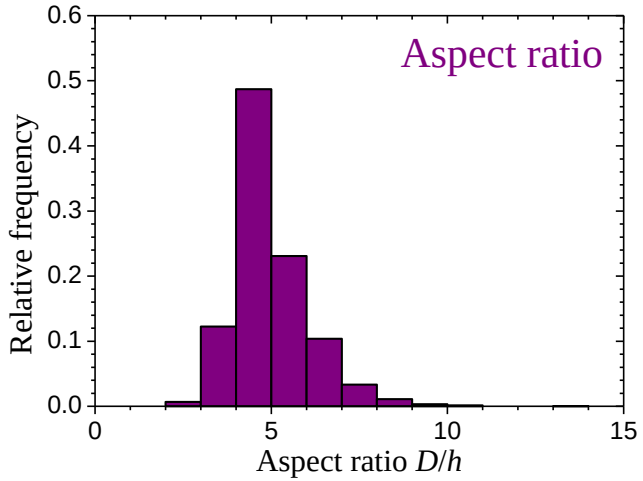
Equivalent sphere

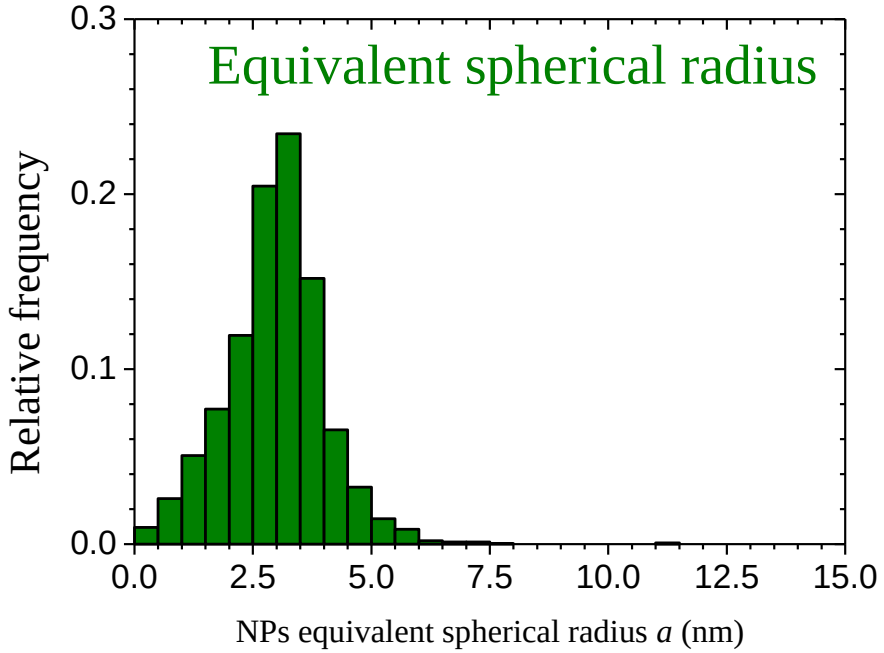


$$a = \sqrt[3]{\frac{3V}{4\pi}}$$







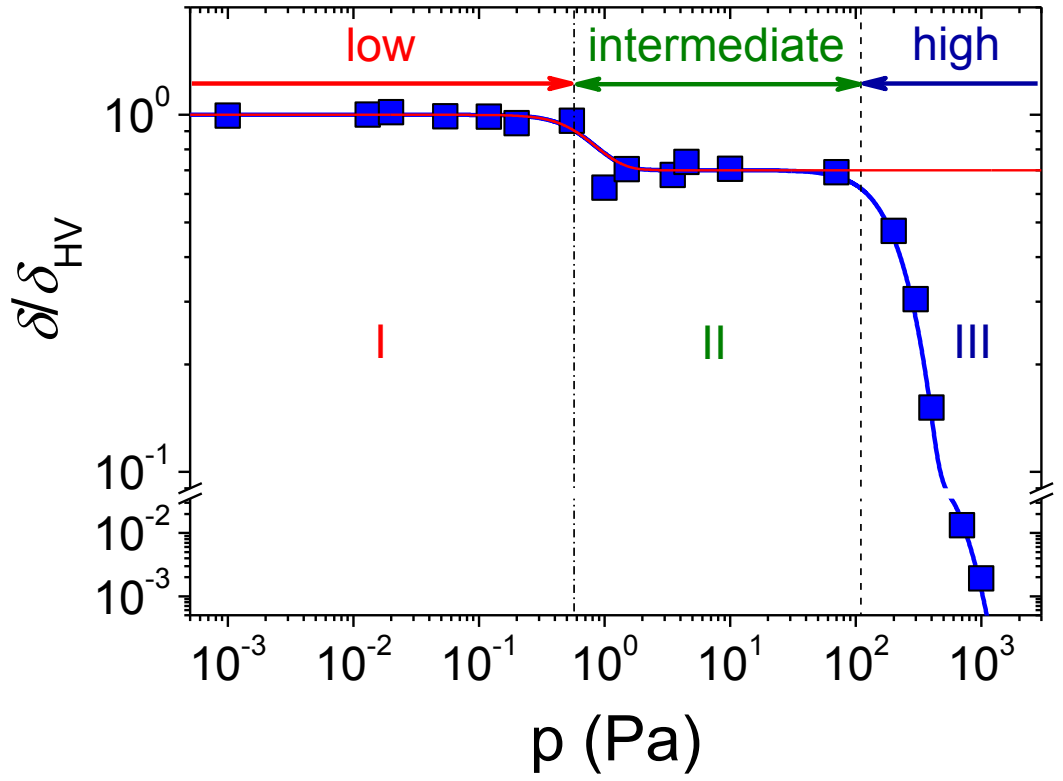


✓ NPs size and size distribution depend slightly on laser fluence

✓ NPs constitute the main part of the ablated material (70-90 %)

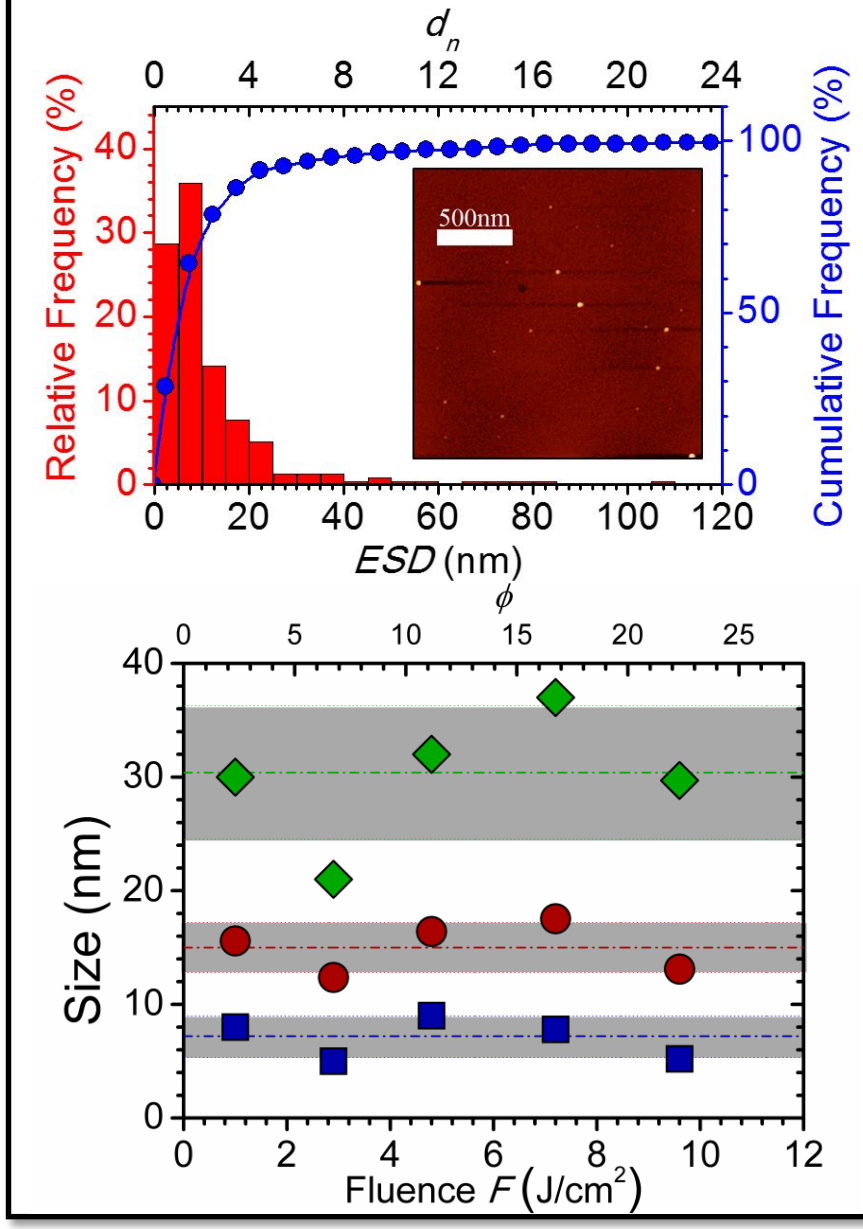
Example: deposition rate vs p

TiO_2 in O_2 background gas



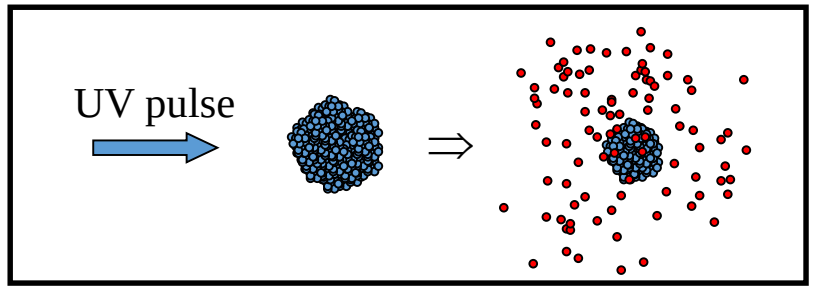
Tsakiris et al., J. Appl. Phys. 115, 243301 (2014)

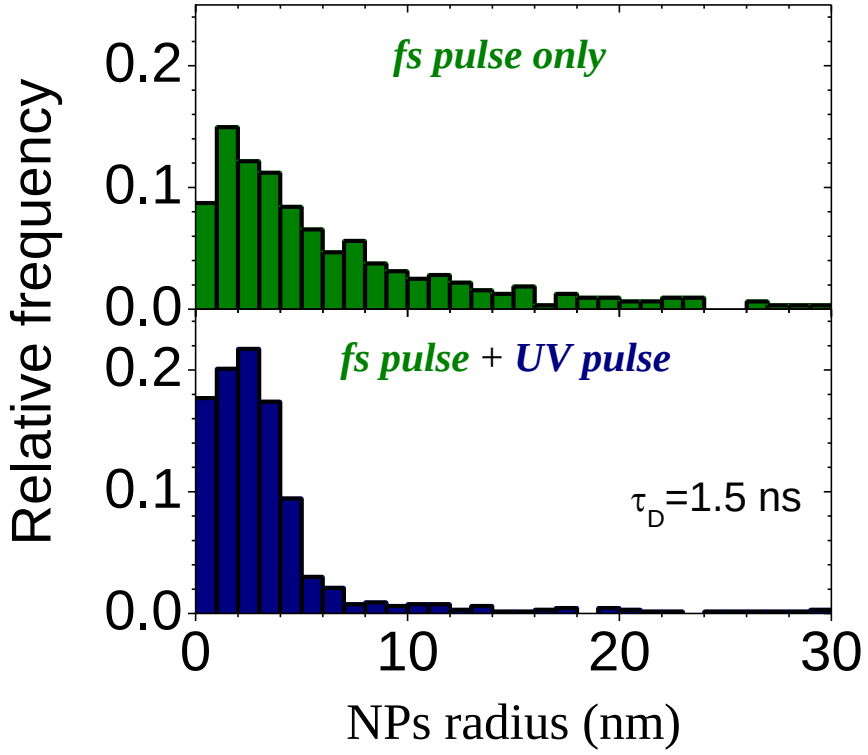
Example: Cu NPs size dependence on F



Possible strategies to control NPs size

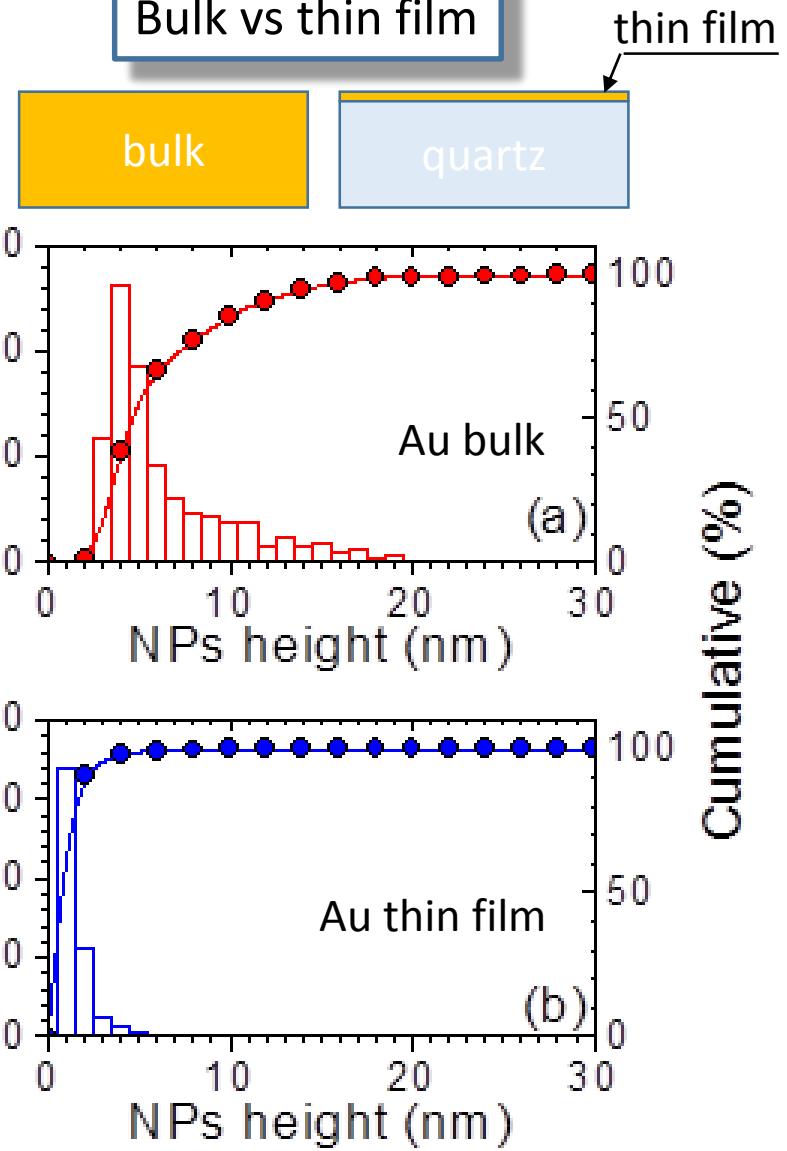
UV laser vaporization





Amoruso et al., J. Phys. B. 4**0**, 1253 (2007)

Bulk vs thin film

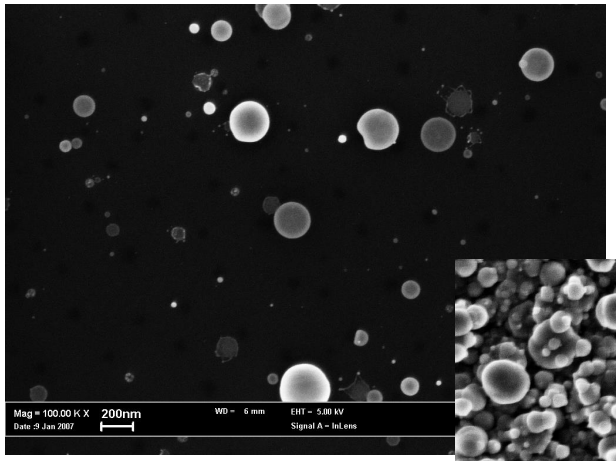


Amoruso et al., J. Appl. Phys. 11**0**, 124303 (2011)

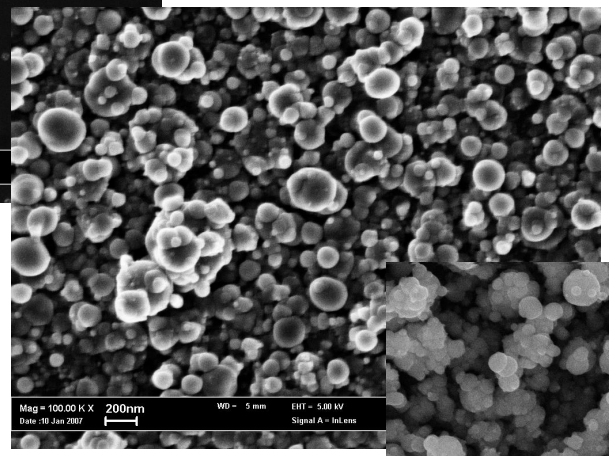
DEPOSITION OF NPS-ASSEMBLED FILMS

SEM images

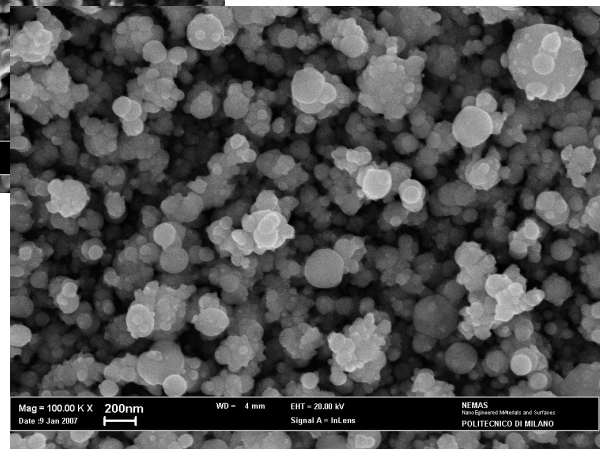
few laser shots



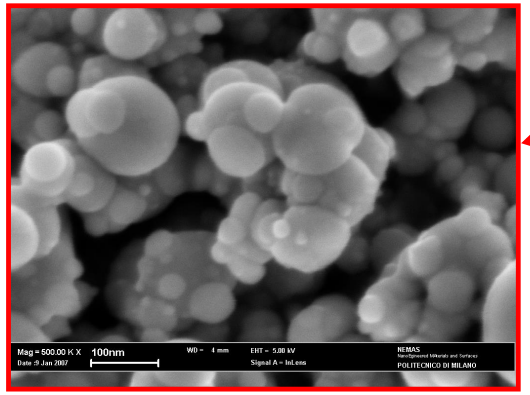
several laser shots

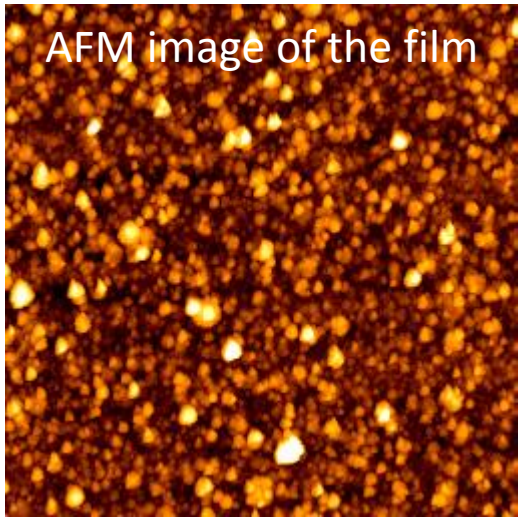


many laser shots (~10^5)



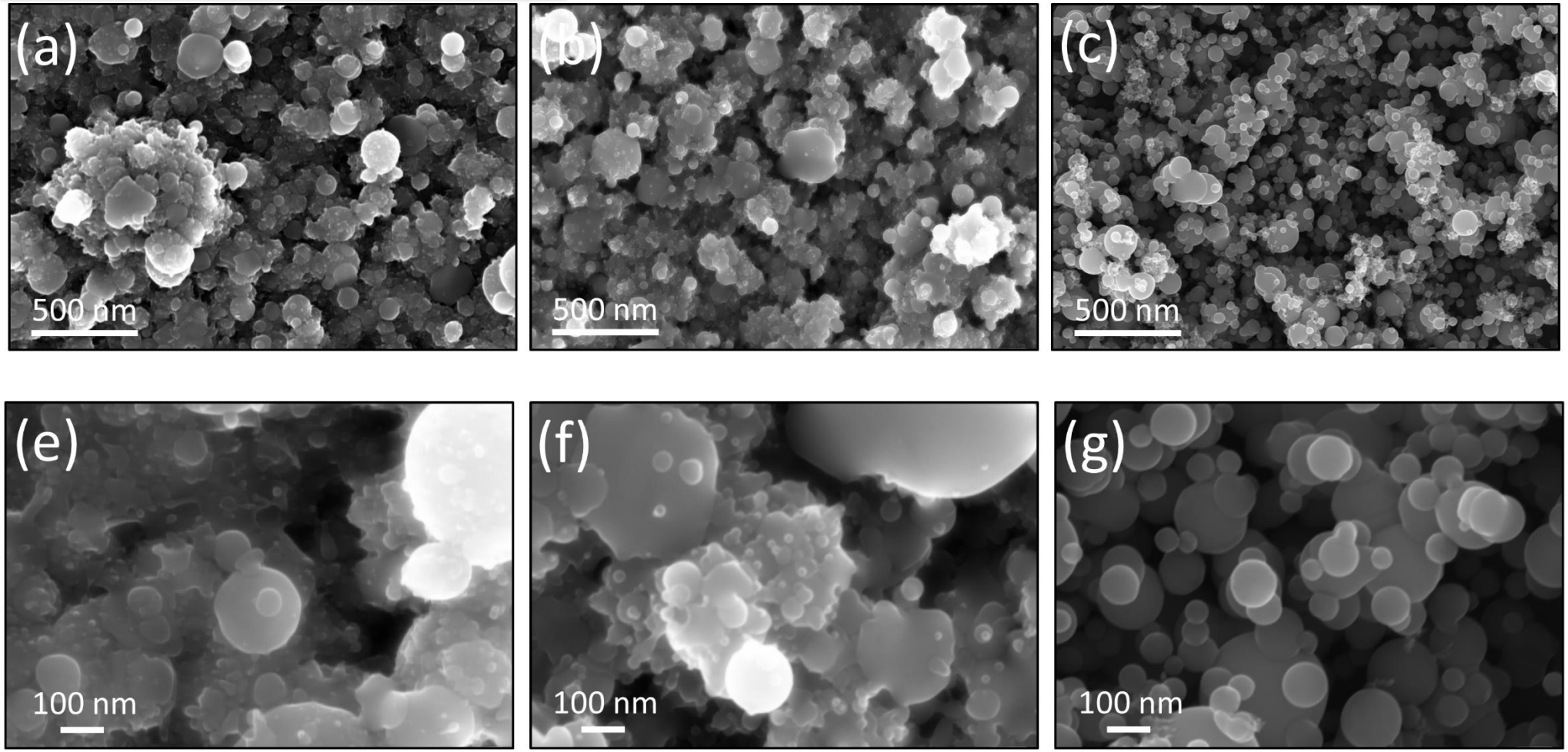
zoomed image





Background pressure can allow controlling the NPs-assembled film morphology

Example: TiO_2 in O_2 background gas



I - low pressure *II - intermediate pressure* *III - high pressure*

Amoruso et al., Appl. Surf. Sci. **270**, 307 (2013)

We studied the generation of NPs and the deposition of NPs-assembled film of diverse material for a number of applications in collaboration with other groups

Domestic Collaborations

- G. Ausanio, V. Iannotti, L. Lanotte
  - ✓ *Magnetic NPs-assembled films*
- C. Altucci & R. Velotta,
  - ✓ *Decoration of QCM for biosensing*
- S. Lettieri & P. Maddalena
  - ✓ *PL and optical-based gas sensors*
- G. Rusciano, A. Sasso,
  - ✓ *NPs of noble metals for SERS/TERS*

International collaborations

- M. Castillejo & C.
  - ✓ ULA of semiconductors
- P. A. Atanasov, N. Nedyalkov
  - ✓ *MD simulations* ✓ *Thin films*
- J. G. Lunney
  - ✓ *Plasma and ions*
  - ✓ *DP ULA*
- Trinity College Dublin
- M. Hu & X. Ni
  - ✓ ULA of metal-oxides
- S. Canulescu & N. Pryds
  - ✓ ULA of metal-oxides
- Université de Montréal
- L. J. Lewis
  - ✓ *Ablation modeling*
  - ✓ *Comparison with experiments*

EXAMPLE #1 - *NPs-assembled films of magnetic materials*

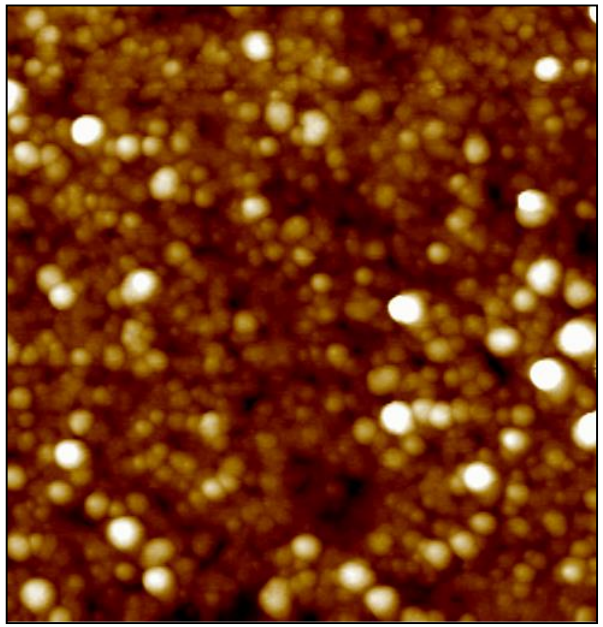
APPLIED PHYSICS LETTERS VOLUME 85, NUMBER 18 1 NOVEMBER 2004

Magnetic and morphological characteristics of nickel nanoparticles films produced by femtosecond laser ablation

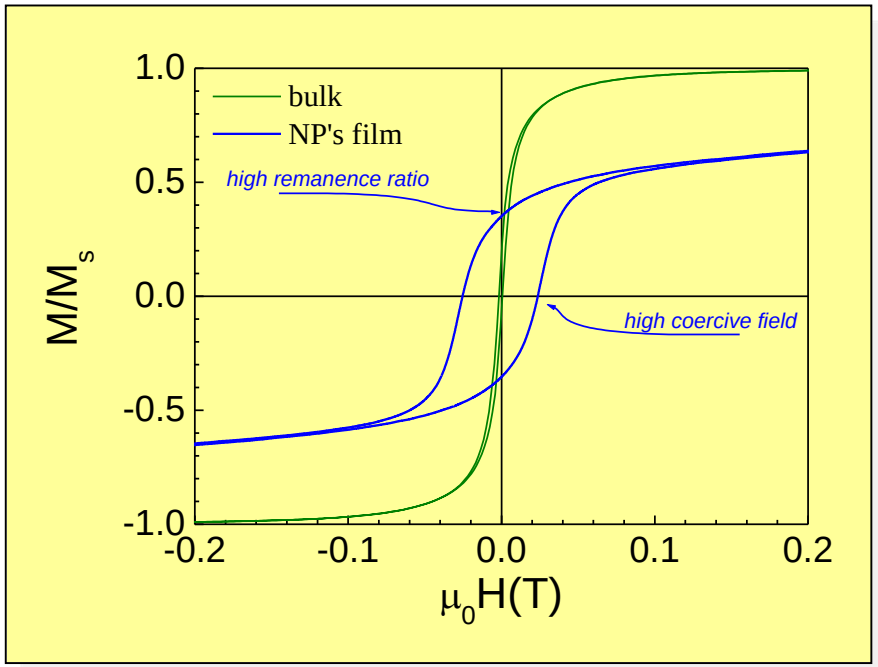
G. Ausanio, A. C. Barone, V. Iannotti, and L. Lanotte[a)]
Coherentia—INFM and Dipartimento di Scienze Fisiche, Università degli Studi di Napoli, Piazzale Tecchio 80, I-80125 Napoli, Italy

S. Amoruso, R. Bruzzese, and M. Vitiello
Coherentia—INFM and Dipartimento di Scienze Fisiche, Università degli Studi di Napoli, Complesso Universitario di Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy

NPs as building blocks of magnetic system with a peculiar response



AFM image of a nickel NPs-assembled film.



Hysteresis loop of a Nickel NPs-assembled film

EXAMPLE #2 - II-VI direct semicondutors (CdS, ZnS)

THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

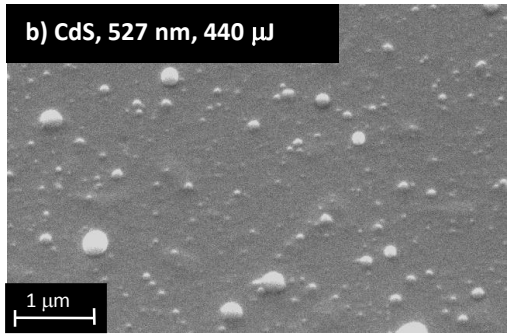
pubs.acs.org/JPCC

Ultrafast Laser Ablation and Deposition of Wide Band Gap Semiconductors

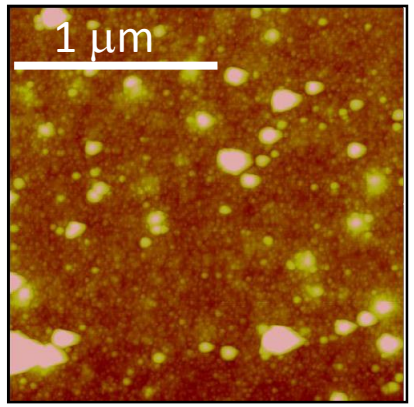
Mikel Sanz,[†] Marien López-Arias,[†,‡] José F. Marco,[†] Rebeca de Nalda,[†] Salvatore Amoruso,[§,∥] Giovanni Ausanio,[§,∥] Stefano Lettieri,[∥] Riccardo Bruzzese,[§,∥] Xuan Wang,[∥] and Marta Castillejo*[,†]

Nanostructures of II-VI semiconductor materials

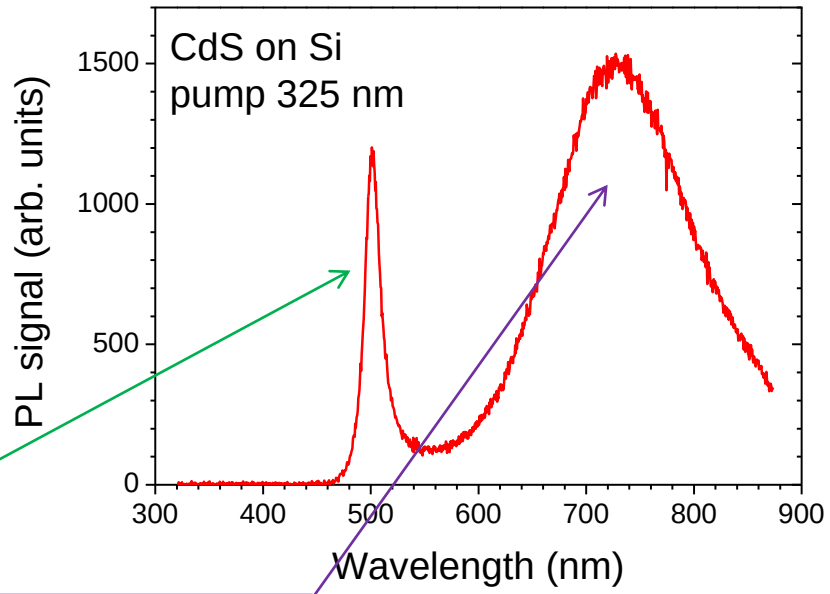
SEM



AFM



Photoluminescence



Decay of photogenerated charge carriers by radiative recombination at the band edge.

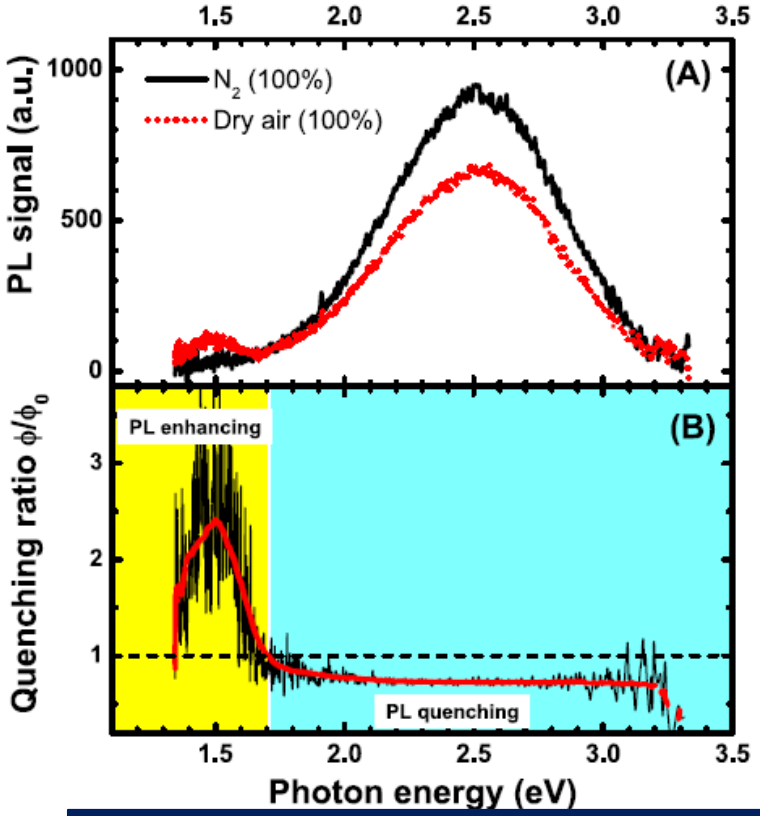
Decay from trap states localized at the surface crystalline defect sites and having energy levels within the forbidden band gap.

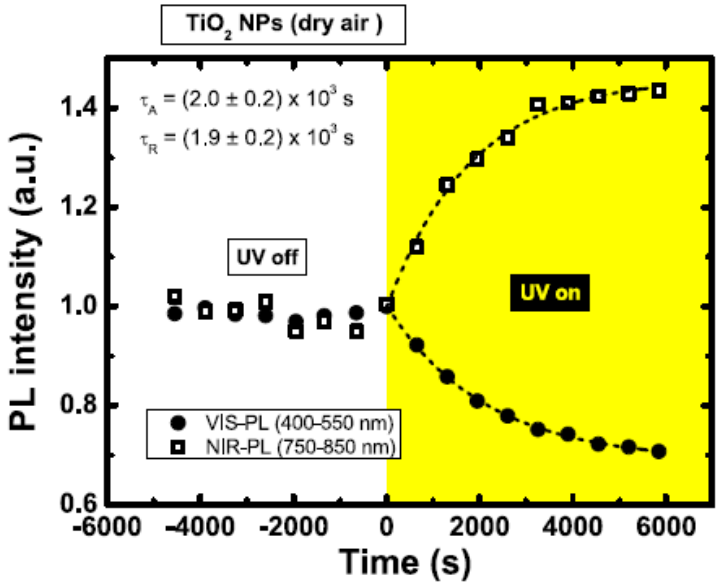
EXAMPLE #3 – *Metal-oxide semicondutors (TiO_2)*

APPLIED PHYSICS LETTERS **105**, 031903 (2014)

Modulation of mixed-phase titania photoluminescence by oxygen adsorption

D. Pallotti,[1,2] E. Orabona,[1,2] S. Amoruso,[1,2] P. Maddalena,[1,2] and S. Lettieri[2,a)]





NPs-assembled metal-oxide semiconductors for PL-based gas sensors

The opposite response to a unique analyte (O_2) offers a valuable example of possible advantages of an optical approach to chemical sensing and appears to be a promising first step towards PL-based sensing with titania.

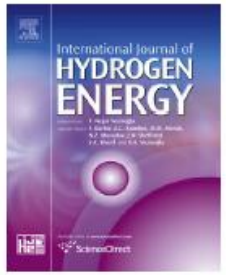
VIS and NIR PL bands of TiO2 NPs-assembled films show an opposite response to oxygen adsorption

EXAMPLE #4 – Metal-oxide semicondutors (TiO_2) on Ti foil

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 779–785

Hydrogen-evolving photoanode of TiO_2 nanoparticles film deposited by a femtosecond laser

Lixia Sang [a,], Hongjie Zhang [a], Xiaochang Ni [b,c,**], K.K. Anoop [c], Rosalba Fittipaldi [d], Xuan Wang [b,c], Salvatore Amoruso [c]*



TiO_2 NPs film for hydrogen production from H_2O splitting

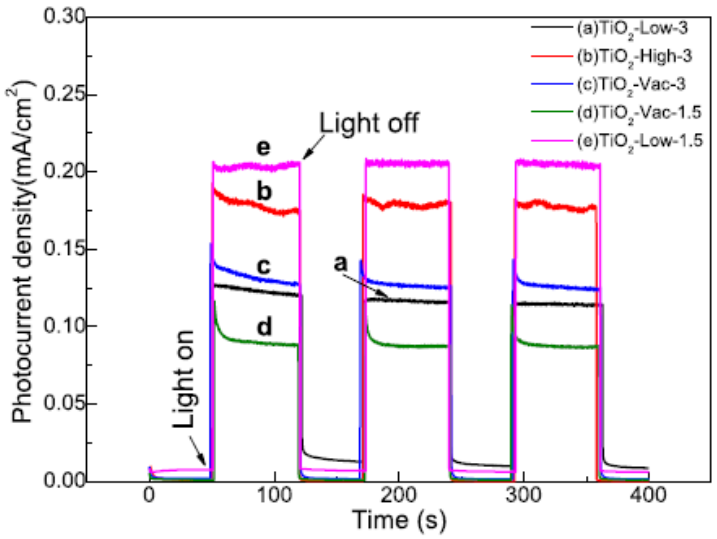


Fig. 4 – Potocurrent density–time curves (I-t) obtained from fs-PLD deposited TiO_2 NPs films in 1 M KOH at 0 V Ag/AgCl under interrupted illumination with a solar simulator (with AM 1.5 filter, 100 mW/cm²) (a:TiO_2-Low-3; b: TiO_2-High-3; c:TiO_2-Vac-3; d:TiO_2-Vac-1.5; e:TiO_2-Low-1.5).

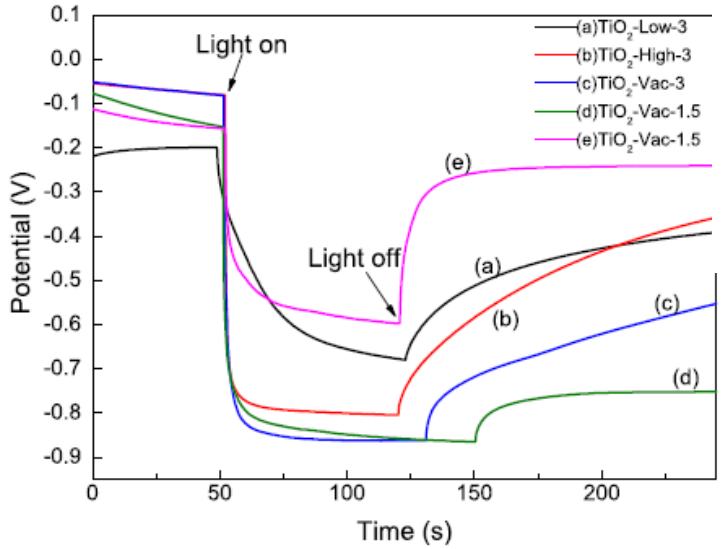


Fig. 5 – Open potential transient curves obtained from fs-PLD deposited TiO_2 NPs films in 1 M KOH at 0 V Ag/AgCl under interrupted illumination with a solar simulator (with AM 1.5 filter, 100 mW/cm²) (a:TiO_2-Low-3; b: TiO_2-High-3; c:TiO_2-Vac-3; d:TiO_2-Vac-1.5; e:TiO_2-Low-1.5).

Table 1 – The deposition conditions of TiO_2 NPs films produced by fs-PLD.

Samples	Chamber pressure (mbar)	Deposition time (h)	Area (cm^2)
TiO_2-Low-3	0.1	3	0.08
TiO_2-High-3	1	3	0.18
TiO_2-Vac-3	10^{-6}	3	0.12
TiO_2-Vac-1.5	10^{-6}	1.5	0.23
TiO_2-Low-1.5	0.1	1.5	0.23

The NPs-assembled films show comparatively higher photocurrent density even if their thicknesses is less than 400 nm.

EXAMPLE #5 – Gold NPs on QCM for biosensing

Biosensing based on a nanostructured quartz-crystal microbalance (QCM) device

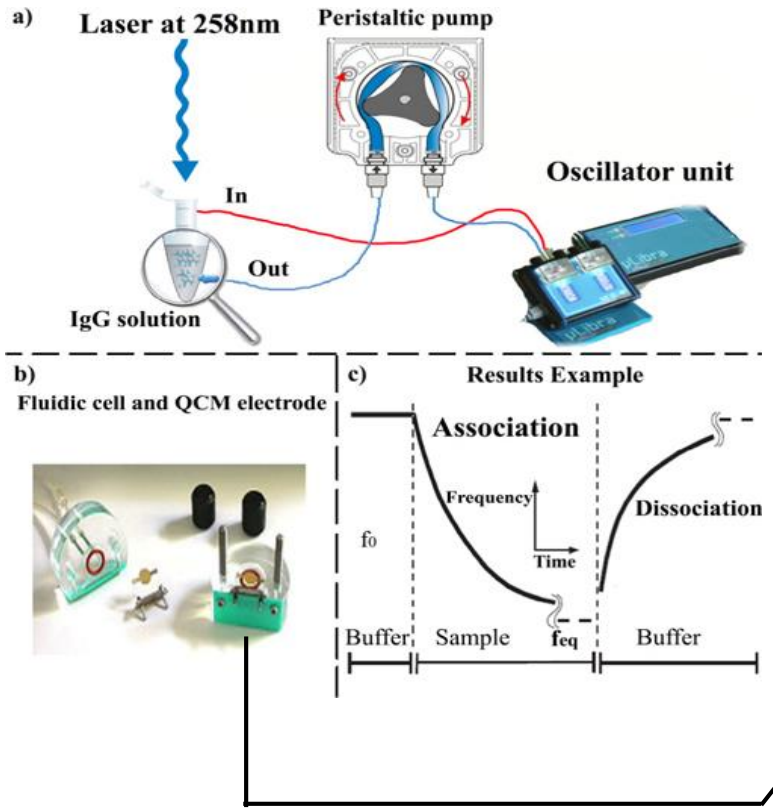
Appl. Phys. B (2015) 119:497–501
DOI 10.1007/s00340-015-6091-3

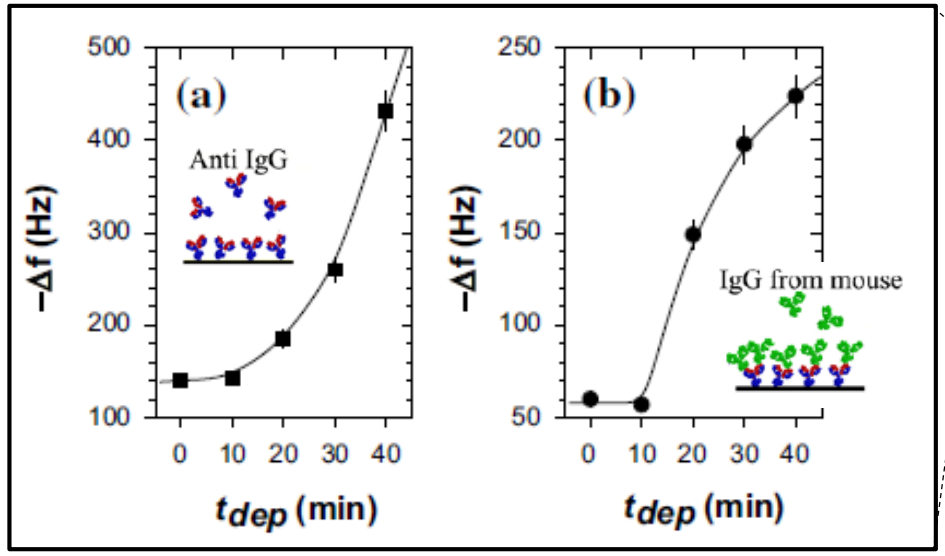
Applied Physics B
Lasers and Optics

Nano-machining of biosensor electrodes through gold nanoparticles deposition produced by femtosecond laser ablation

B. Della Ventura[1] · R. Funari[1] · K. K. Anoop[1,2] · S. Amoruso[1,2] · G. Ausanio[1,2] · F. Gesuele[1] · R. Velotta[1] · C. Altucci[1]

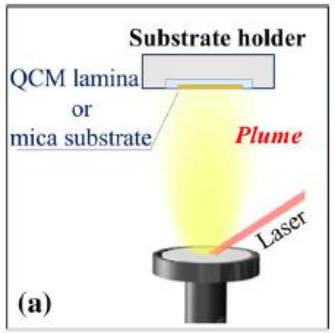
QCM experimental setup

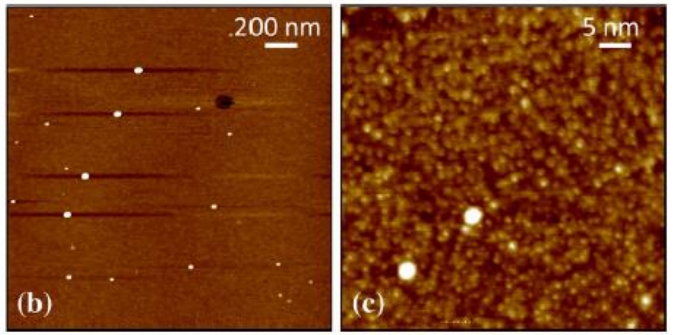


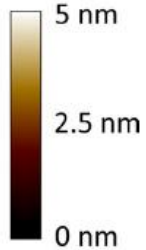


(a) functionalization with anti-IgG from goat
(b) recognition of the IgG antigen from mouse

<u>Proof of principle</u>
The NPs-assembled films on QCM surface allows increasing the sensitivity!







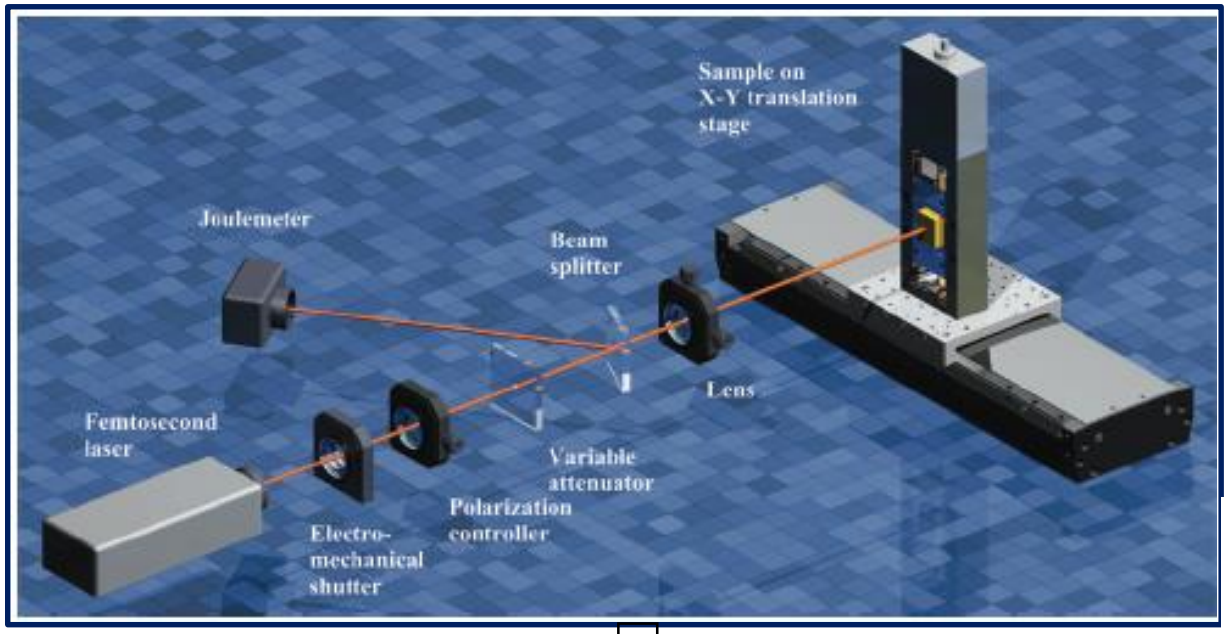
DIRECT FS LASER SURFACE STRUCTURING

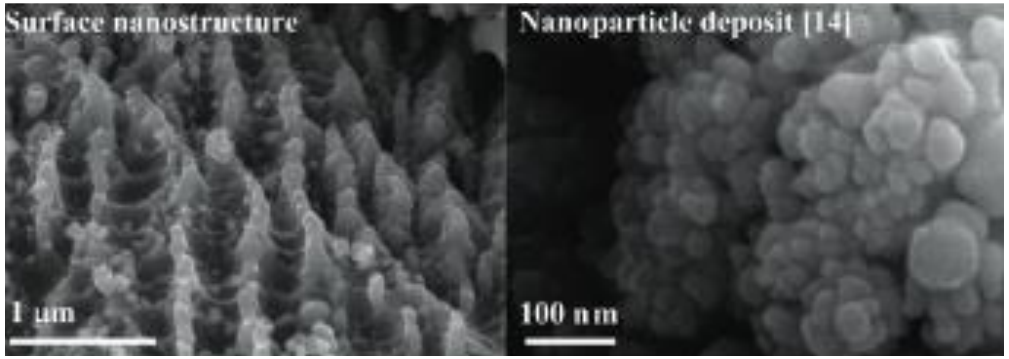
LASER & PHOTONICS REVIEWS

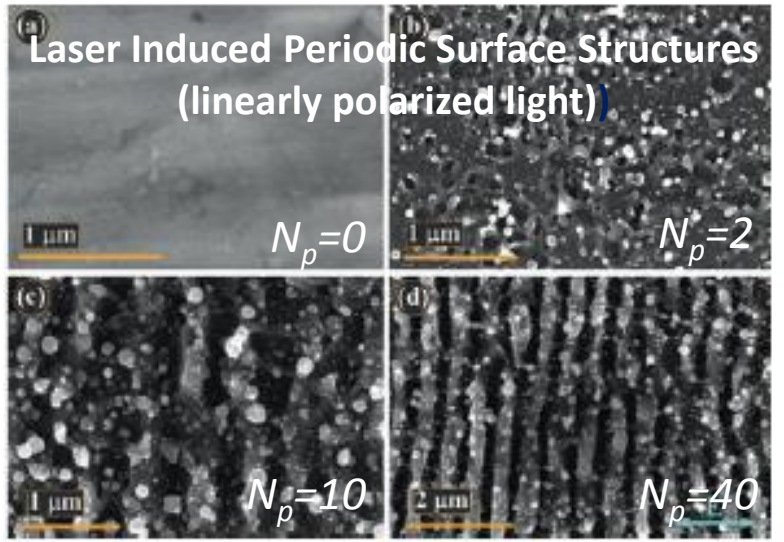
Direct femtosecond laser surface nano/microstructuring and its applications

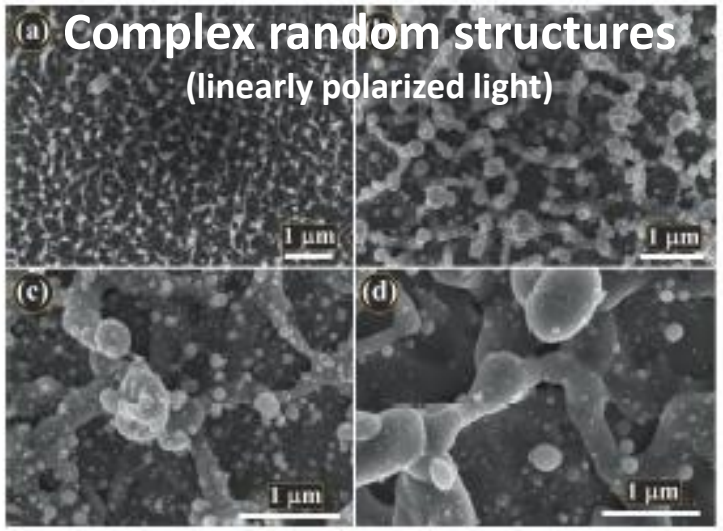
Laser Photonics Rev. 7, No. 3 , 385–407 (2013) / DOI 10.1002/lpor.201200017

Anatoliy Y. Vorobyev and Chunlei Guo*





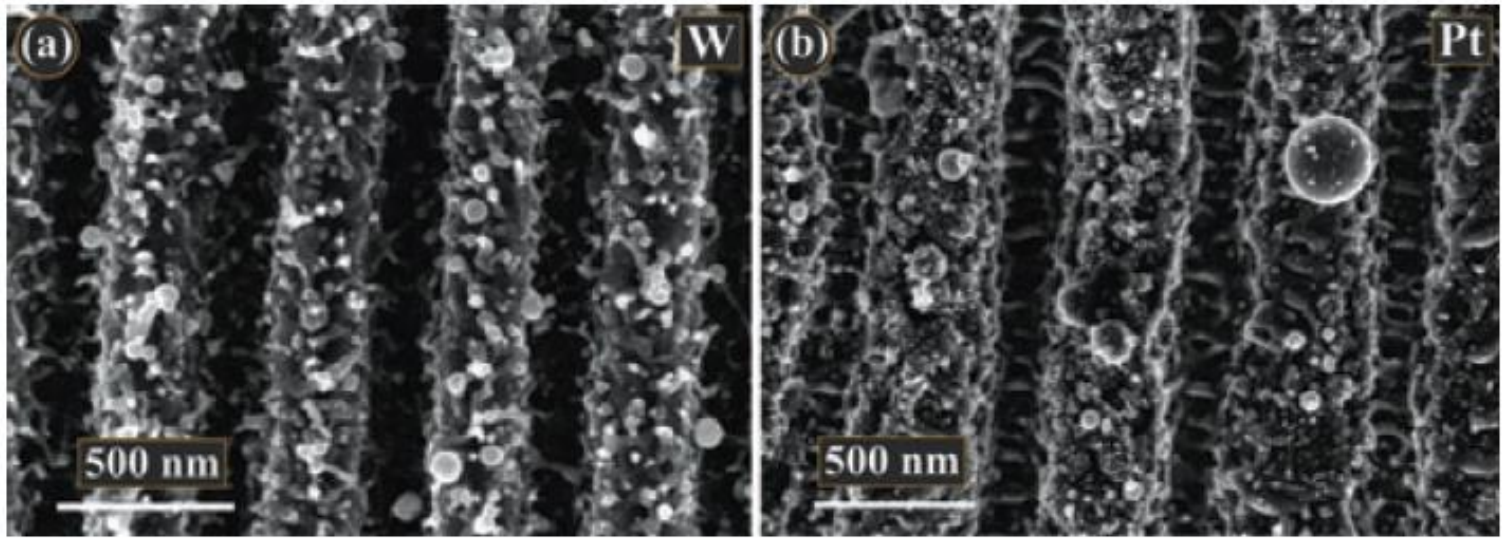




Examples of nano/micro structures

General features of fs LIPSS

- **hierarchical structures** are formed (micro & nano)
- The period and structure depend on the **number of laser shots**
- Gaussian beam: LIPSS at center or periphery depending on F_L



Ridges and valleys are extensively textured with nanostructures

Surface structures affect physical and chemical properties

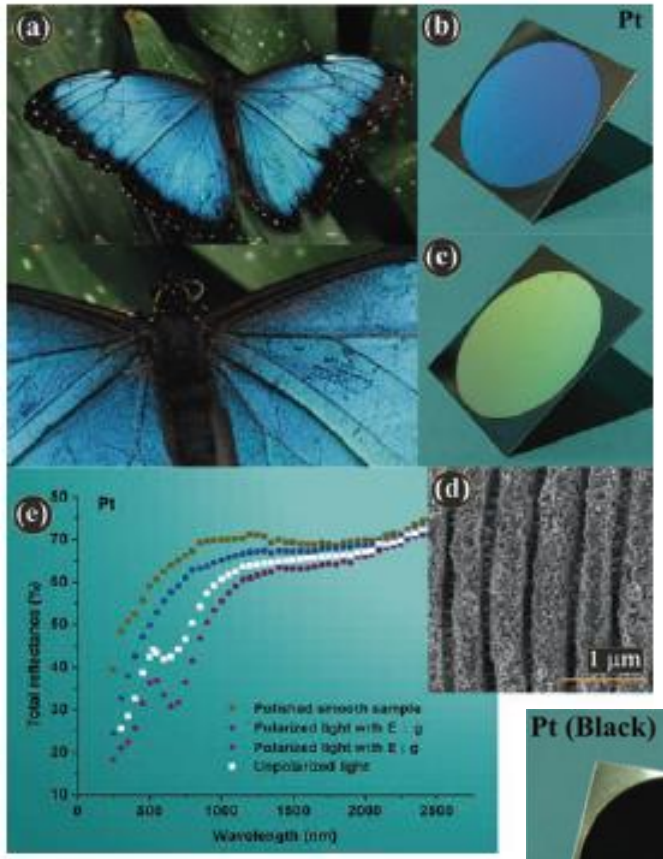
Surface functionalization

LASER & PHOTONICS REVIEWS

Some optical properties of the structured surfaces…

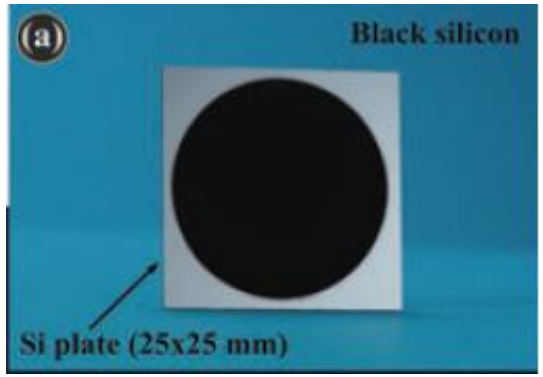
Colorizing or blackening of Metals

Morpho Butterfly wings like effect on Pt



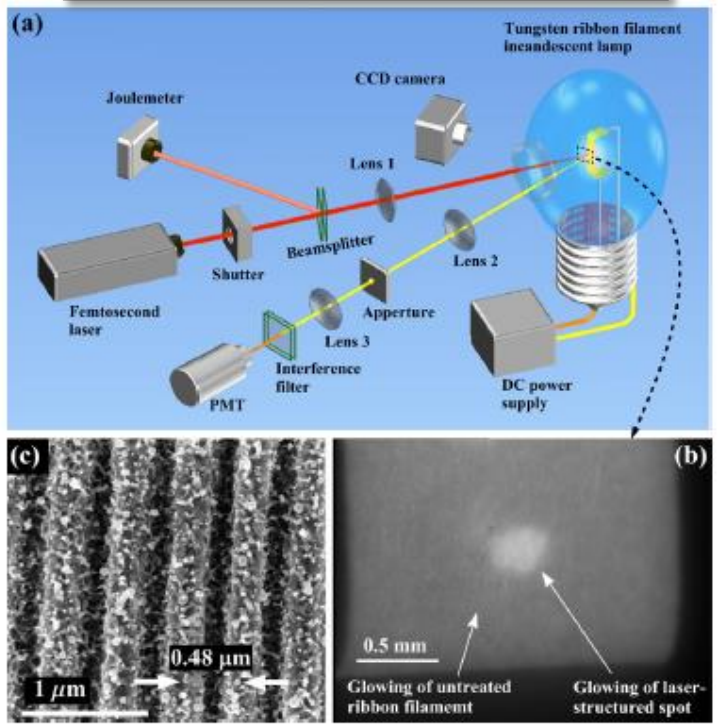
(a) Morpho butterfly iridescent blue wings. (b) and (c) iridescent colors of a Pt sample with LIPSS-textured surface. (d) SEM image of LIPSS texture on Pt. (e) Reflectance spectrum of the LIPSS texture. Side panel: black Pt.

Black Silicon



Black Al as absorber for TEG module

Light bulbs with nanostructured filaments

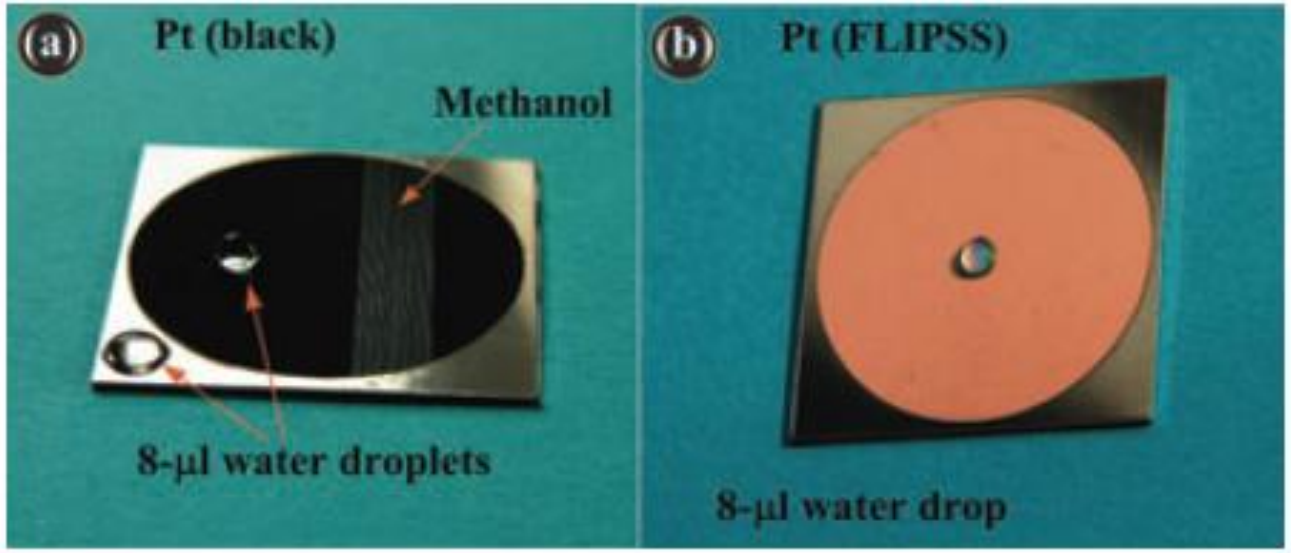


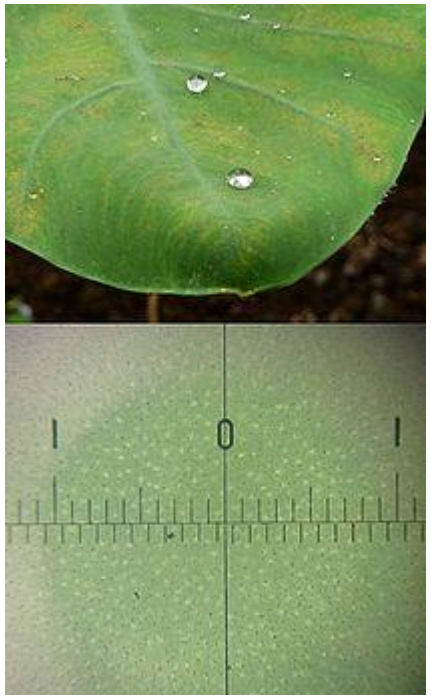
Improved efficiency on W-filament for incandescent bulb lights

LASER & PHOTONICS REVIEWS

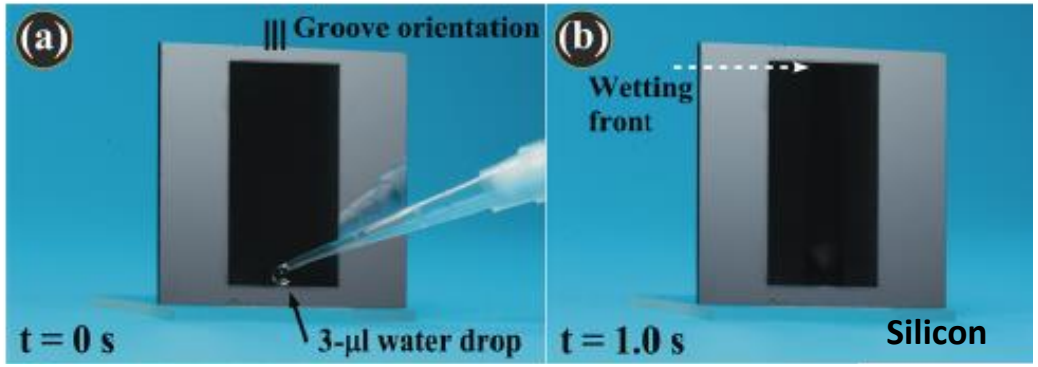
Wetting properties of the nanostrucutred surfaces…

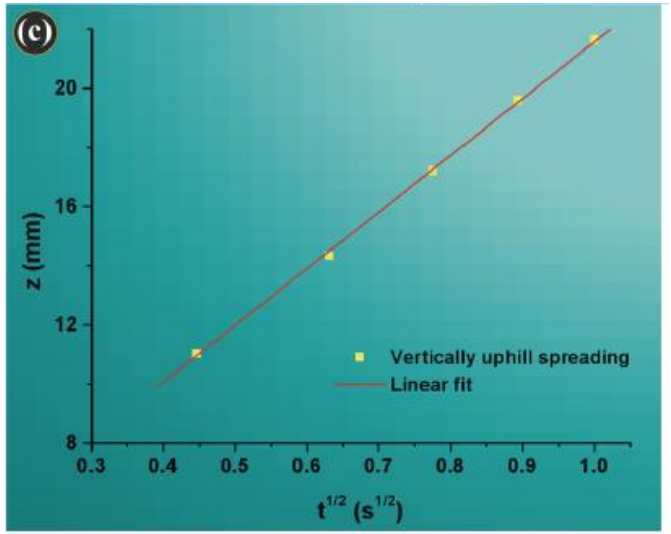
Lotus leaf effect: hydrophobic and hydrophilic surfaces





Pumping water (liquids) uphill with surface μ/n-structrues





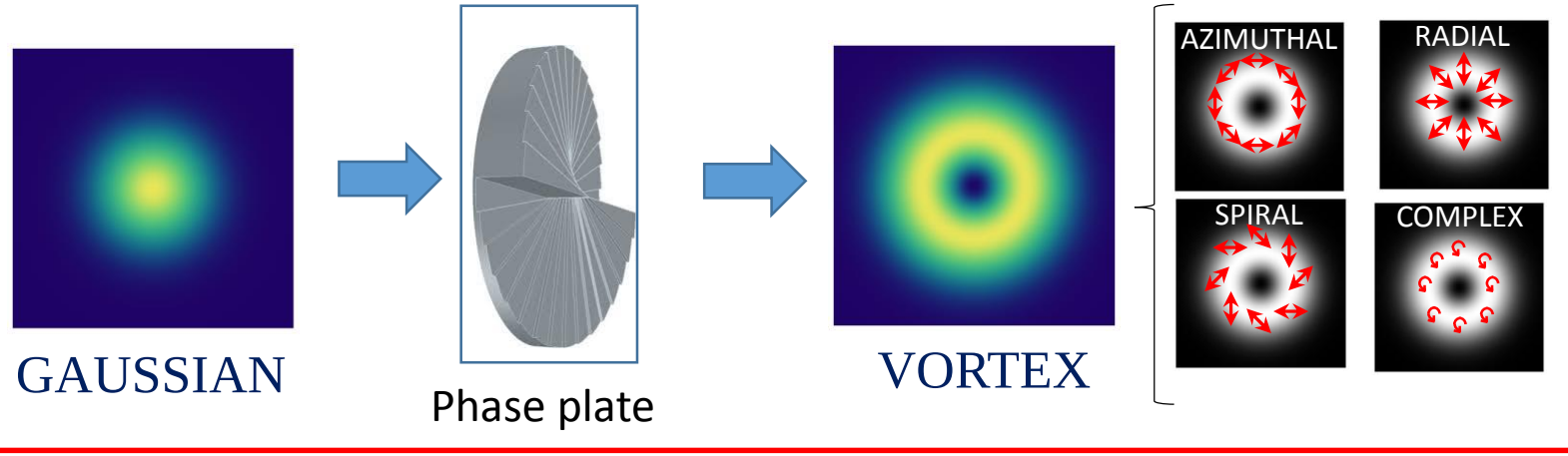
LASER & PHOTONICS REVIEWS

We are pursuing the use of fs laser beams with complex State of Polarization

Shaped optical beams offer novel routes in material ablation and processing

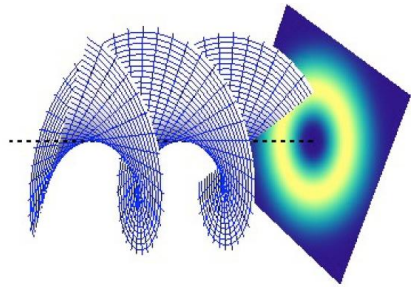
(*e.g. Temporal pulse tailoring has been already explored at a rather large extent*)

Optical Vortex beams carrying Orbital Angular Momentun can open up further opportunities!

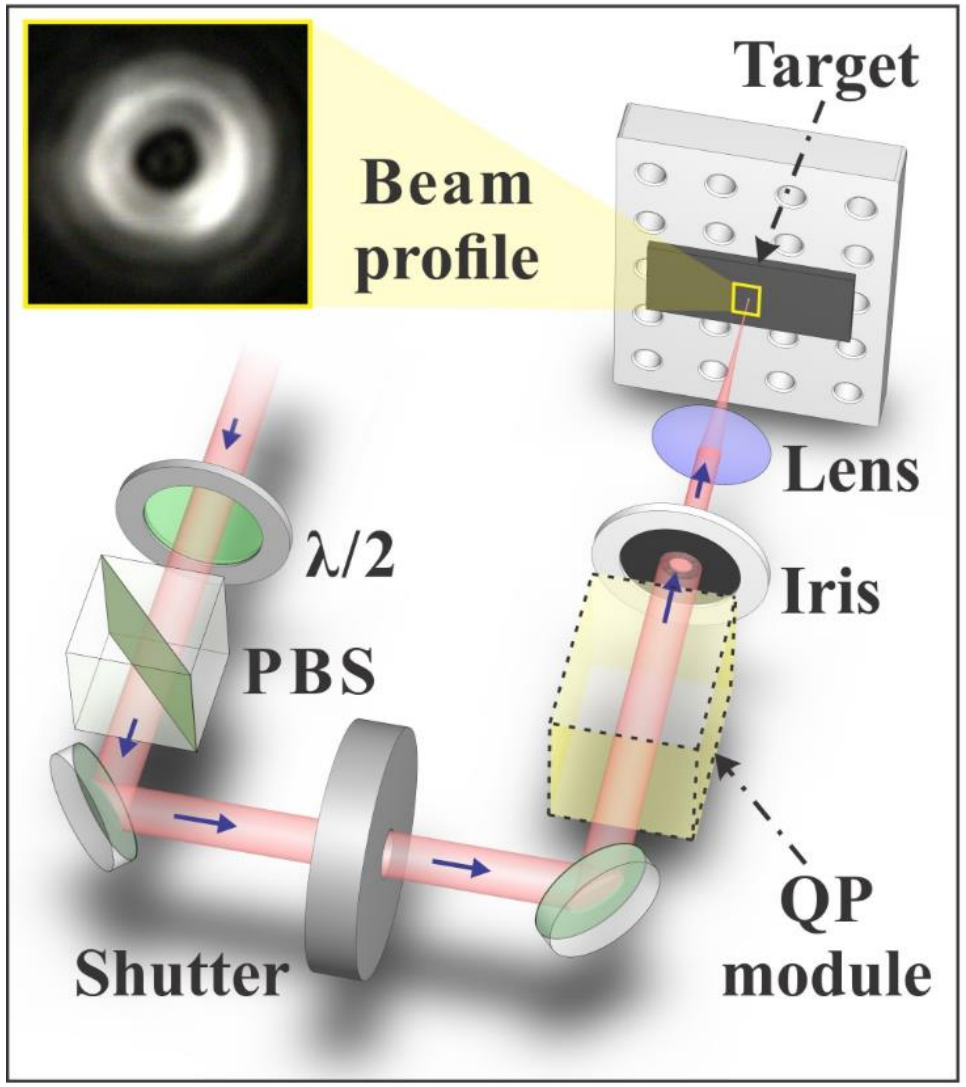


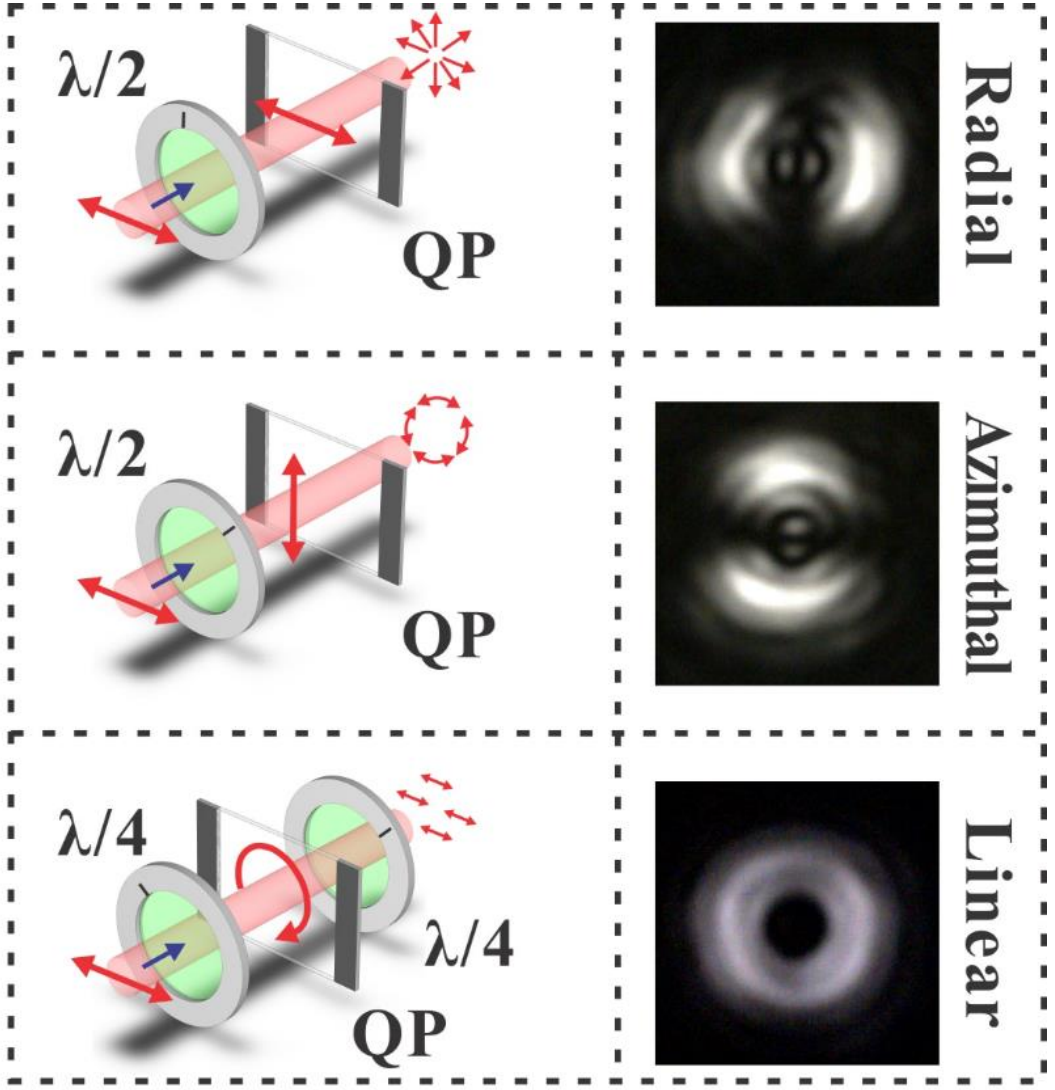
OPTICAL FUSILLI

"pasta spirals"



In collaboration with Nonlinear Optical Spectroscopy Group (L. Marrucci, D. Paparo)

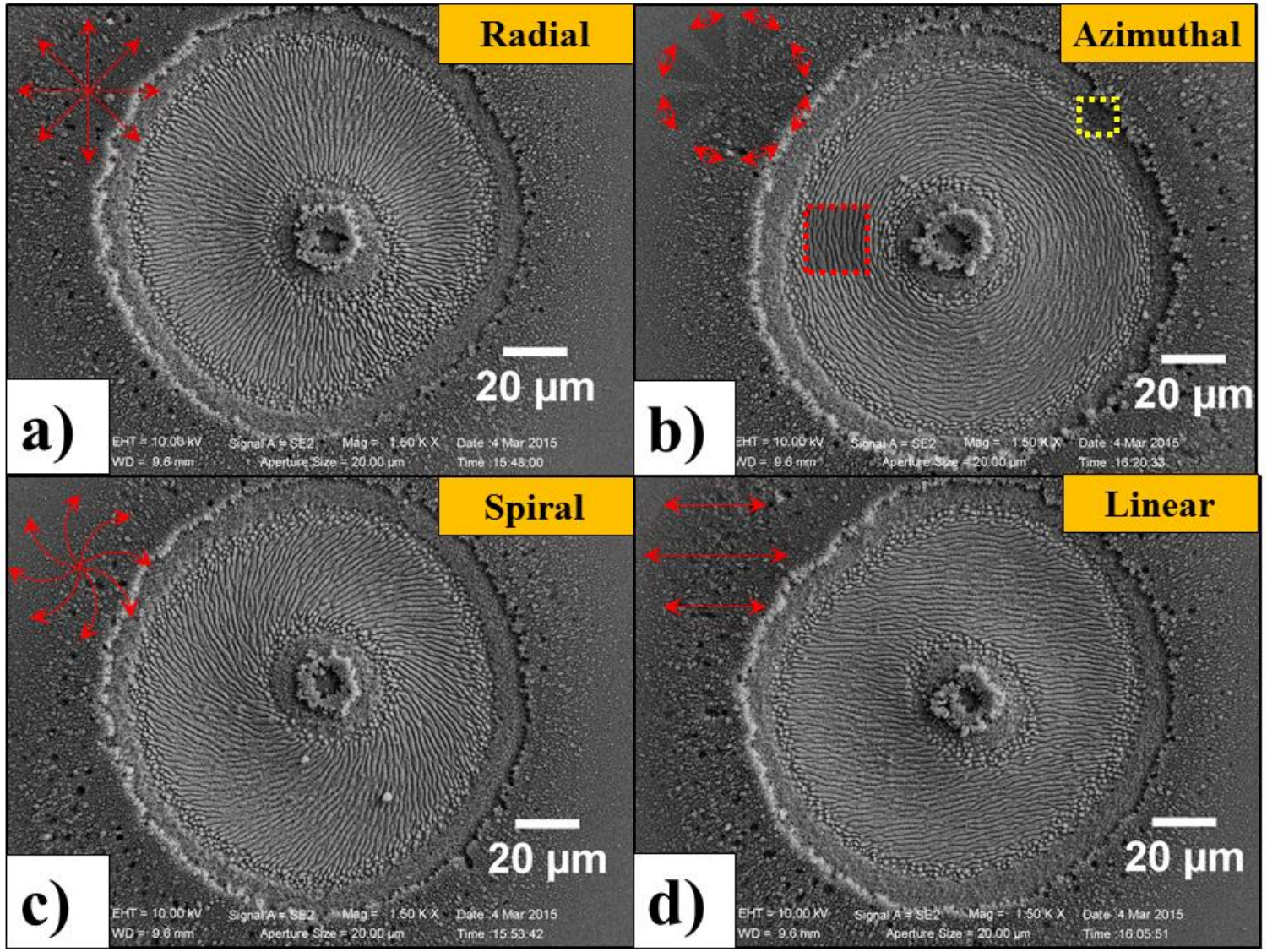


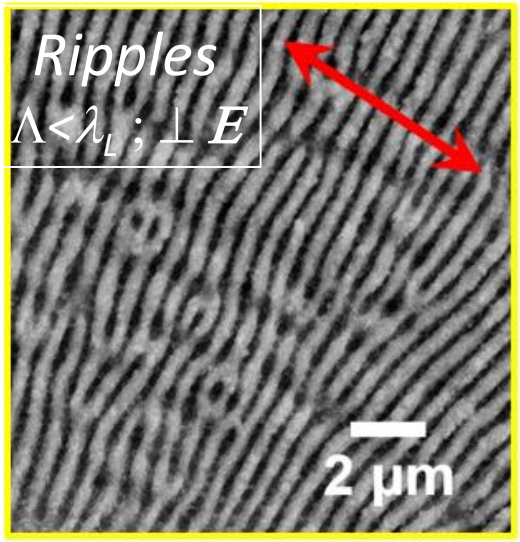


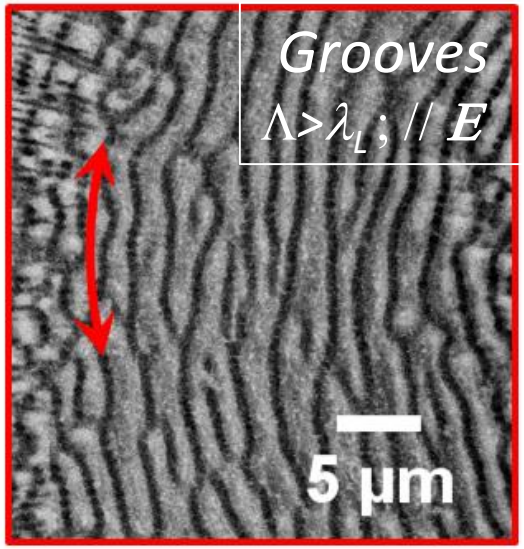
(a) (b) (c)

Sketch of the experimental setup | Q-plate module | Check of SoP

Examples of surface ordered structures on Silicon



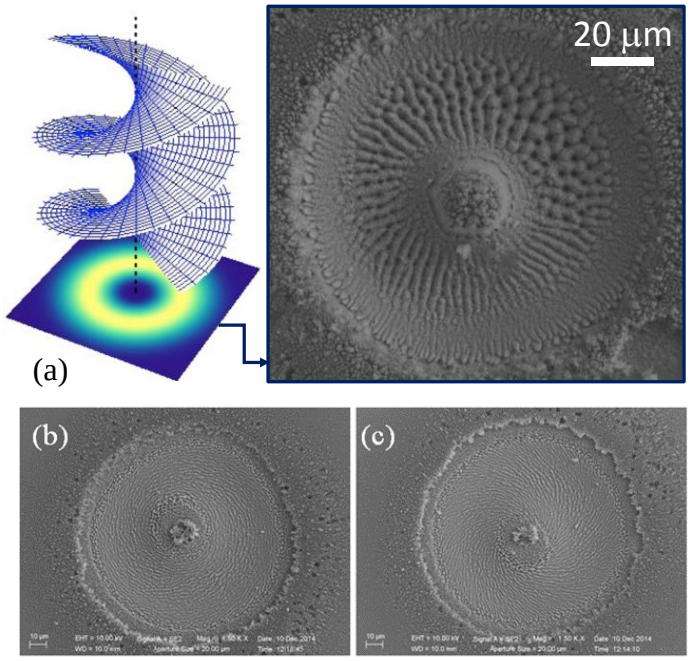




APPLIED PHYSICS LETTERS **104**, 241604 (2014)

Femtosecond laser surface structuring of silicon using optical vortex beams generated by a *q-plate*

K. K. Anoop,[1,2] A. Rubano,[1,2] R. Fittipaldi,[3] X. Wang,[2] D. Paparo,[2] A. Vecchione,[3]
L. Marrucci,[1,2] R. Bruzzese,[1,2] and S. Amoruso[1,2,a)]

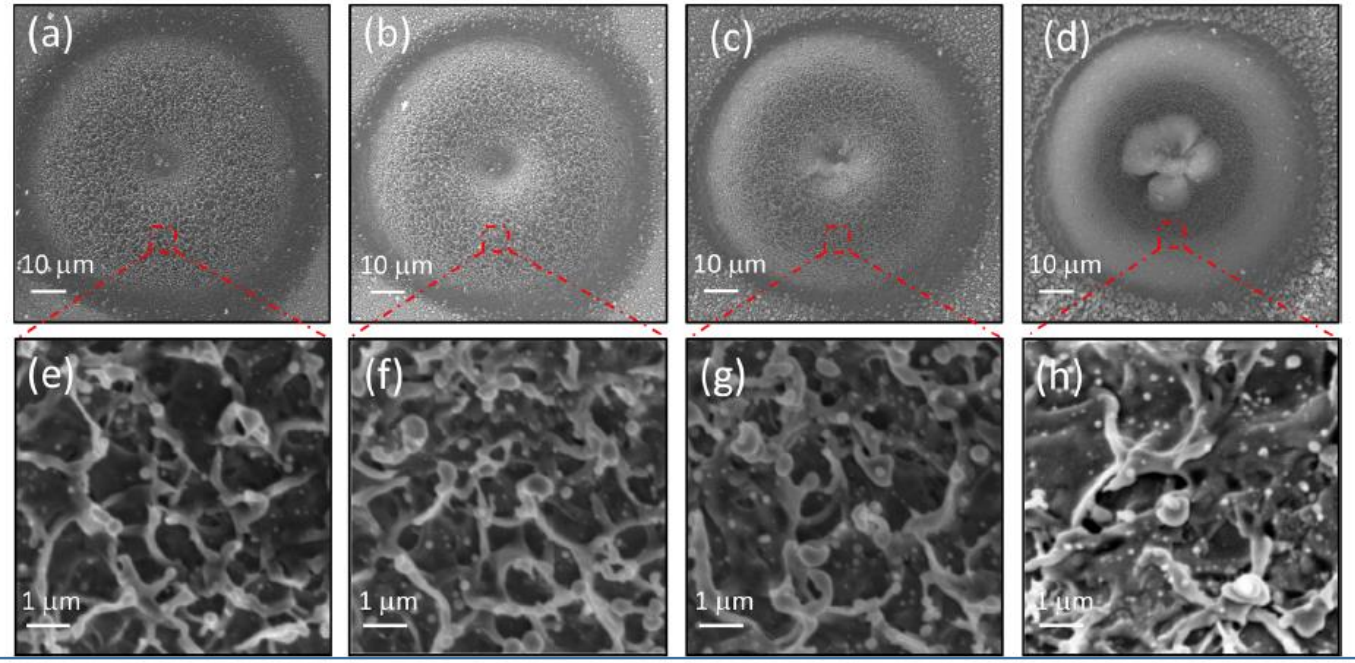


Direct patterning/structuring of complex surfaces

JOURNAL OF APPLIED PHYSICS **116**, 113102 (2014)

Direct femtosecond laser ablation of copper with an optical vortex beam

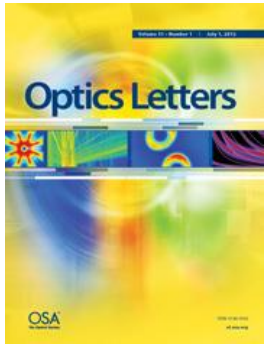
K. K. Anoop,[1,2] R. Fittipaldi,[3] A. Rubano,[1,2] X. Wang,[2] D. Paparo,[2] A. Vecchione,[3]
L. Marrucci,[1,2] R. Bruzzese,[1,2] and S. Amoruso[1,2,a)]



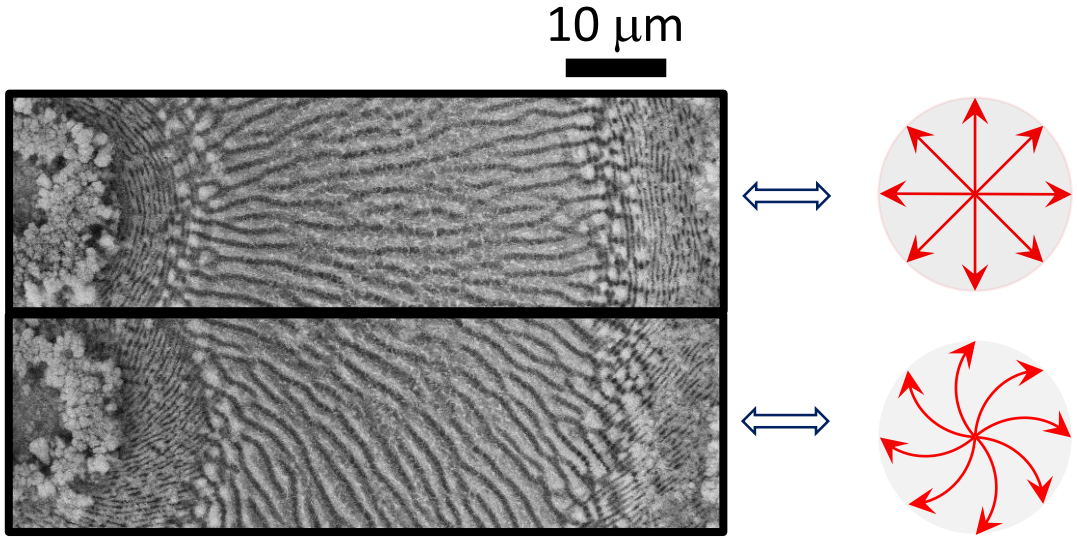
Diagnostics of cylindrical vector beams

Laser ablation of silicon induced by a femtosecond optical vortex beam

OL - in press



JIJIL JJ NIVAS,[1,2] HE SHUTONG,[1,3] ANOOP K.K.,[1,2] A. RUBANO,[1,2] R. FITTIPALDI,[4] A. VECCHIONE,[4] D. PAPARO,[2] L. MARRUCCI,[1,2] R. BRUZZESE,[1,2] AND S. AMORUSO[1,2,*]



We seek for applications

- ✓ ……..
- ✓ … ……..
- ✓ ……..
- ✓ ….. ……. ……..
- ✓ ……..
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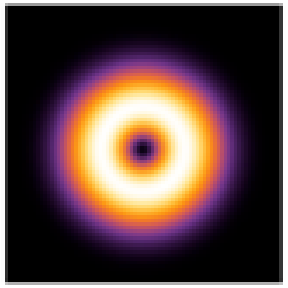
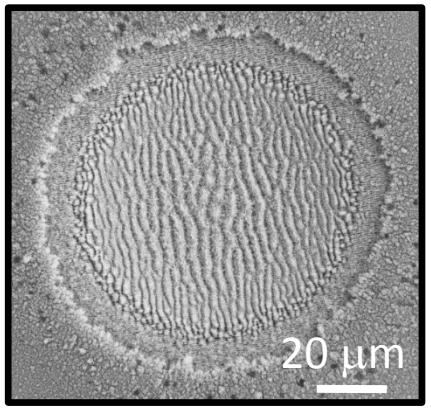
GRAPHIC SUMMARY - Laser ablation with ultrashort pulses

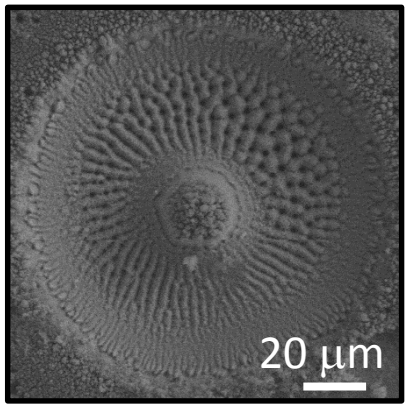
① Imprinting surface micro/nano-strucures with diverse morphologies

Gaussian beam

Vortex beam

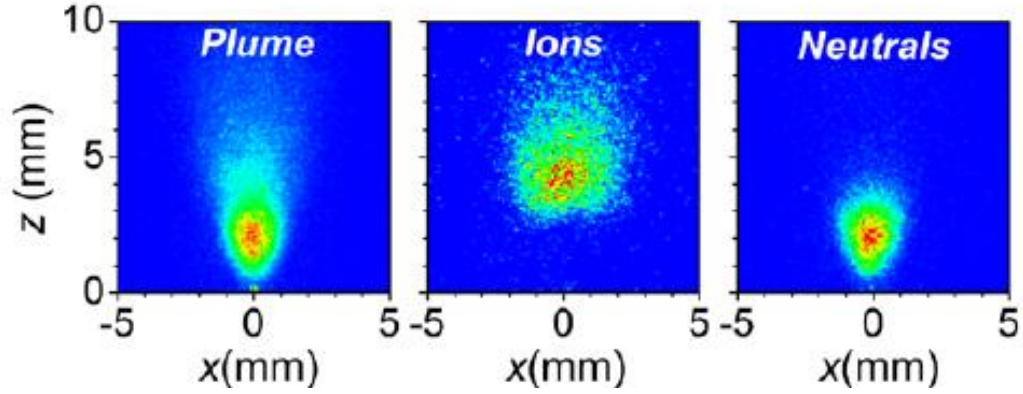




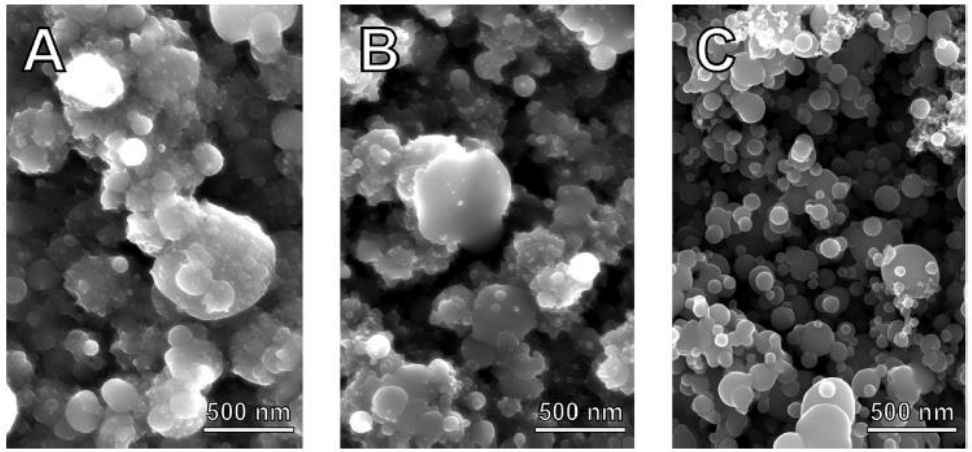


Control and tailor physical properties of surfaces and probe vector laser beams

② Peculiar plasma states



③ NP-assembled films



Magnetism, Optics, Gas-sensing, H_2O-splitting for H_2 production, etc..

Acknowledgements

G. Ausanio, V. Iannotti, L. Lanotte

Magnetic NPs-assembled films

C. Altucci & R. Velotta,

Decoration of QCM for biosensing

S. Lettieri & P. Maddalena

PL and optical-based gas sensors

L. Marrucci, D. Paparo, A. Rubano

Direct fs laser structuring with Vortex beams

CSIC

M. Castillejo & C.

✓ ULA of semiconductors

INSTITUTE OF ELECTRONICS BULGARIAN ACADEMY OF SCIENCES

P. A. Atanasov

N. Nedyalkov

✓ *MD simulations* ✓ *Thin films*

TIANJIN UNIVERSITY (PEIYANG UNIVERSITY) 1895

M. Hu & X. Ni

✓ ULA of metal-oxides

THANK YOU!

FLAG – Femtosecond Laser Ablation Group

S. Amoruso, R. Bruzzese, X. Wang

K.K. Anoop, J. JJ Nivas, S. He

(web site: people.na.infn.it/amoruso/labpage)

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