8th International School on Lasers in material science
SLIMS

Matrix-assisted laser-based analysis and deposition techniques

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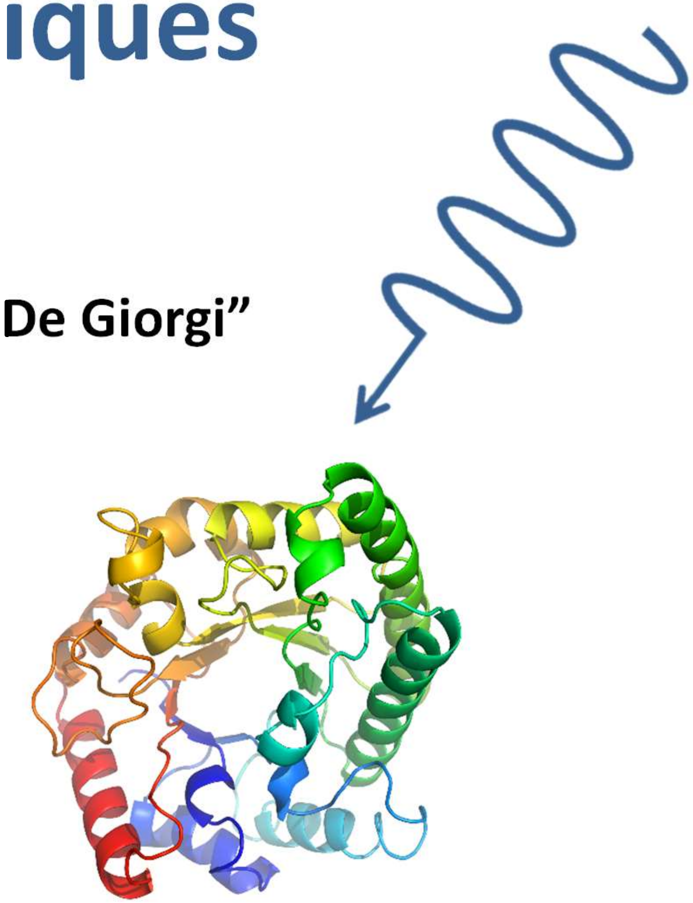

S. Servolo, July 19 2024


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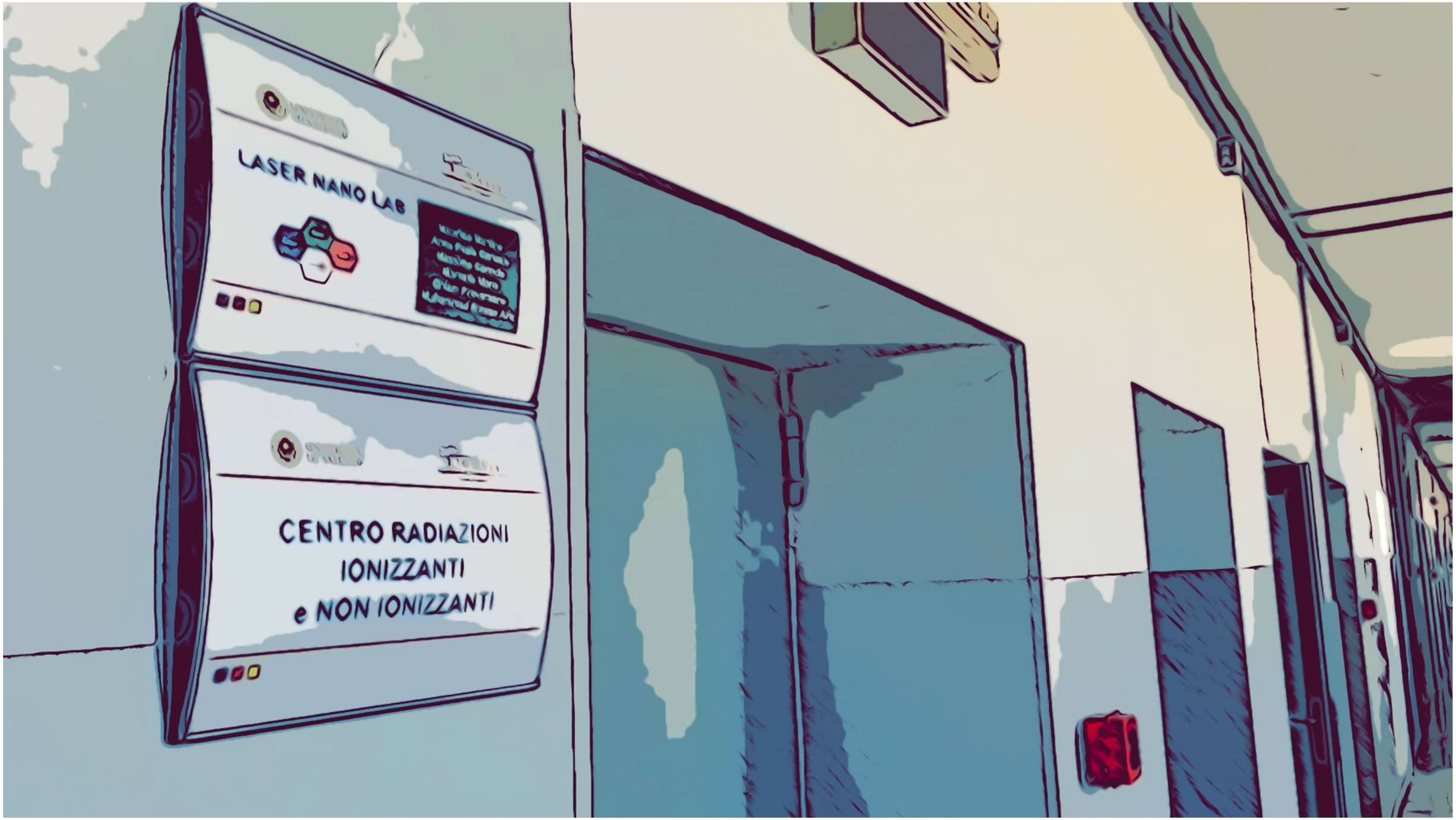
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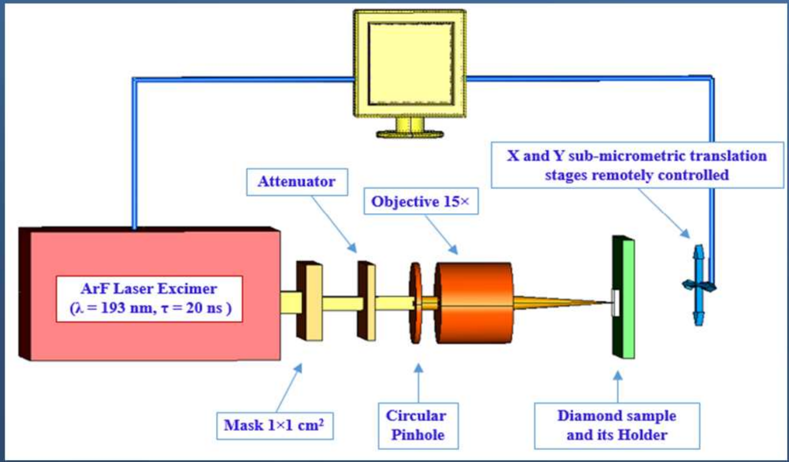
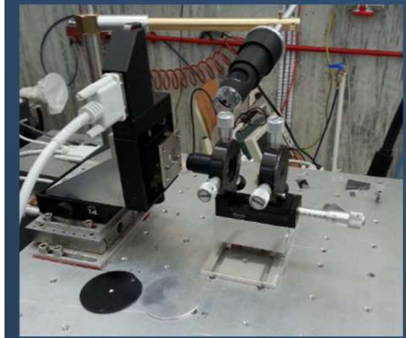
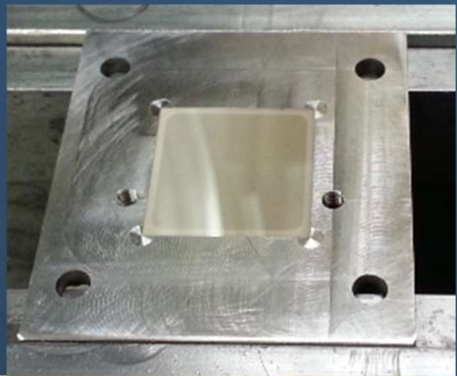
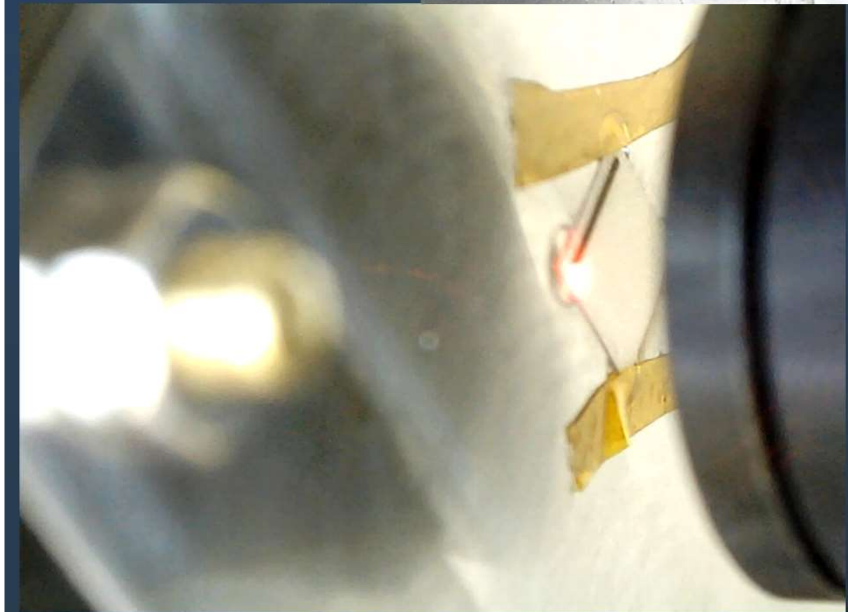
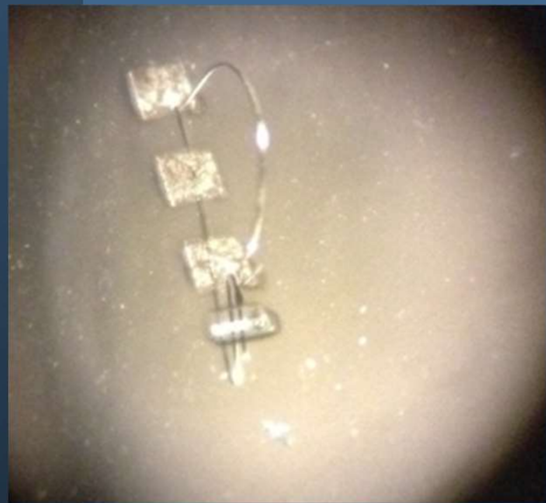
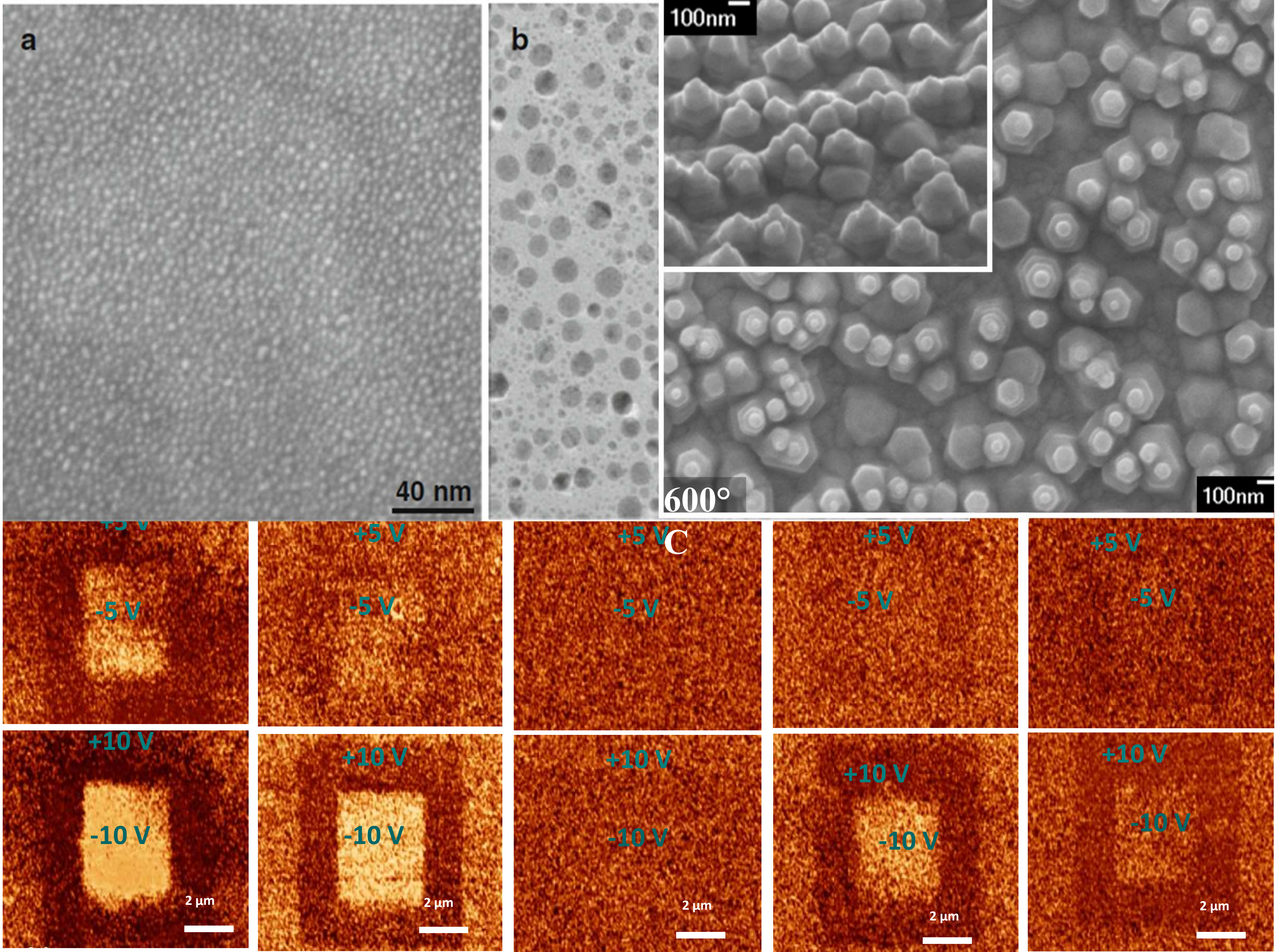

X and Y sub-micrometric translation stages remotely controlled
Attenuator
Objective 15×
ArF Laser Excimer
(λ = 193 nm, τ = 20 ns)
Mask 1×1 cm²
Circular Pinhole
Diamond sample and its Holder





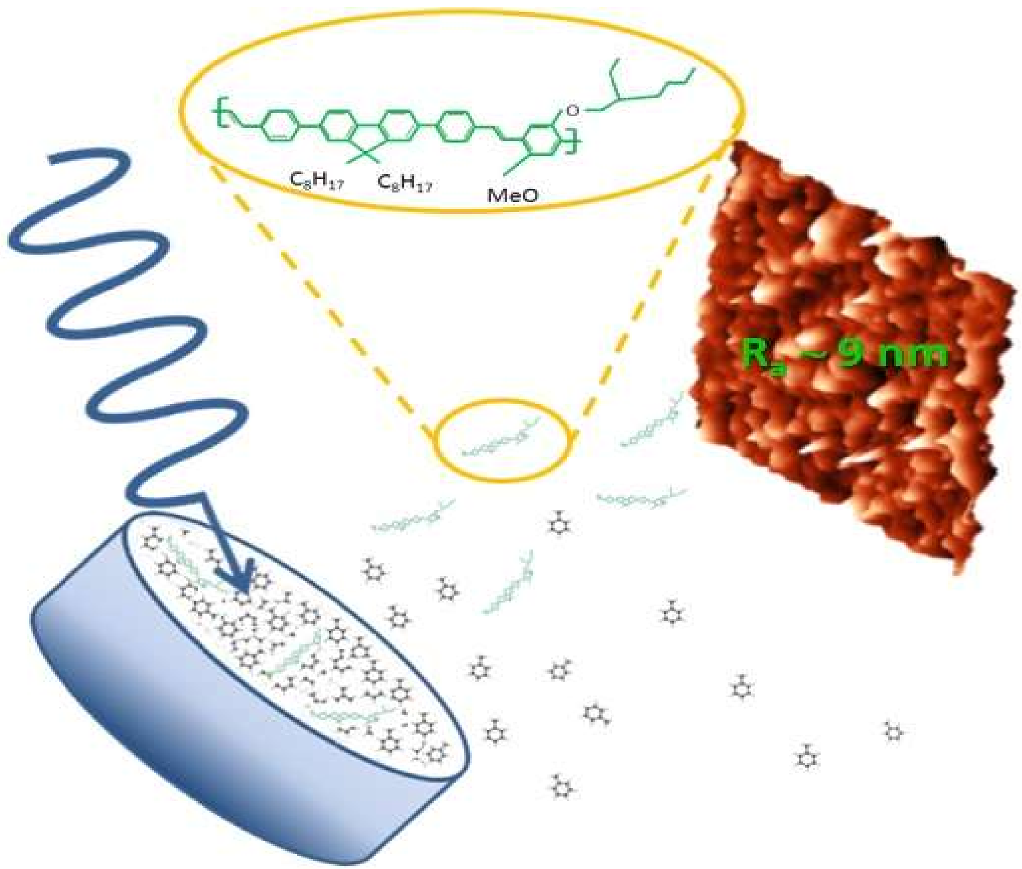





a
40 nm
b
100nm
600°
100nm
C
+5 V
-5 V
+10 V
-10 V
2 µm

MAPLE

Matrix-assisted pulsed laser evaporation



Outline

Matrix-assisted Pulsed Laser Evaporation (MAPLE):

- overview of the basic principles (first idea, experimental set up, simulations);
- advantages/drawbacks;
- influence of some of the deposition parameters;
- applications (deposition of polymers and biomaterials);
- MAPLE for nanomaterial deposition;

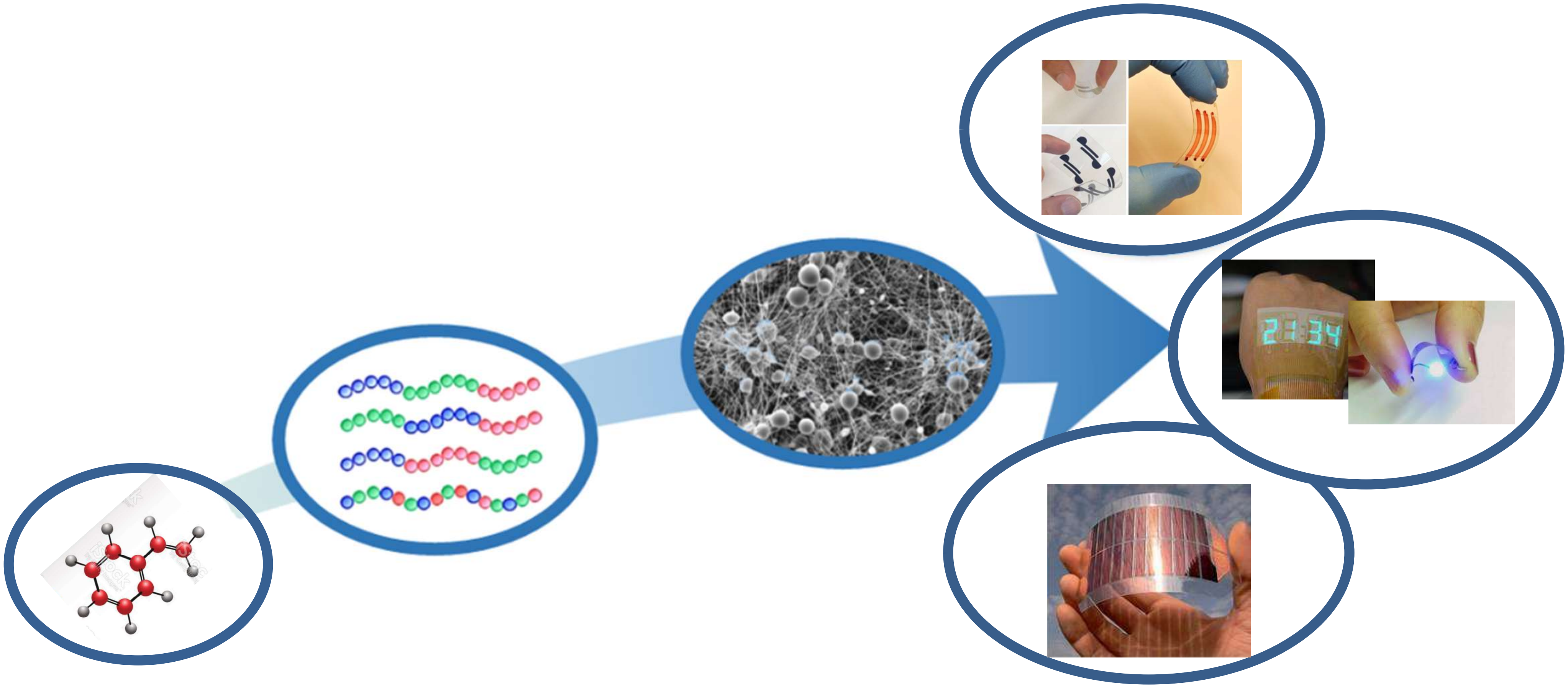
Matrix-assisted Laser Desorption Ionization(MALDI):

- overview of the basic principles

CONCLUSIONS

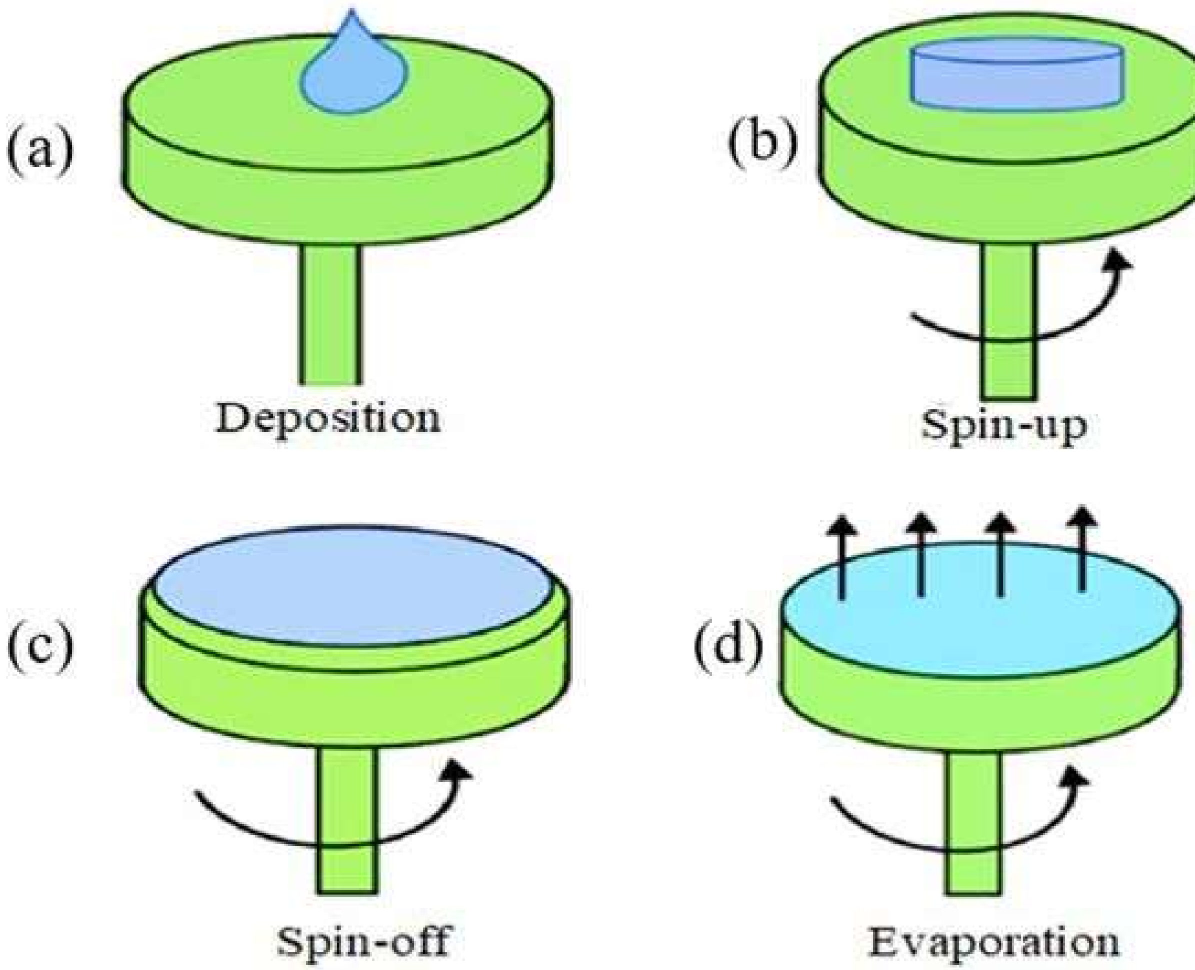
MAPLE: motivation and working principle

Polymers are macromolecules, which are synthesized from one or more different monomers using different types of polymerization



MAPLE: motivation and working principle

Spin coating procedure for polymer deposition



Easy

Cheap

BUT

Solvent related problems

Difficult thickness control

Deposition on patterned substrates

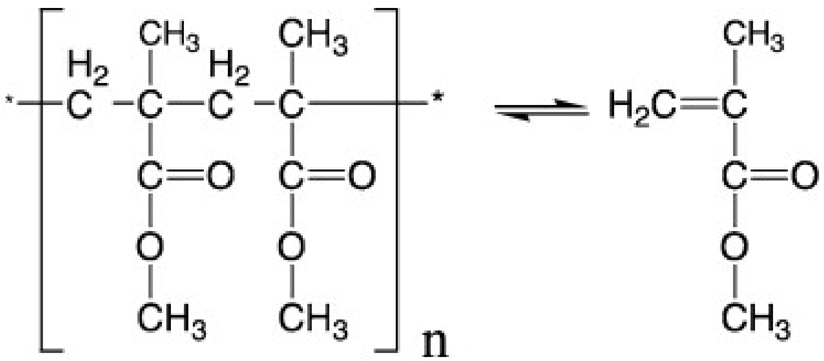
Multilayer deposition

MAPLE: motivation and working principle

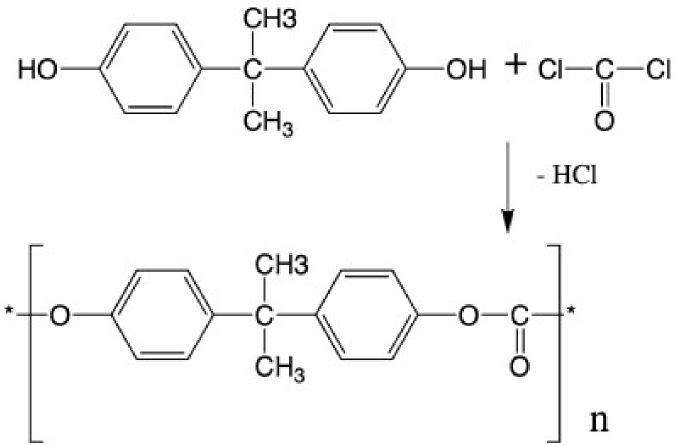
Is it possible to deposit polymer films by PLD?

The PLD deposition is limited to only certain polymers.

Polymers that are produced by radical polymerization from monomers, which contain double bonds, are likely to depolymerize into monomers, while polymers that have been formed by reactions such as polycondensation will not depolymerize into monomers upon irradiation but will be decomposed into different fragments. **The second group cannot be used to produce films with the same structure or molecular weight as the original material**



Monomers with double bond (PMMA)



Polycondnsation

MAPLE: motivation and working principle

Laser ablation of polymers: a very complex mechanism!

Absorption of the UV laser → direct bond breaking (fs-ps)

The photon energy not resulting in bond breaking is transferred to the polymer matrix → increase of T.

Primary decomposition products can also be decomposed directly by the laser photons

Energy can be released from exothermic decomposition reactions (up to kJ g−1) of secondary products → increase of T

Small reaction/decomposition products are formed → increase of p

The increase of T results in thermal decomposition of the polymer → increase of p

The fast increase of T can also increase the QY and subsequent reactions (unzipping: for PMMA 6 monomers at RT and over 200 above Tg) ➠ increase of p.

Ablation starts when a certain number of bonds are broken in a volume element (before: decomposition/incubation) ➠ delayed ablation of a modified (not original) polymer.

All of these processes are dependent on the polymer

MAPLE: motivation and working principle

In PLD the UV high <u>energy photon</u> and the <u>high fluence values</u> (~ J/cm^2) are such to induce very high T on the target at the laser spot

We need something to smooth the interaction!!

Matrix

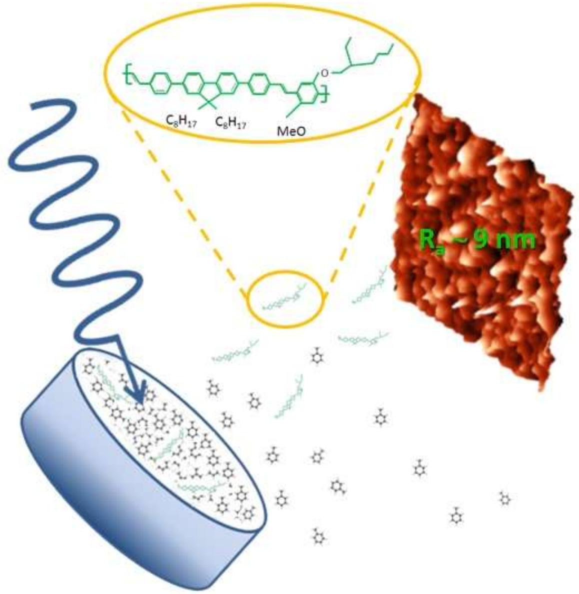
MAPLE: motivation and working principle

1990 BREAKTHROUGH:

D. Chrisey* and co-workers at the U.S. Naval Research Laboratory gave birth in 1990 to the:

Matrix Assisted Pulsed Laser Evaporation
(MAPLE technique)

Goal: achieving a soft **molecule-by-molecule** deposition of high-quality ultrathin organic, bioorganic, and composite films with **minimum chemical modification of the target material**

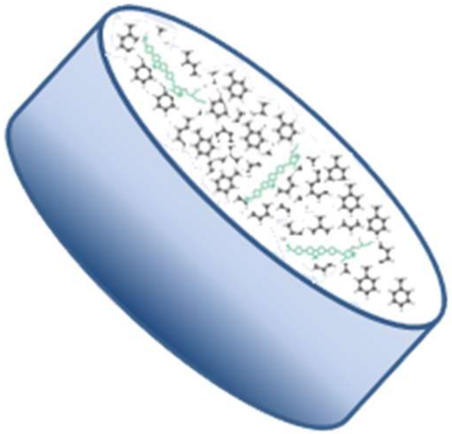


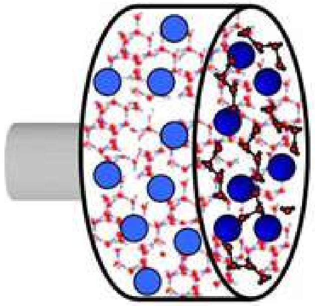
*R.A. McGill and D.B. Chrisey, Method of Producing a Film Coating by Matrix Assisted Pulsed Laser Deposition, Patent No. 6,025,03 (2000).

MAPLE: motivation and working principle

The material of interest (solute) is diluted in a volatile absorbing solvent (**matrix**) to form a homogeneous solution (concentration up to a few wt %)

The solution is frozen at LN2 temperature





Then it is placed into a vacuum chamber and submitted to pulsed laser irradiation.

MAPLE: motivation and working principle

Assumed mechanism: photothermal process

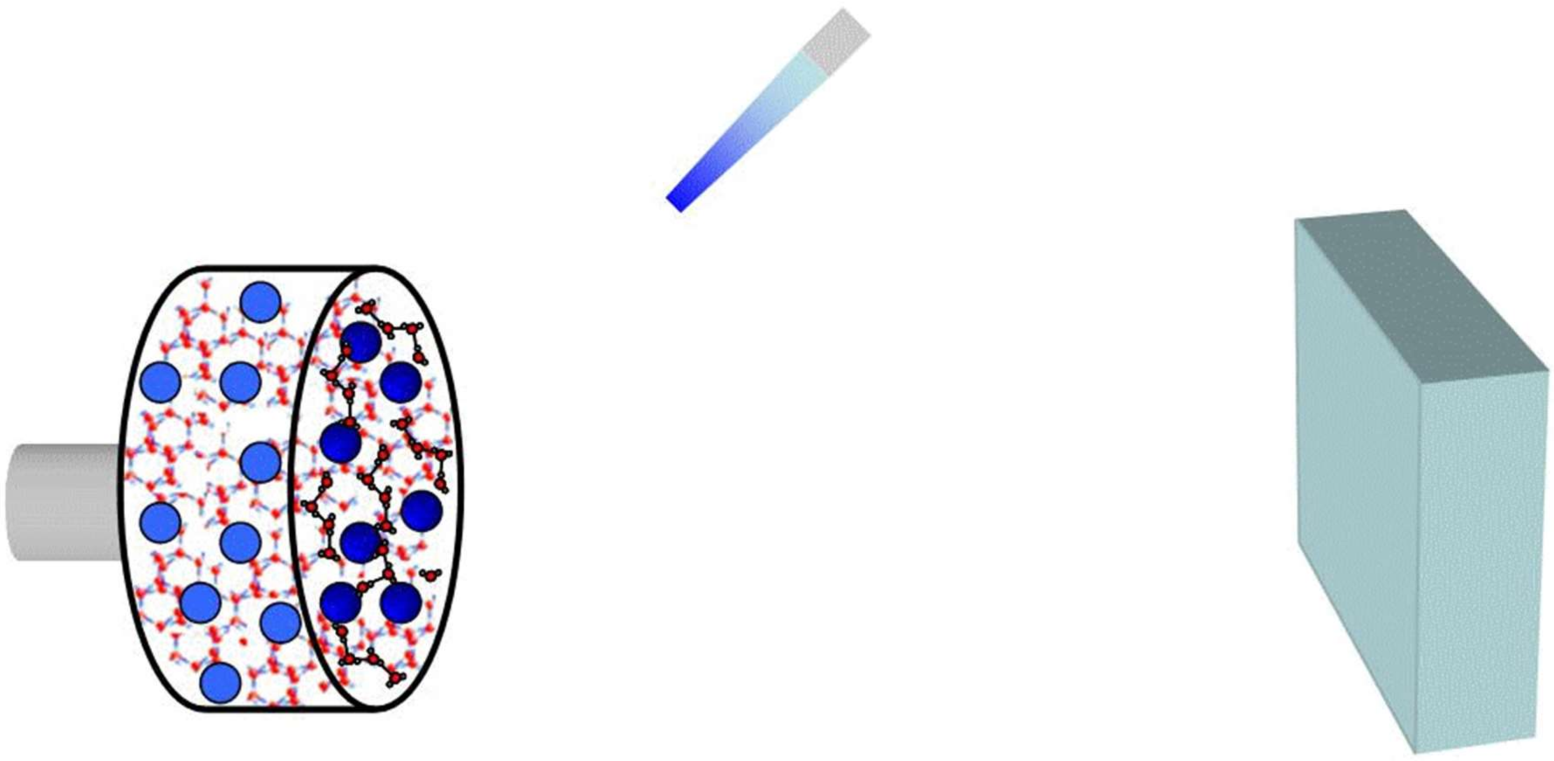
Most of the laser energy is absorbed by the volatile solvent (matrix) and converted into thermal energy

This laser pulse energy causes the vaporization of the solvent layer and only a moderate heating of the solute.

The collective motion of the many solvent molecules, evaporated by a single laser pulse, carries the few solute molecules present in the evaporated layer to the substrate

The solvent molecules (volatile) are pumped away from the deposition chamber during the time of flight (low sticking coefficient).

MAPLE: motivation and working principle



MAPLE: motivation and working principle

Difference with respect to PLD?

Essentially, the TARGET.

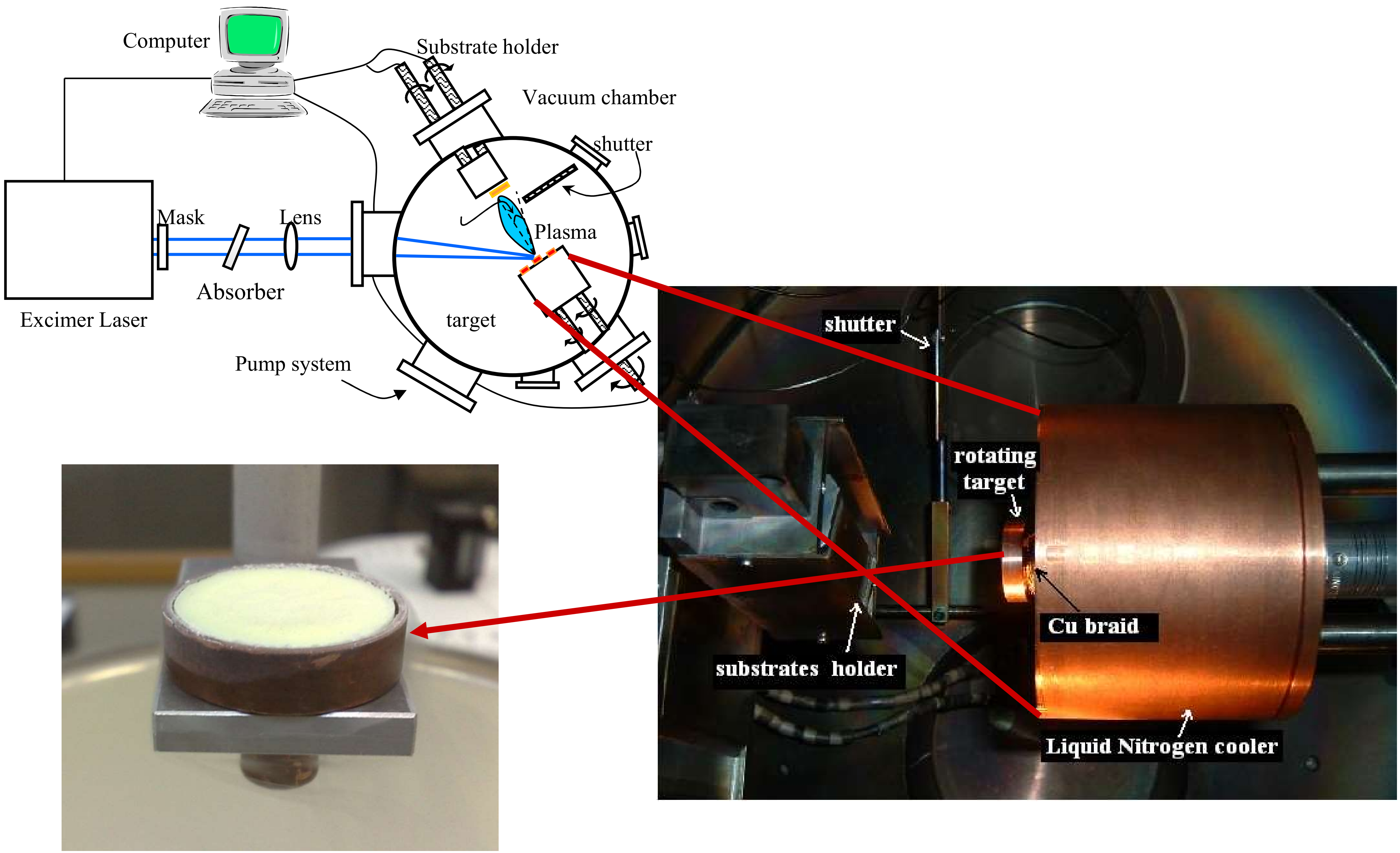
The solute material is **diluted** in a **volatile** and **absorbing** (at the used laser wavelength) solvent in order to produce a **homogeneous solution**

few wt% of the solute → Minimization of the photochemical damage

absorbing and volatile solvent → Minimization of the photothermal damage*

*The ablation onset is defined by the thermodynamic parameters of the solvent ⇒ depositions can proceed at much lower fluences, as compared to conventional PLD: 0.05 – 1 J/cm^2

MAPLE: experimental set-up



MAPLE: most used deposition parameters

Laser	Type/wavelength	KrF (λ=248 nm), ArF (λ=193 nm), Ng:YAG (λ=355 nm), Nd:YAG (λ=266) RIR-MAPLE (2.94 μm, 8.2 μm)
	Fluence	**0.05 – 1 J/cm^2**
	Frequency	1 – 20 Hz
	Spot dimension	1 -15 mm^2
Solvent	Isopropanol, deionized water, toluene, acetone, tetrahydrofuran, ter-butyl alcohol, dimethyl sulfoxide, ethyl acetate, chlorobenzene, methanol, dimethoxyethane, phosphate buffer solution, chloroform	
Target-substrate distance	3 – 7 cm	
Background pressure	Vacuum – 70 Pa	

MAPLE: advantages and drawbacks

Advantages:

→ quite simple procedures;

→ in principle good control of film thickness;

→ different independent deposition parameters;

→ deposition on non-planar substrates with good uniformity;

→ possibility to deposit mulilayer and composite polymeric films;

Drawbacks

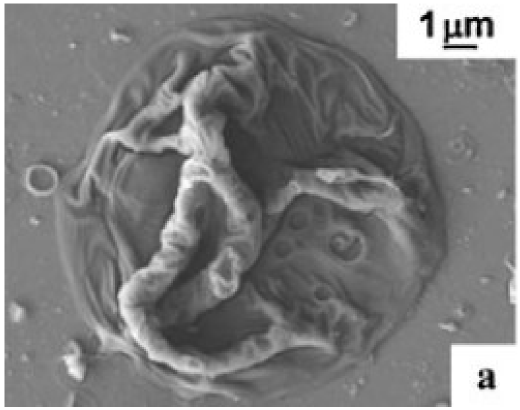
→ low deposition rates with UV laser (one order of magnitude lower than those for PLD)

→ possible formation of reactive radicals due to photochemical reactions of the solvent molecules which can react with the solute material

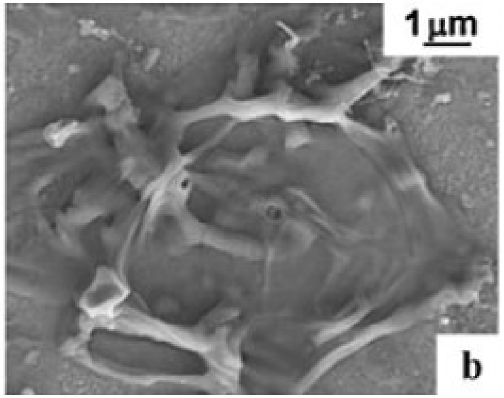
→ high roughness values: very often the surface of MAPLE-deposited films shows a high density of micronsized droplets

MAPLE: a really simple evaporative process?

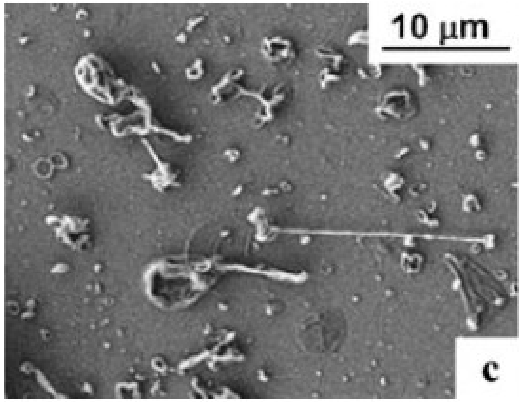
The AFM and SEM images of MAPLE deposited polymer films reveal significant surface roughness, aggregates or clusters with sizes ranging from tens of nanometers to tens of microns.



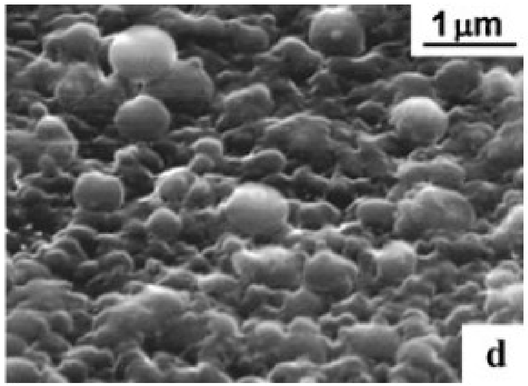
Deflated ballons



Interconnetted filaments



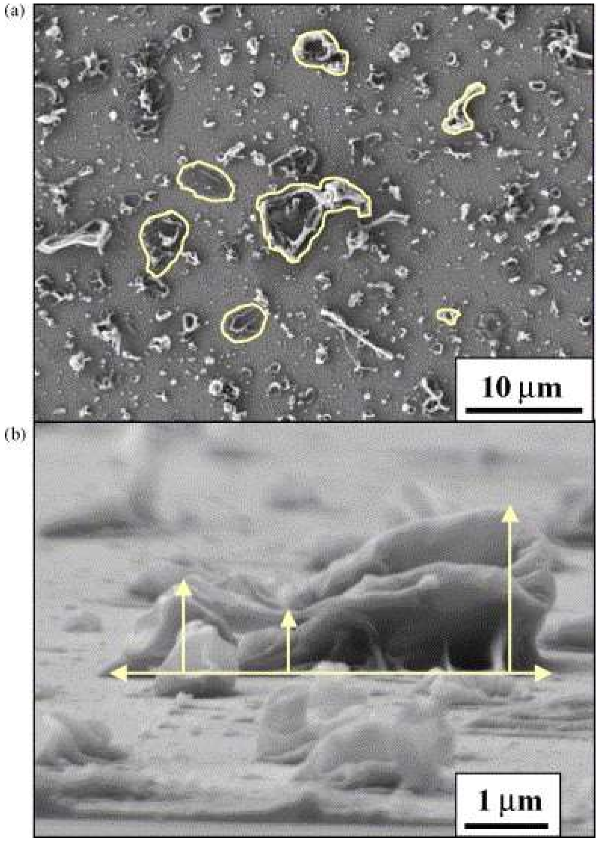
Elongated nanofibers



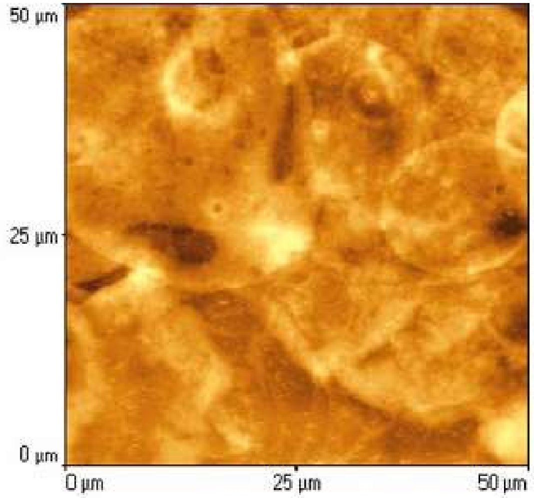
Nanostructures

K.B. Shepard, Appl. Phys. A 110, 771 (2013)

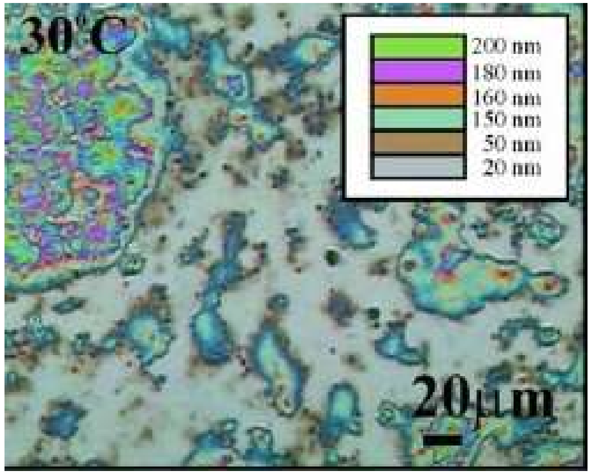
MAPLE: a really simple evaporative process?



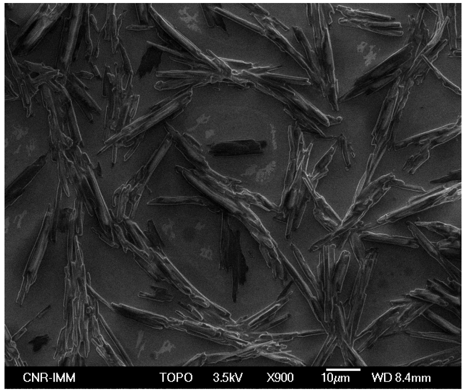
E. Leveugle, L.V. Zhigilei, A. Sellinger, J.M. Fitz-Gerald, Appl. Surf. Sci. 253 (2007) 6456



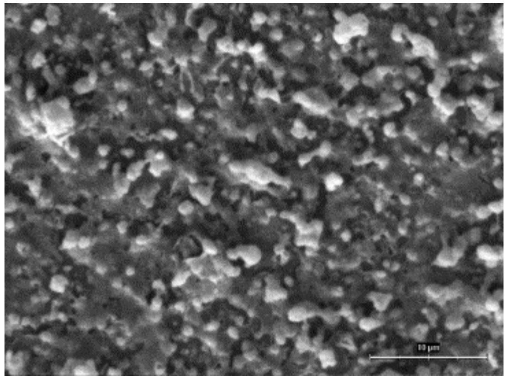
A.P. Caricato, et al. Appl. Phys. A 93 (2008) 651.



K. Rodrigo et al., Applied Surface Science 252 (2006) 4824.



A.P. Caricato et al. J. Phys. D, Appl. Phys. 42, 095105 (2009).



G. Socol et al. Appl. Surf. Sci. 255 (2009) 5611

MAPLE: a really simple evaporative process?

The simple model of the ejection and transport of individual molecules is often in contradiction with the results of high-resolution SEM and AFM images of MAPLE deposited films.

The formation of large polymer features is rather unexpected:

- the polymer concentration in the target is low polymer molecules are dissolved in the matrix down to the molecular level

- the expanding plasma plume should not provide a suitable environment for condensation of polymer clusters.

MAPLE: a really simple evaporative process?

Revision of the physical picture of the molecular transfer in MAPLE

E. Leveugle, L.V. Zhigilei, A. Sellinger, J.M. Fitz-Gerald, *"Computational and experimental study of the cluster size distribution in MAPLE"*, Appl. Surf. Sci. 253 (2007) 6456.

E. Leveugle, L.V. Zhigilei, *"Molecular dynamics simulation study of the ejection and transport of polymer molecules in matrix-assisted pulsed laser evaporation"*, J. Appl. Phys. 102 (2007) 074914.

………

Leveugle and Zhigilei consider that the concentrations of polymer molecules (typically 0.1–5 wt %) and the collective behaviour of polymer molecules may play an important role in defining the mechanisms of molecular ejection and the morphological characteristics of the deposited films.

MAPLE: a really simple evaporative process?

Matrix → breathing sphere model

Polymer → Bead-and spring model

Very different conditions from what used in conventional MAPLE experiments but such to reproduce similar physical conditions

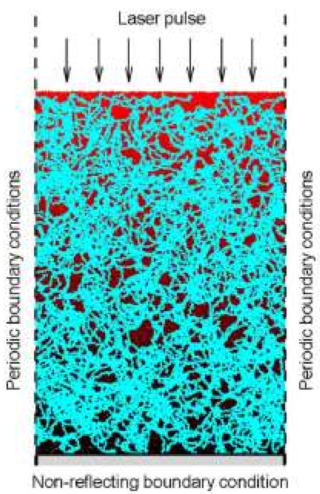
Thermal confinement: $$\tau_p < \tau_{th} = \frac{L_p^{\,2}}{AD_T}$$ $\tau_{p=}$ laser pulse duration, D_T=thermal diffusivity,L_p=laser penetration depth, A=costant

No stress confinement: $$\tau_p > \tau_s \approx \frac{L_p}{C_S}$$ $\tau_{p=}$ laser pulse duration, C_S=speed of sound in target material,L_p=laser penetration depth

*The natural limit of the applicability of the model are defined by the conditions for the onset of multiphoton absorption, phtochemical fragmentation, ionization and plasma formation

MAPLE: a really simple evaporative process?

Some values for theory and experiment:



Simulations*:

τ_p = 50 ps

L_p = 50 nm

τ_{th} = 7 ns

τ_s = 20 ps

$$\tau_s < \tau_p < \tau_{th}$$

Experiments*:

T_p= 20 - 30 ns

$L_{p=}$= 4 µm

τ_{th} = 181 µs

$\tau_{\ s}$ = 3 ns

$$\tau_s < \tau_p < \tau_{th}$$

The ejection mechanisms revealed in the simulations also work in experiments, albeit at much larger time and length scales*!

* E. Leveugle and L.V. Zhigilei, J. Appl. Phys. 102, 074914 (2007)

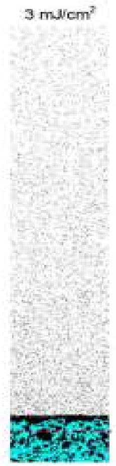
MAPLE: a really simple evaporative process?

From the simulation, at the early stage of the laser-target interaction, it results:

Below a threshold fluence: evaporative process

- Thermal evaporation of individual matrix molecules

- No ejection of polymer molecules

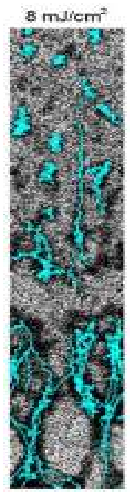


Above a threshold fluence: explosive process

- Prompt ejection of small cluster and liquid droplets of matrix-polymer structures as well as of matrix molecules

- Polymer molecules are <u>only ejected</u> as part of matrix-polymer clusters;

- The polymer molecules have a clear tendency to extend along the flow in the ablation plume.



http://www.faculty.virginia.edu/CompMat/maple/

MAPLE: influence of deposition parameters

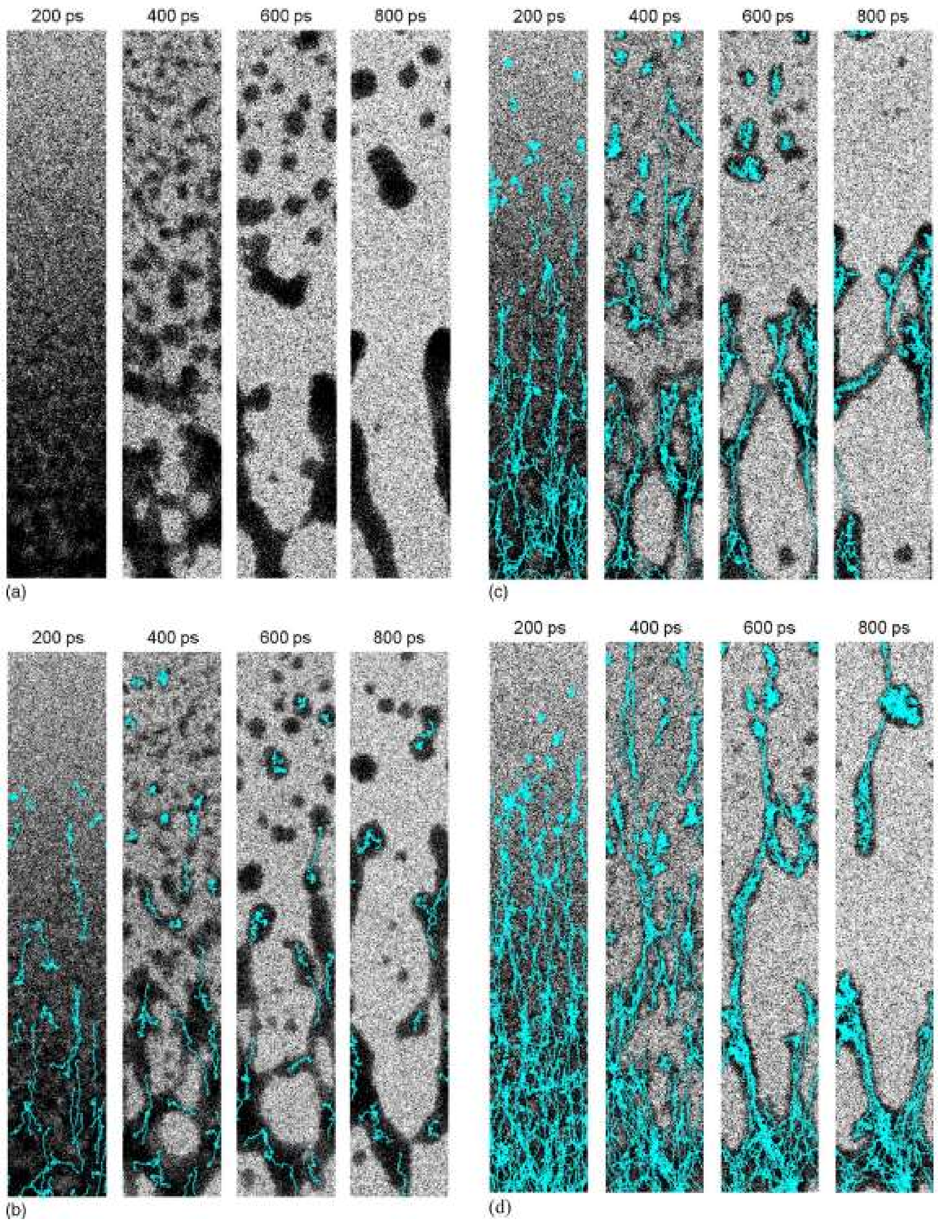
Polymer concentration

pure matrix

3 wt %

1 wt %

6 wt %



complex matrix-polymer liquid structures elongated in the direction of the ablation plume expansion and stabilized by the presence of polymer molecules

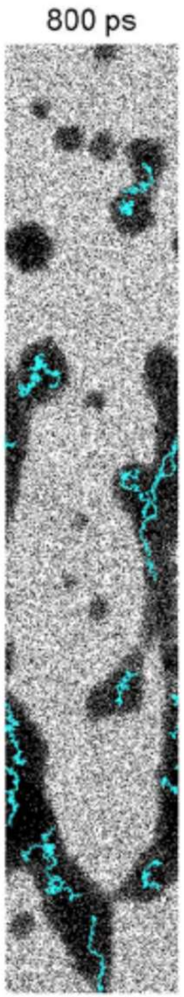
as the polymer concentration increases, the chains become more entangled → formation of intricate elongated structures → complex surface morphology

* E. Leveugle and L.V. Zhigilei, J. Appl. Phys. 102, 074914 (2007)

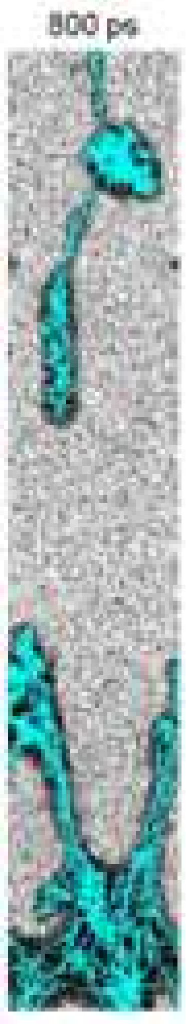
MAPLE: a really simple evaporative process?

Above a threshold fluence: explosive process

1 wt %



3 wt %



- the polymer molecules have a clear tendency to extend along the flow in the ablation plume.

- active evaporation of matrix molecules from the surface of the droplets contributes to the formation of polymer rich surface layer hampering, at first, the escape of the remaining matrix molecules which then escape from polymer voids

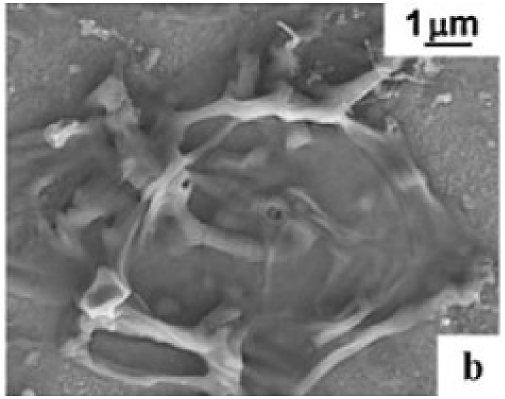
- High internal temperatures are reached by the ejected cluster which then decrease, because of evaporative cooling, until an equilibrium temperature is obtained of the order of 0.7T*(1)

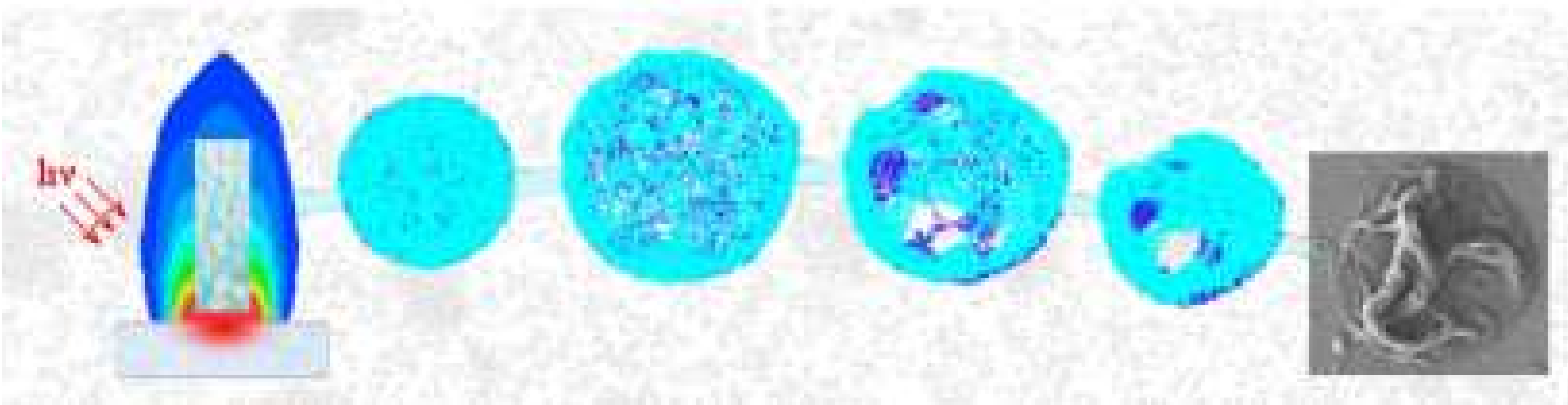
* E. Leveugle and L.V. Zhigilei, J. Appl. Phys. 102, 074914 (2007)

MAPLE: a really simple evaporative process?

From laser interaction to film deposition

Long filament resulting by the ablation process

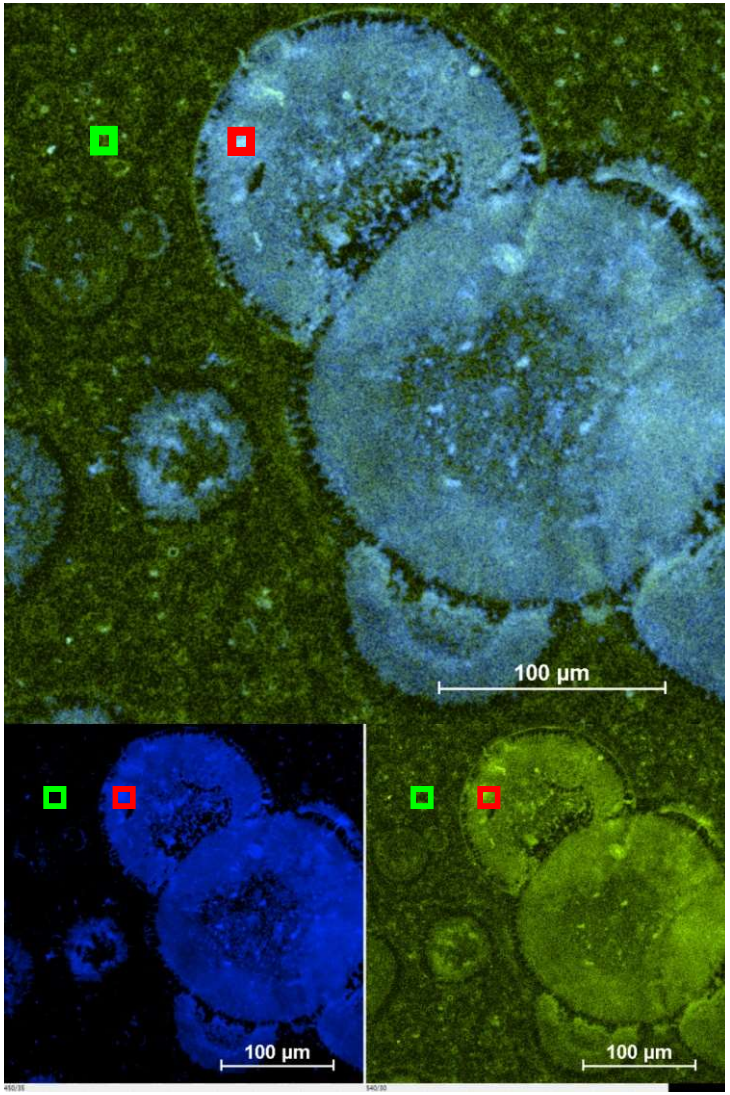


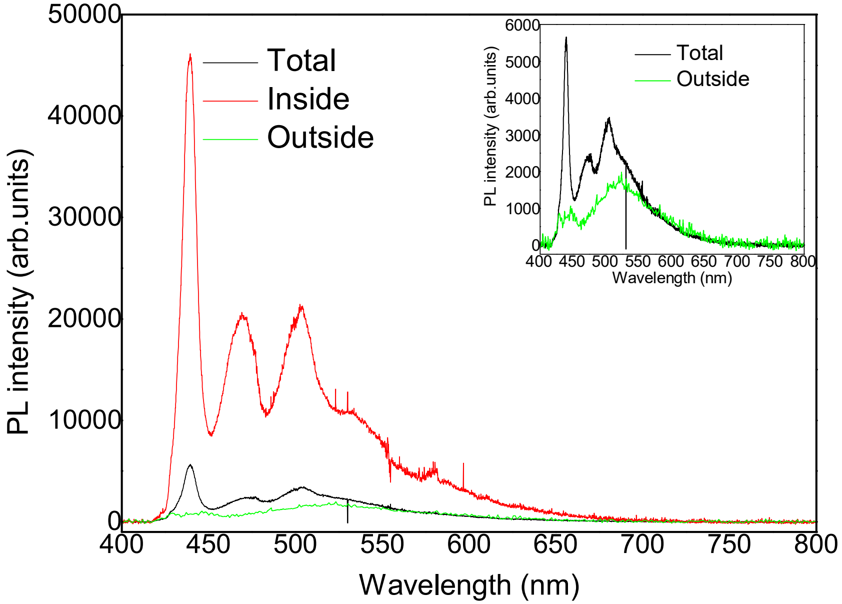


* E. Leveugle and L.V. Zhigilei, J. Appl. Phys. 102, 074914 (2007)

MAPLE: a really simple evaporative process?

Droplet landing velocity vs morphology





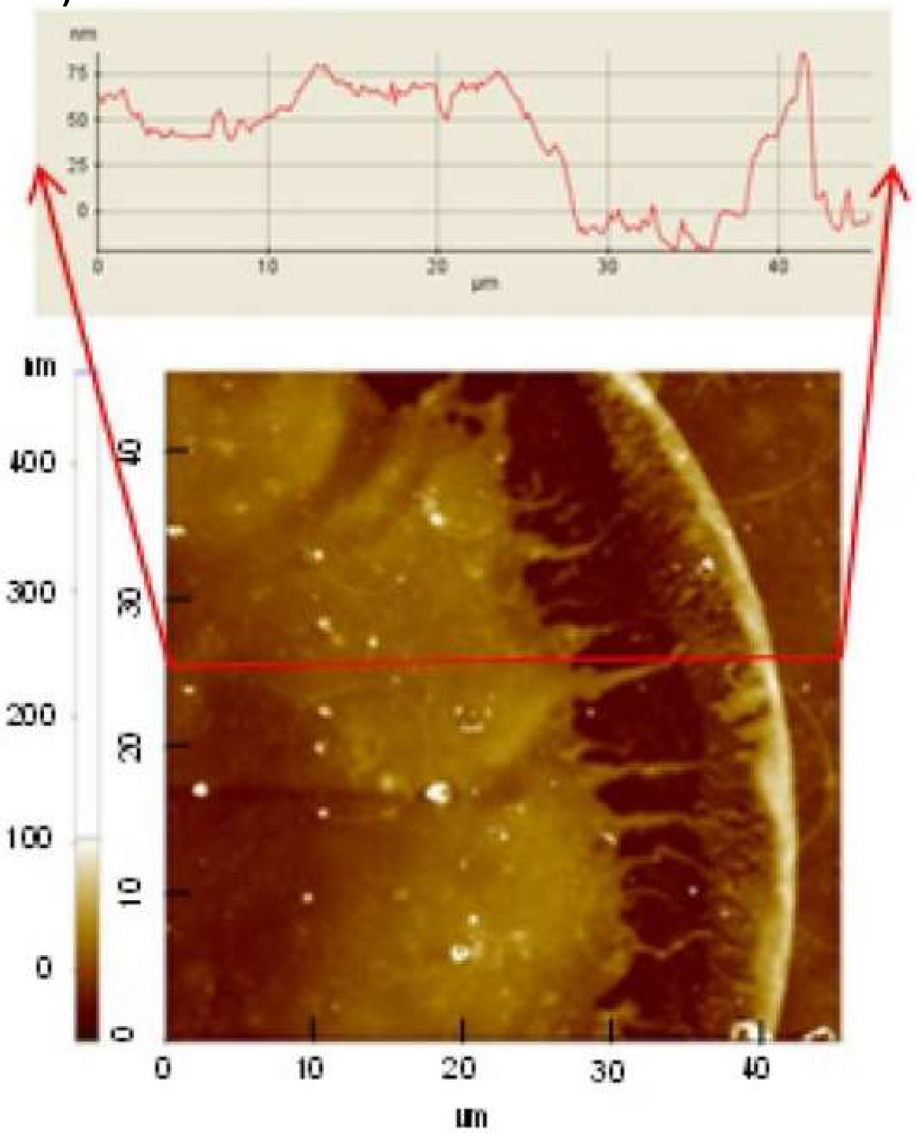
A.P. Caricato Appl. Phys. B (2015) 119:453–461

MAPLE: a really simple evaporative process?

Droplet landing velocity vs morphology

(poly(9,9-dioctylfluorene) — PFO film

Fluence 450 mJ/cm^2



coffee ring evaporation model

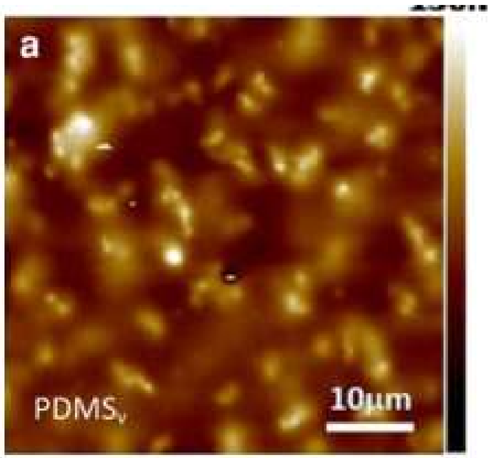
A.P. Caricato, Appl. Phys. B (2015) 119:453

MAPLE: a really simple evaporative process?

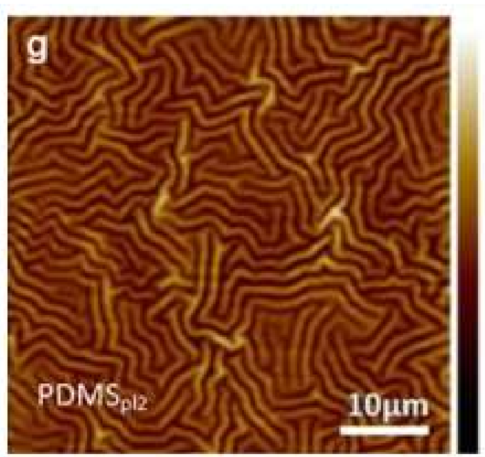
From the simulations → part of the solvent reaches the substrate.

This aspect has been observed experimentally using a substrate (6 cm) on which a polymer (polydimethylsiloxane-PDMS) “sensitive” to the solvent has been used as test and placed in front of the substrate

A frozen toluene target was irradiated with an excimer laser at the conventional fluences used in MAPLE depositions (60-250 mJ/cm^2)



Unexposed



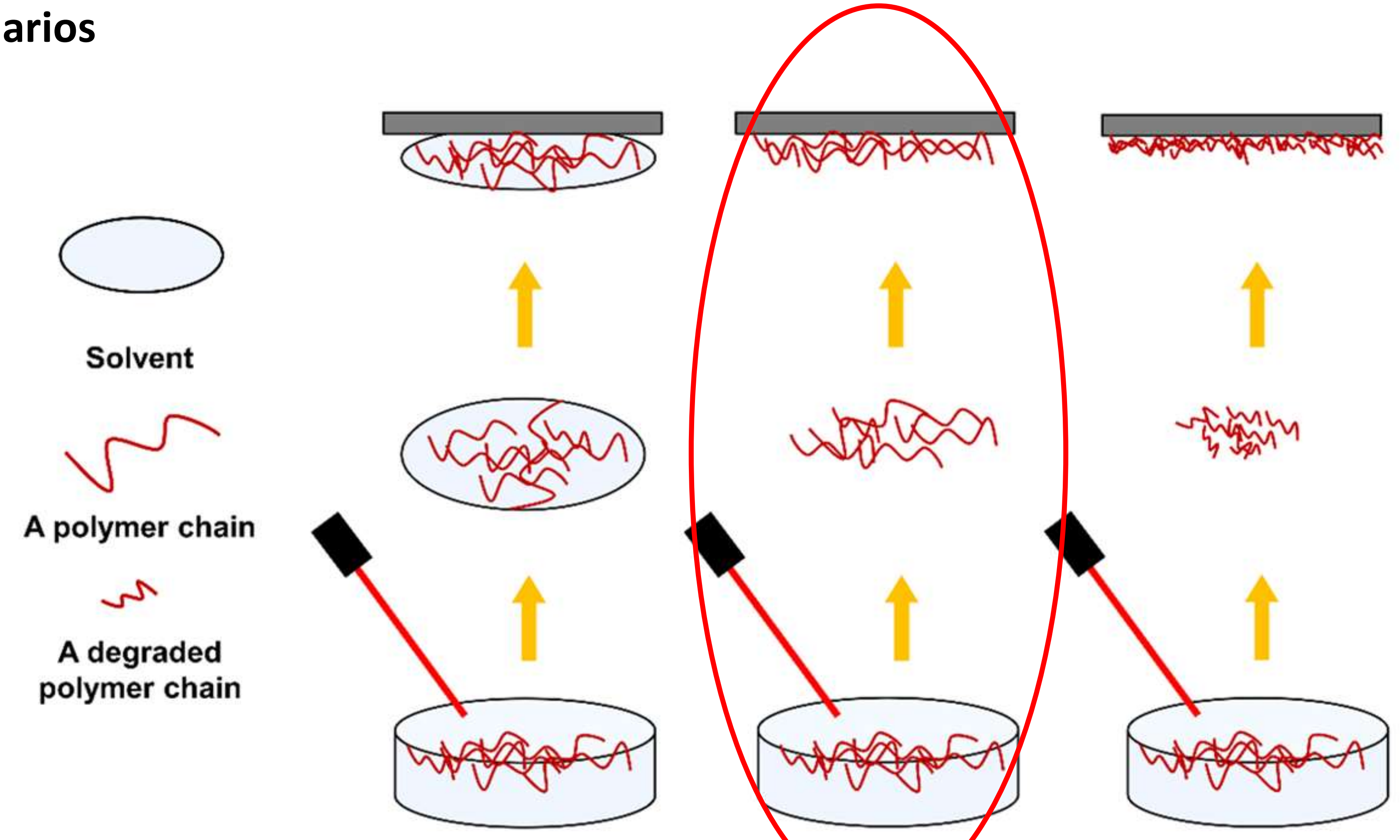
Exposed

The solvent, if sufficiently volatile, is not present in liquid phase at the substrate position, but in form of vapor molecules (neutral, ionized and possibly dissociated)

A.P. Caricato et al. Appl. Phys. B 113, 463 (2013)

MAPLE: influence of deposition parameters

The use of a solvent matrix to absorb laser energy leads to three possible deposition scenarios



laser energy is not able to completely vaporize the frozen solvent matrix

laser energy is completely and solely absorbed by the solvent matrix

the laser energy is absorbed by both the solvent matrix and target polymer

MAPLE: relevant applications/properties

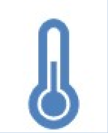
What is important for a successful applications?

N. Bulkakova 1Q

Control

MAPLE: influence of deposition parameters

The choice of the right deposition parameters can play important roles in determining which deposition scenario occurs.
The main involved deposition parameters are:

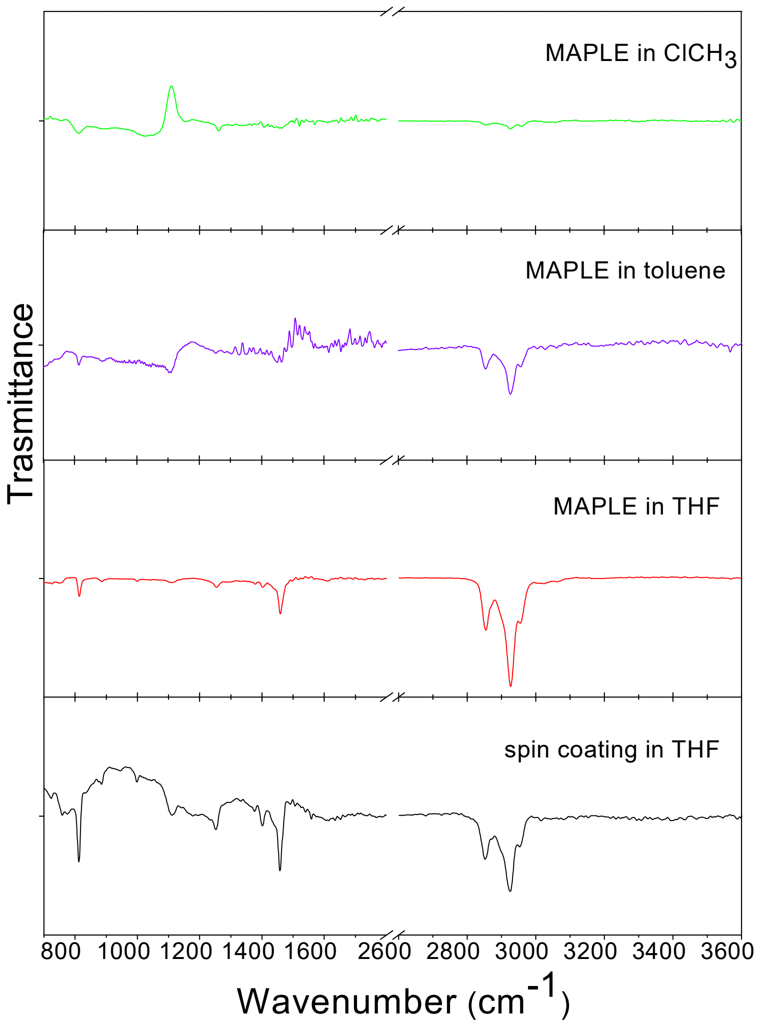
Laser parameters		Wavelength
		Fluence
		Pulse duration
Solvent		**Volatility**
		Absorption properties
		Capacity to dissolve the solute
		Chemical stability
Solute		Molecula weight
		Wt%
Substrate		Substrate temperature
		Target-substrate distance
		…..

MAPLE: influence of deposition parameters

Role of the kind of solvent on the polymer structure and integrity

Poly(9,9-dioctylfluorene) - (PFO)

FTIR spectra



F = 200 mJ/cm^2, polymer concentration 0.5 wt%

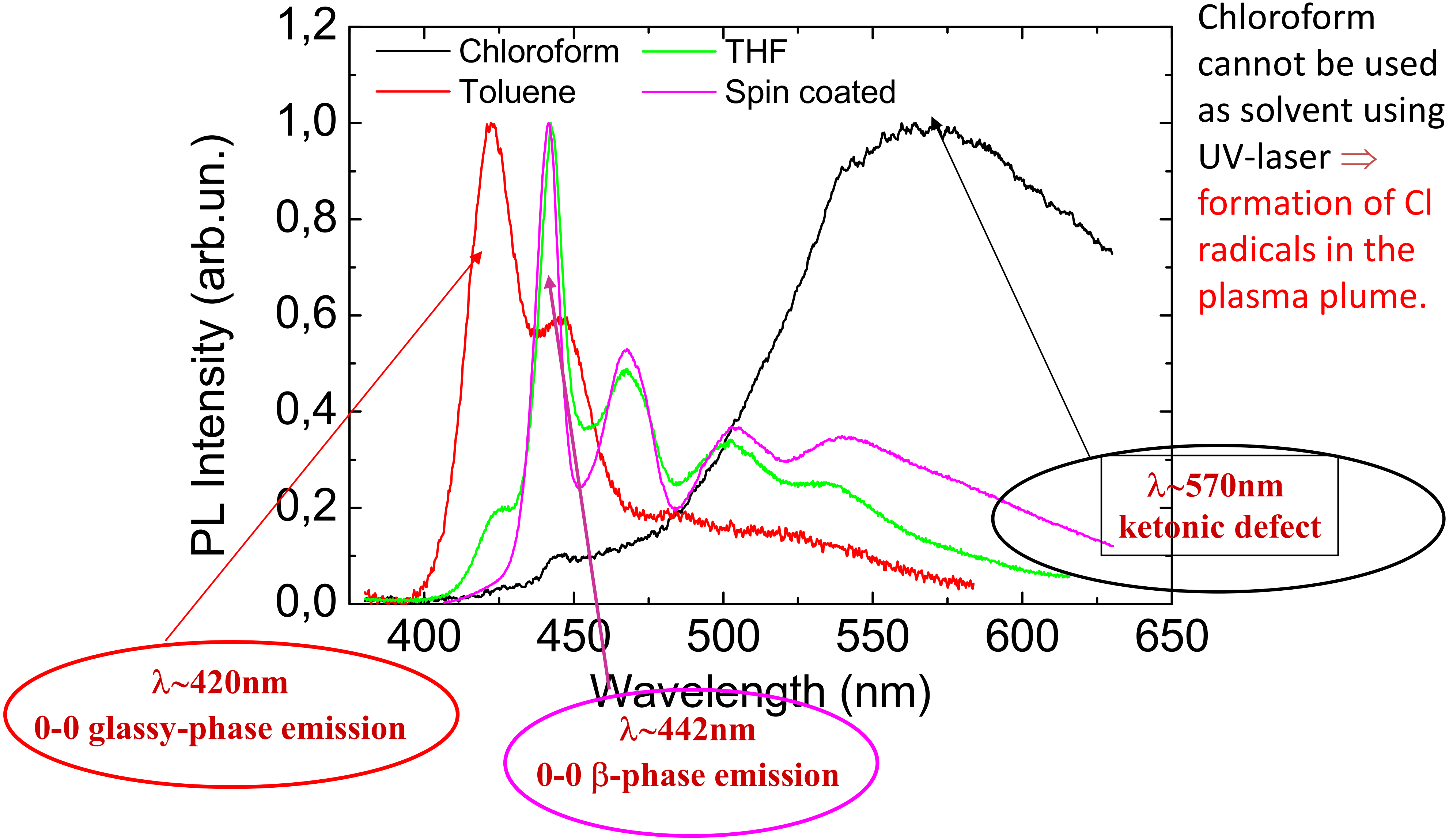
The sample deposited starting from chloroform solution does not present the PFO characteristic peaks!

T. Tunno, et al, Appl. Surf. Sci. 253 (2007) 6461.

MAPLE: influence of deposition parameters

Role of the solvent on the polymer structure and integrity

Poly(9,9-dioctylfluorene) - (PFO)

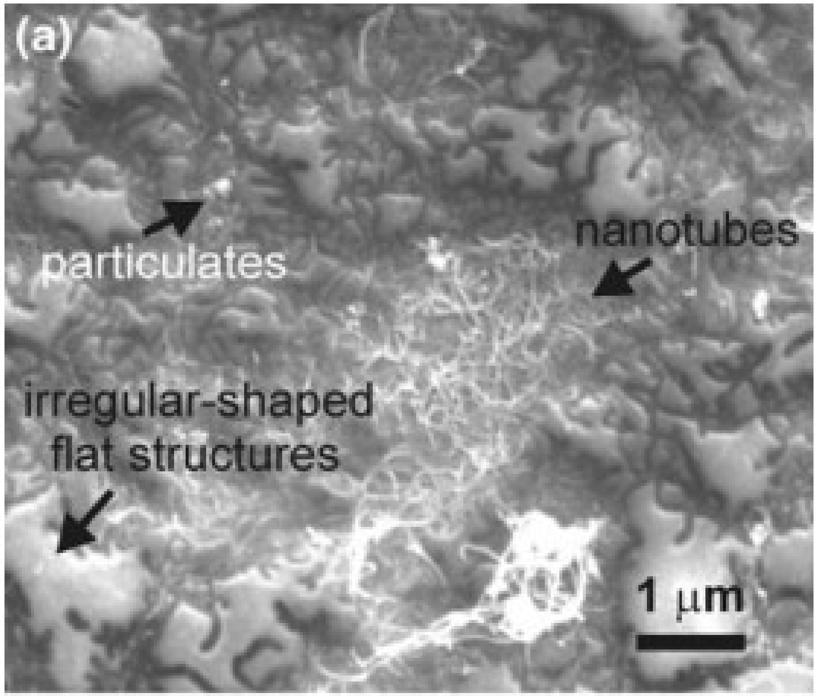


Chloroform cannot be used as solvent using UV-laser ⇒ formation of Cl radicals in the plasma plume.

MAPLE: influence of deposition parameters

Role of the solvent

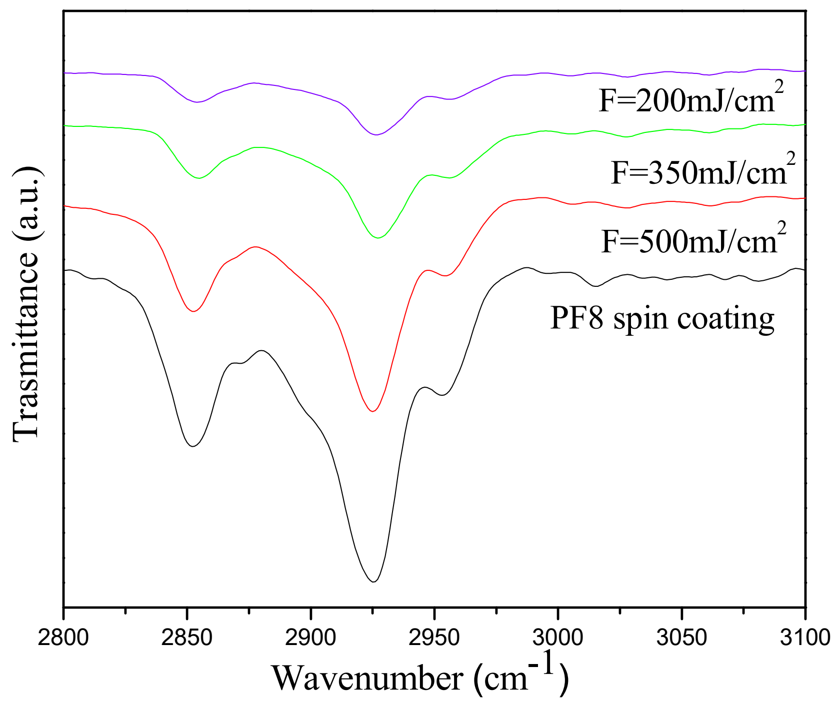
….however also conventionally and volatile used solvents, like toluene, are responsible of the co-deposition of organic material which can be successively removed by UV-Ozone etching



E. Gyorgy et al, J. Nanopart. Res. (2013) 15:1852

MAPLE: influence of deposition parameters

Role of the laser fluence on the polymer structure and integrity



FTIR spectra

PFO films deposited by spin coating and MAPLE at different laser fluences. The solvent: toluene

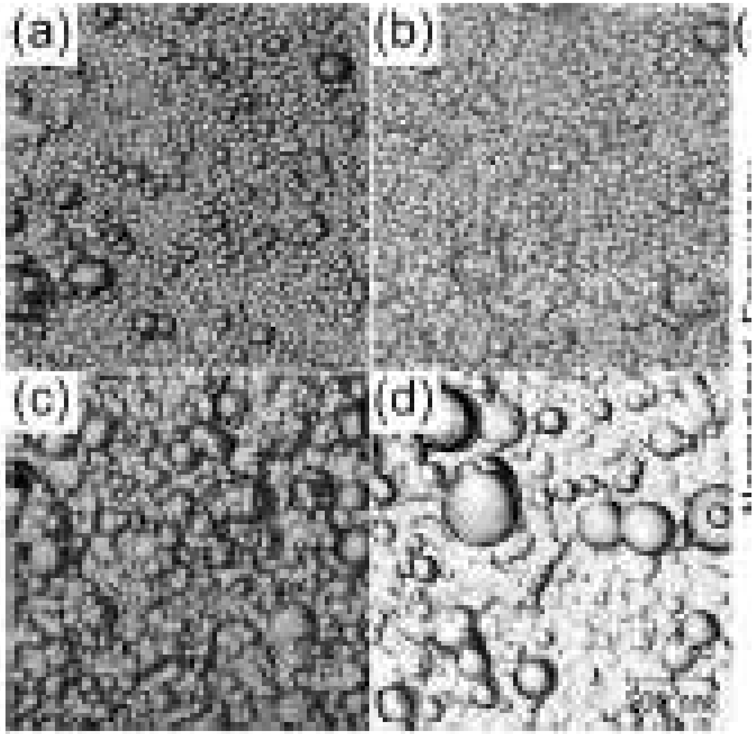
The increase of laser fluence (up to 500 mJ/cm^2) does not influence the spectra features but influences the film thickness.

MAPLE: influence of deposition parameters

Polymer concentration

AFM images of PMMA.

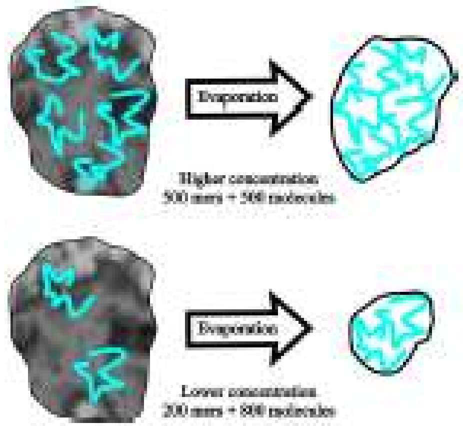
0.05 wt%



0.1 wt%

0.5 wt%

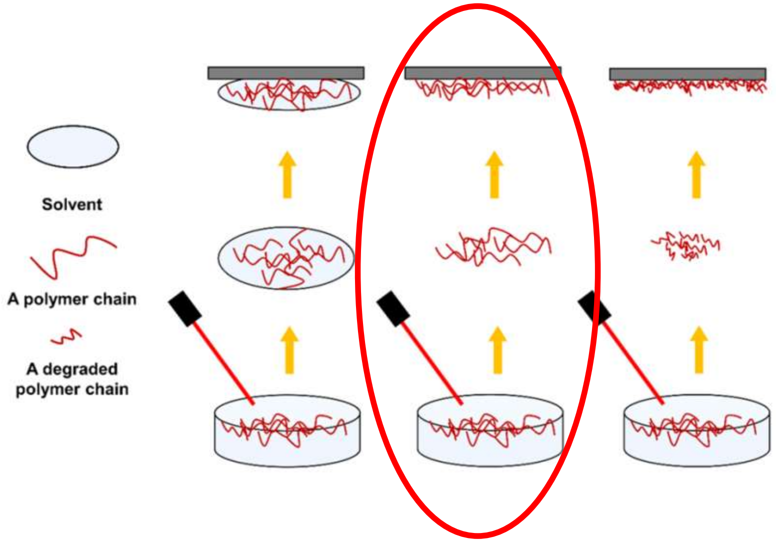
1 wt%



As solvent evaporates, polymers assemble and/or collapse forming globular clusters to optimize the attractive bead-bead interactions.

K.B. Shepard, et al., Appl. Phys. Lett. 103, 123105 (2013)

Resonant Infrared MAPLE (RIR-MAPLE)

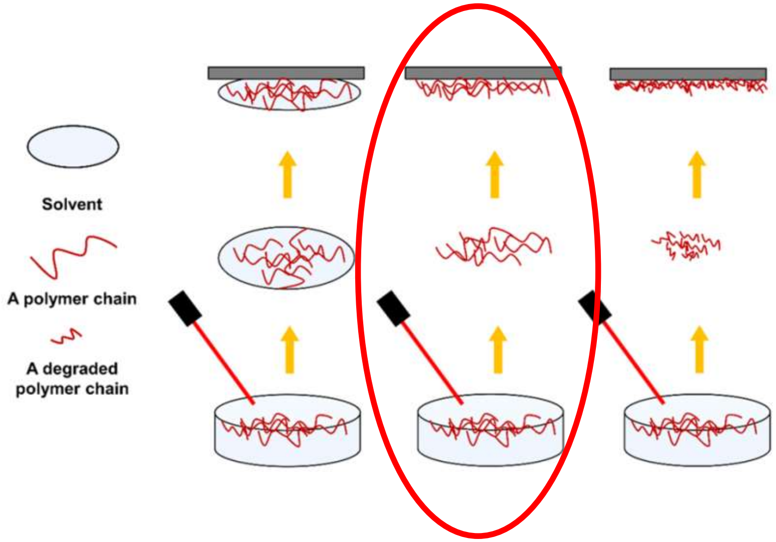


How is it possible to minimize the damage induced by laser material-interaction?

Tune the laser wavelength to be resonant only with molecular vibrational modes in the solvent matrix that are not present in the polymer to be deposited.

Resonant Infrared MAPLE (RIR-MAPLE)

Resonant Infrared MAPLE (RIR-MAPLE)



O-H bending and C-H stretch vibrations: 10 µm (**CO_2 laser**)

C=O stretch vibrations: between 5.5 and 6.5 μm (**FEL**)

O-H or N-H stretch vibrations : ~ 3 µm (**Er:YAG laser**)

Moreover, for a given organic target material, the chosen solvent matrix must also account for the solubility of the organic material

R. D. Torres, Critical Reviews in Solid State and Materials Science 36, 16 (2011)

Resonant Infrared MAPLE (RIR-MAPLE)

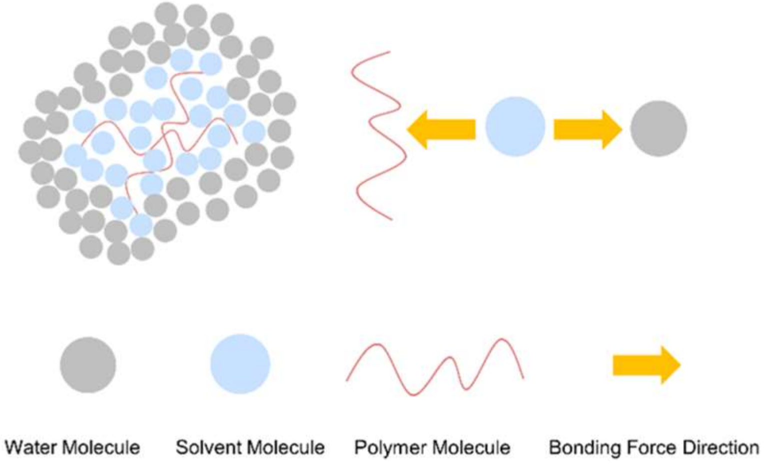
To help make RIR-MAPLE a more universal technique that can deposit most organic material systems, Pate, et. al. developed a novel approach to prepare the deposition target.

emulsion-based RIR-MAPLE

Instead of using a frozen solution, a frozen emulsion, or mixture of two or more liquids that are normally immiscible, is used as the deposition target

Good idea but you have a prize to pay!

A very complex target material

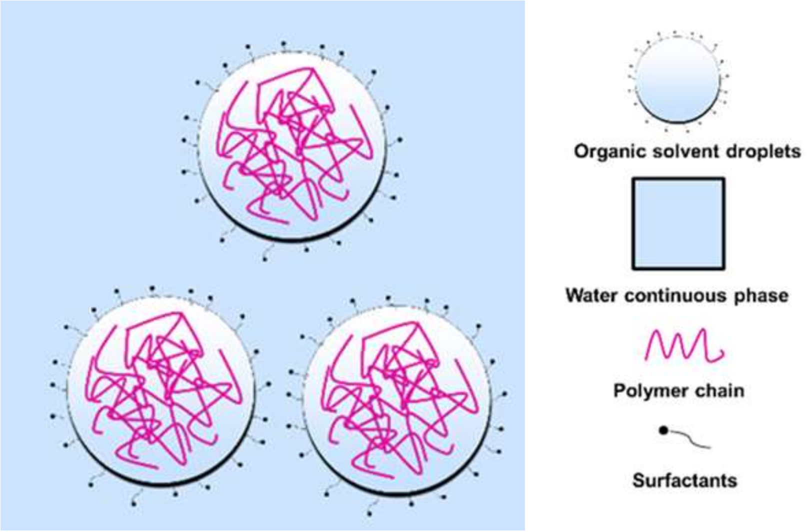


More difficult to control!!

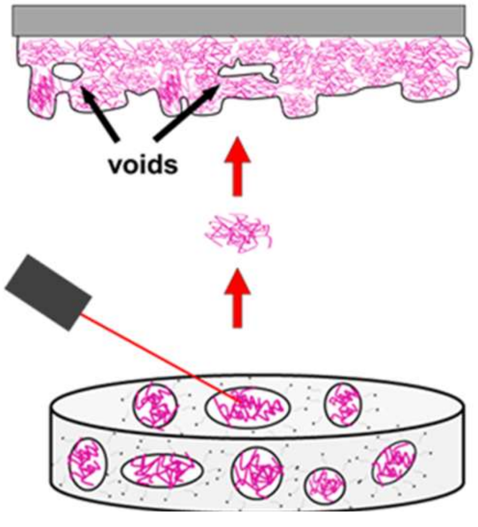
Resonant Infrared MAPLE (RIR-MAPLE)

The composition of an emulsion for the deposition of an hydrophobic polymer by RIR-MAPLE is

✓ guest organic material (0,5 wt%);
✓primary solvent (to dissolve the guest material. These solvents generally have a high vapor pressure);
✓deionized (DI) water (to enrich the hydroxyl (OH) bond concentration);
✓Surfactant ~ 0.001 wt. % (to stabilize the emulsion for flash freezing).



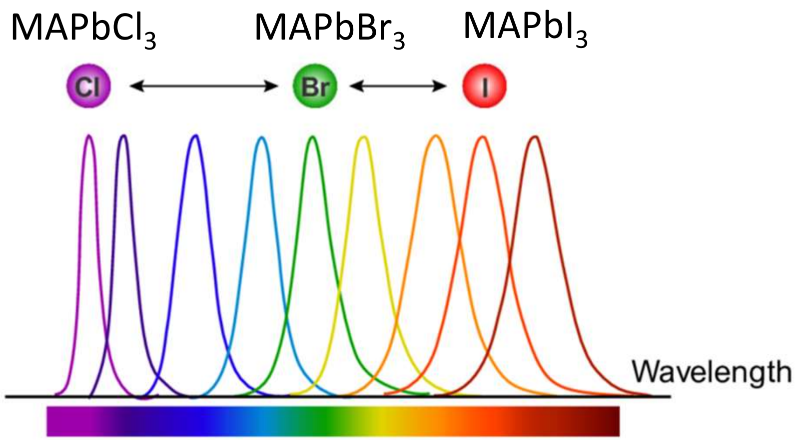
Deposition mechanism

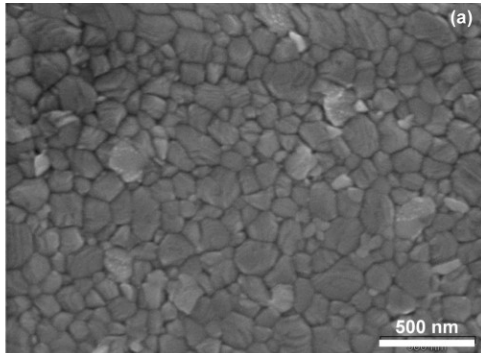


The film deposited from the frozen emulsion target results from the cluster-by-cluster stacking of the polymer

Resonant Infrared MAPLE (RIR-MAPLE)

Hybrid organic-inorganic perovskite (HOIP) deposition by emulsion based RIR_MAPLE





Target: stoichiometric ratio of precursor materials in a 1:1 (by volume) mixture of DMSO:MEG.

Dimethyl sulfoxide (DMSO) = primary solvent

Monoethylene glycol (MEG), with two hydroxyl bonds, is used to provide multiple functions within the target solution

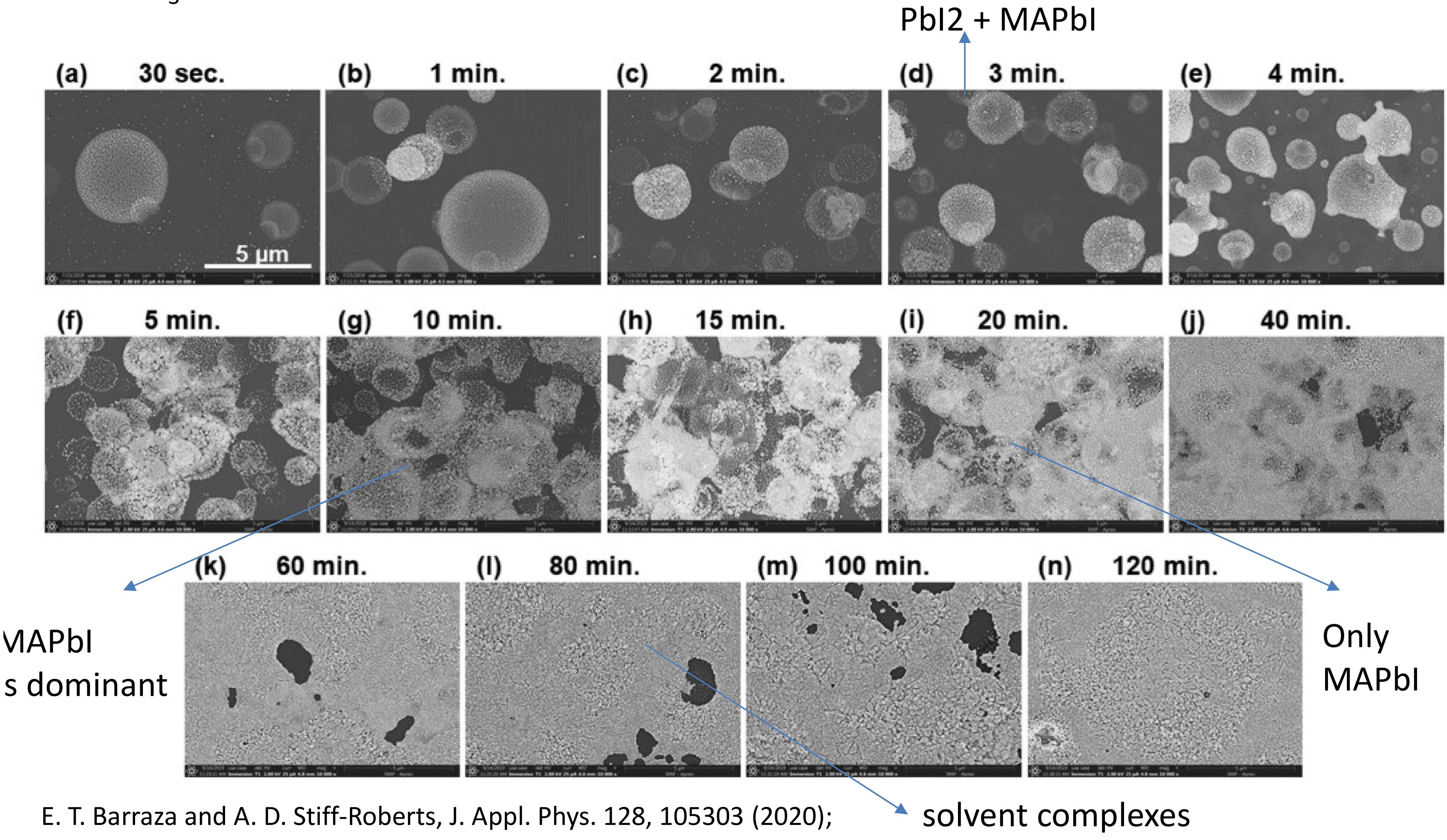
HOIP precursor materials are transferred intact and the desired crystal forms on the substrate after deposition.

E. T. Barraza and A. D. Stiff-Roberts, J. Appl. Phys. 128, 105303 (2020);

Resonant Infrared MAPLE (RIR-MAPLE)

Hybrid organic-inorganic perovskite deposition by emulsion based RIR_MAPLE

$MAPbI_3$ dense concentration

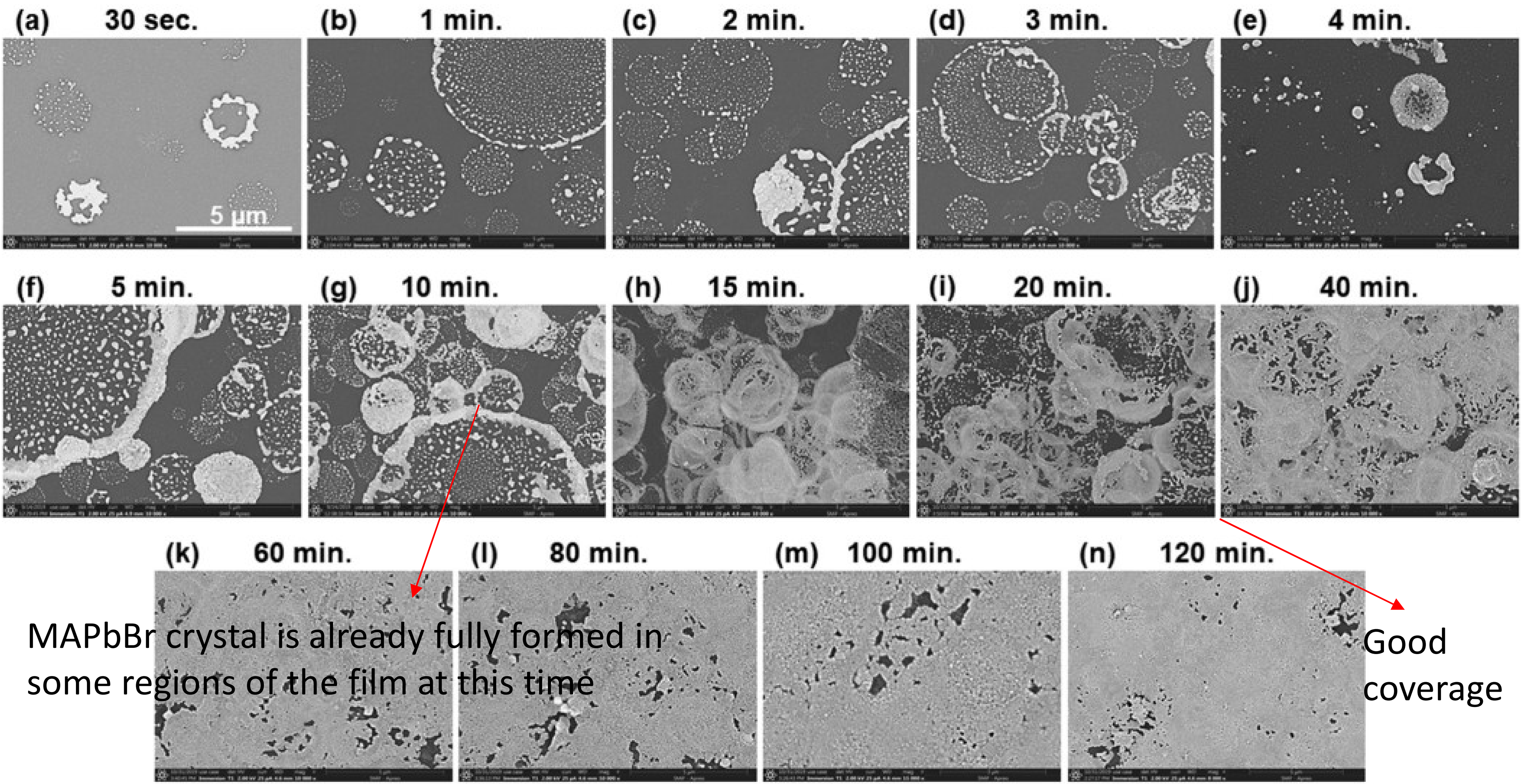


E. T. Barraza and A. D. Stiff-Roberts, J. Appl. Phys. 128, 105303 (2020);

Resonant Infrared MAPLE (RIR-MAPLE)

Hybrid organic-inorganic perovskite deposition by emulsion based RIR_MAPLE

$MAPbBr_3$ sparse concentration of material

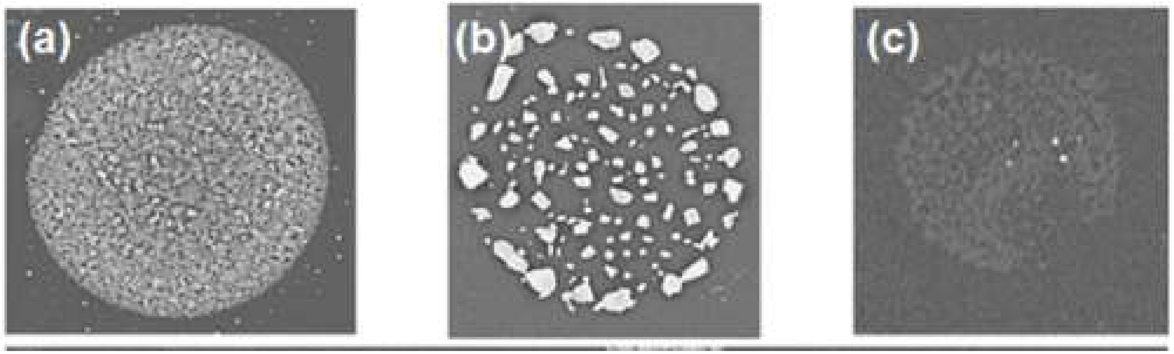


MAPbBr crystal is already fully formed in some regions of the film at this time

Good coverage

E. T. Barraza and A. D. Stiff-Roberts, J. Appl. Phys. 128, 105303 (2020);

Resonant Infrared MAPLE (RIR-MAPLE)



Dense Sparse Solvent Droplets

MAPI film forms later

The contact angle decreases with decreasing halide atomic number

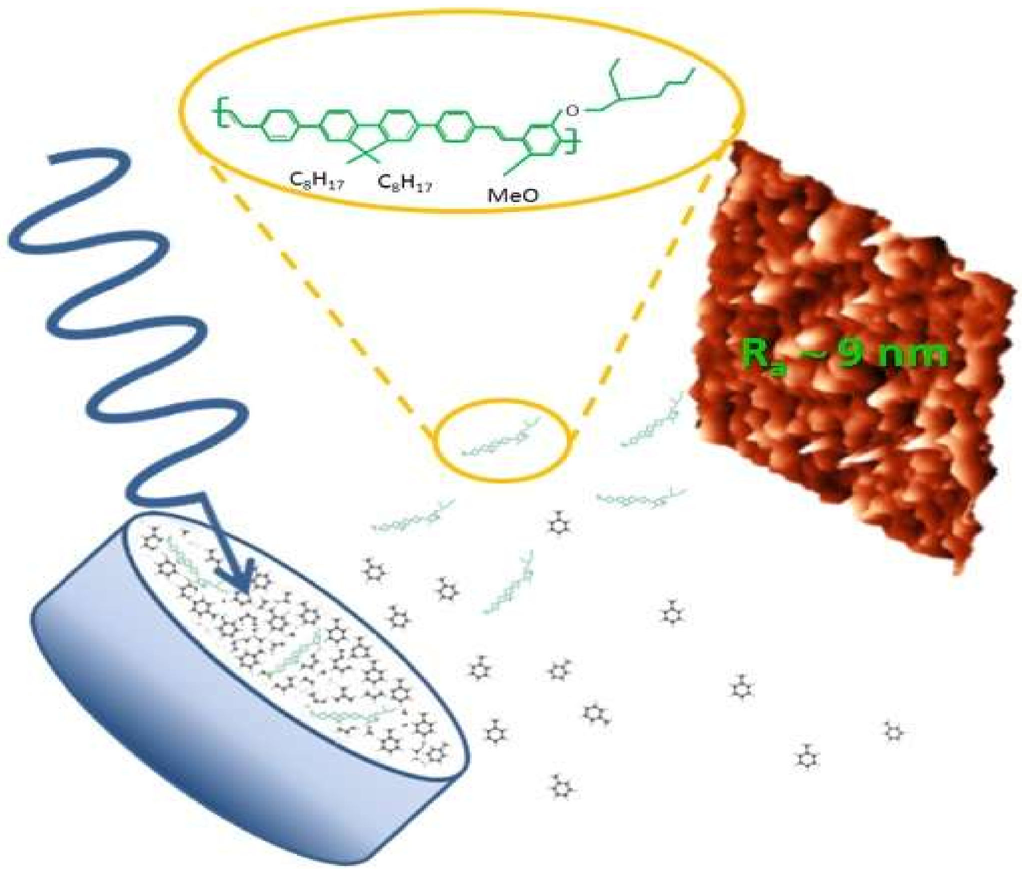
Gibbs free energy of formation for each HOIP system, which decreases with decreasing halide atomic number

the dense droplets of MAPbI result from less surface wetting and slower crystal nucleation/formation, while the sparse droplets of MAPbBr and MAPbCl result from more surface wetting and faster crystal nucleation/formation

E. T. Barraza and A. D. Stiff-Roberts, J. Appl. Phys. 128, 105303 (2020);

MAPLE

Applications



MAPLE: relevant applications/properties

Maple deposition of bilayer/trylayer structures

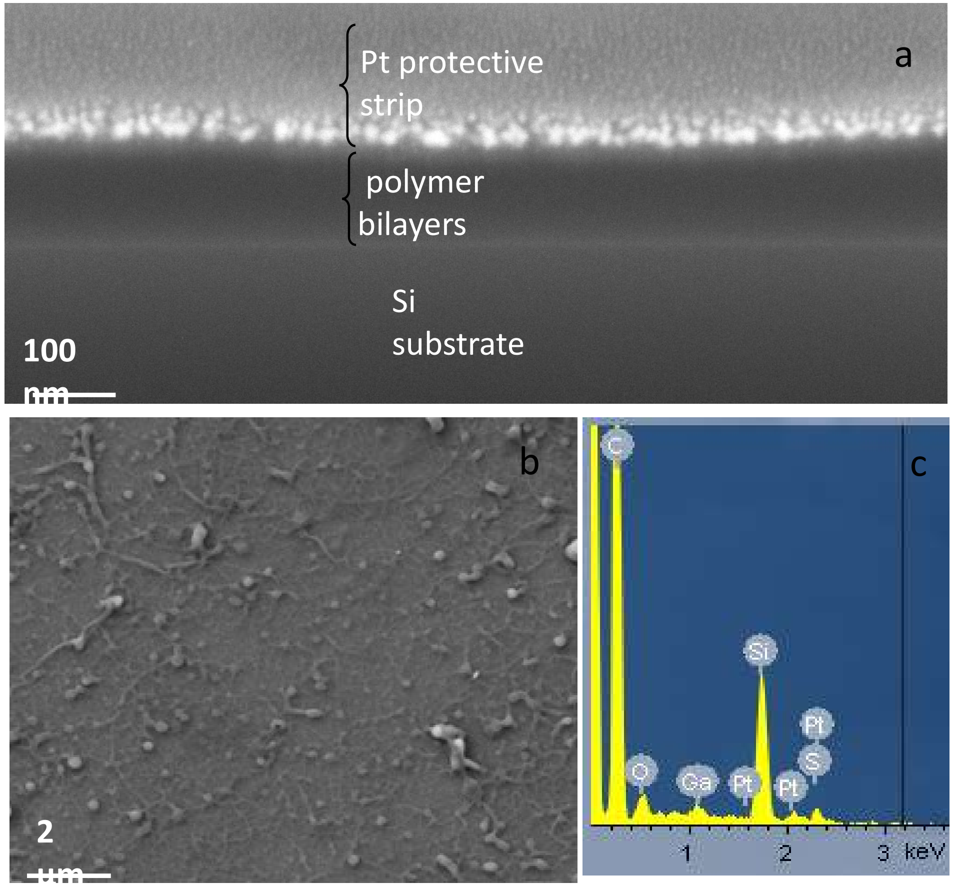
The fabrication of polymer multilayer is not an easy tasks with conventional deposition techniques since an underlying layer can be damage by spin coating the overlying layer.

What about MAPLE?

MAPLE: relevant applications/properties

Maple deposition of bilayer/trylayer structures

A poly-(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM) bilayer structure has been realized by single step matrix-assisted pulsed laser evaporation (ss-MAPLE) technique using the **same solvent** (toluene) for both the polymers under vacuum conditions*.



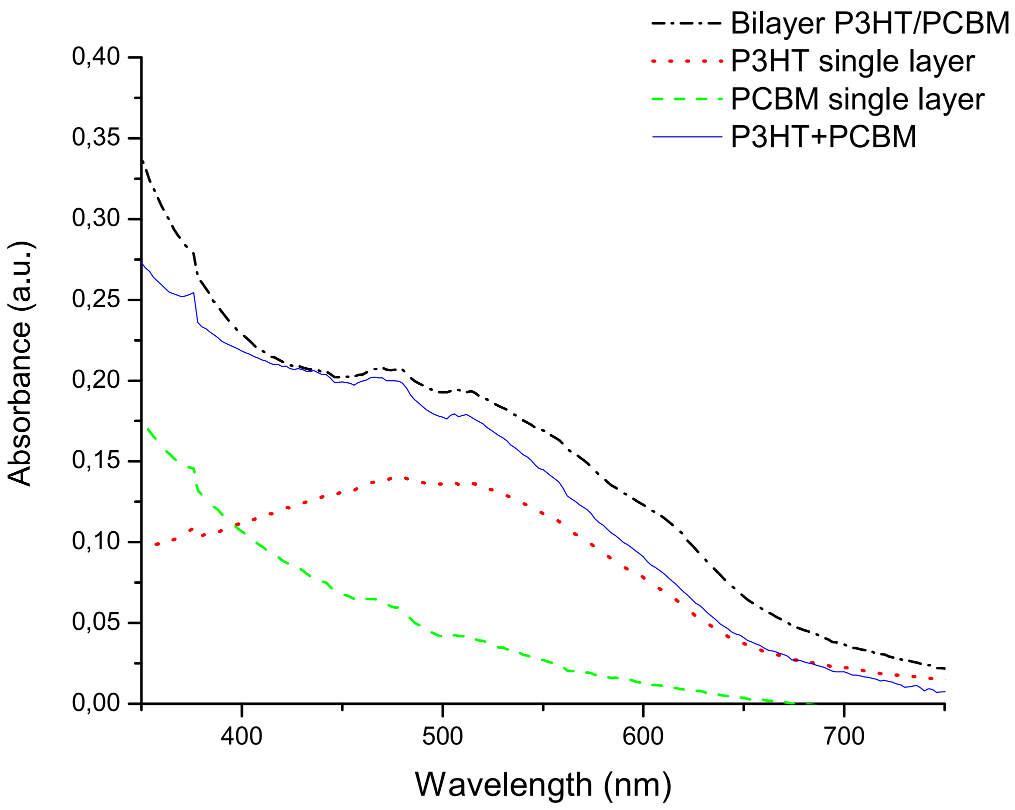
SEM cross section of the two layers

* A.P. Caricato et. al., Appl. Phys. Lett. 100, 073306 (2012)

MAPLE: relevant applications/properties

Maple deposition of bilayer structures

UV – Vis absorption spectra of the single layers P3HT or PCBM, and of the bilayer P3HT/PCBM



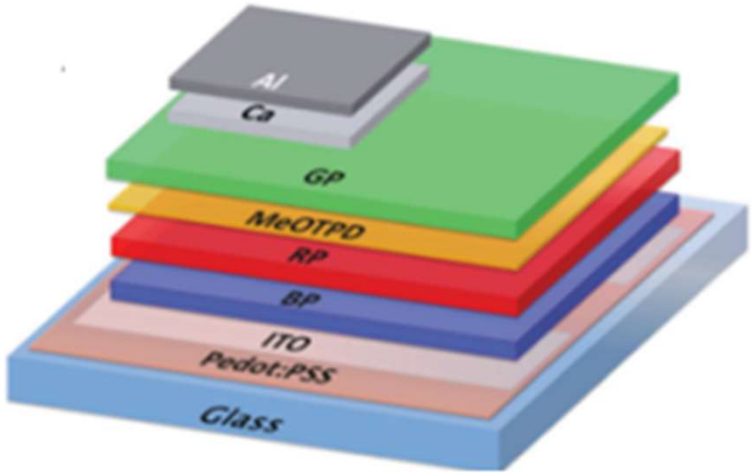
The arithmetical sum of the single layer spectra, labeled as P3HT+PCBM, well reproduces the behavior of the experimental spectrum for the bilayer structure

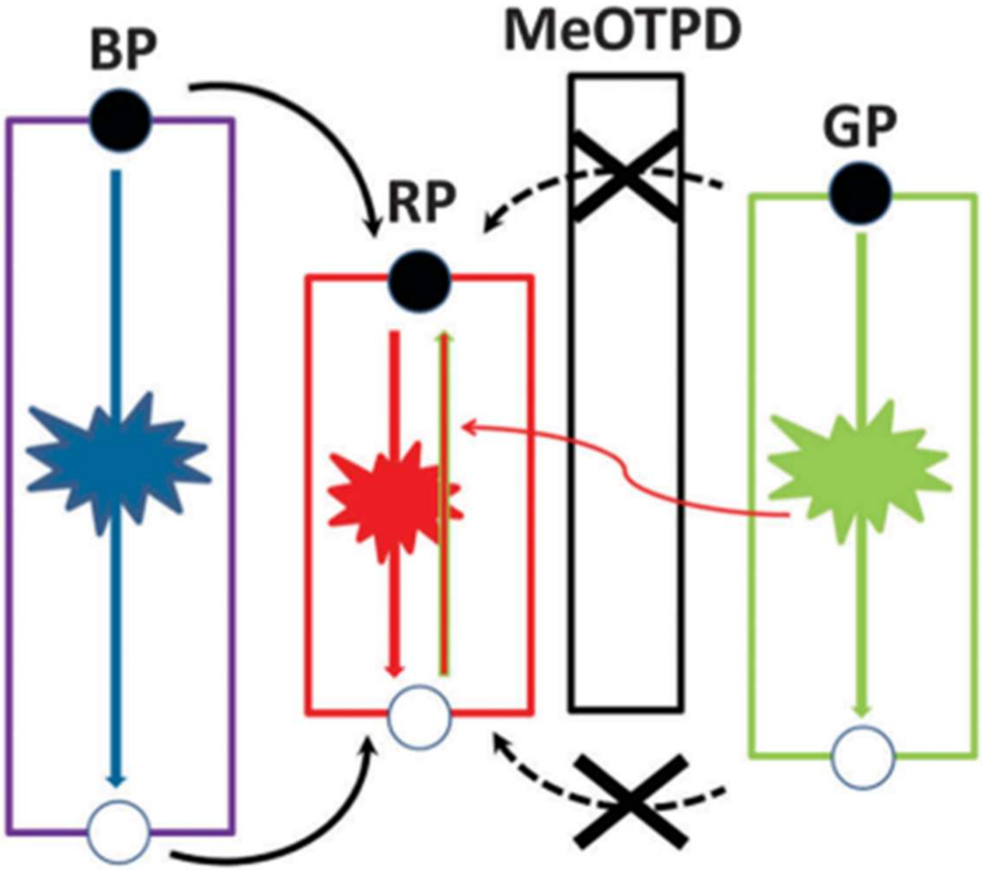
* A.P. Caricato et. al., Appl. Phys. Lett. 100, 073306 (2012)

MAPLE: relevant applications/properties

White multi-layered polymer light emitting diode through matrix assisted pulsed laser evaporation

First evidence of white emission by a heterostructured three-layer polymeric system





F. Mariano et al., J. Mater. Chem. C, 2016, 4, 7667--7674

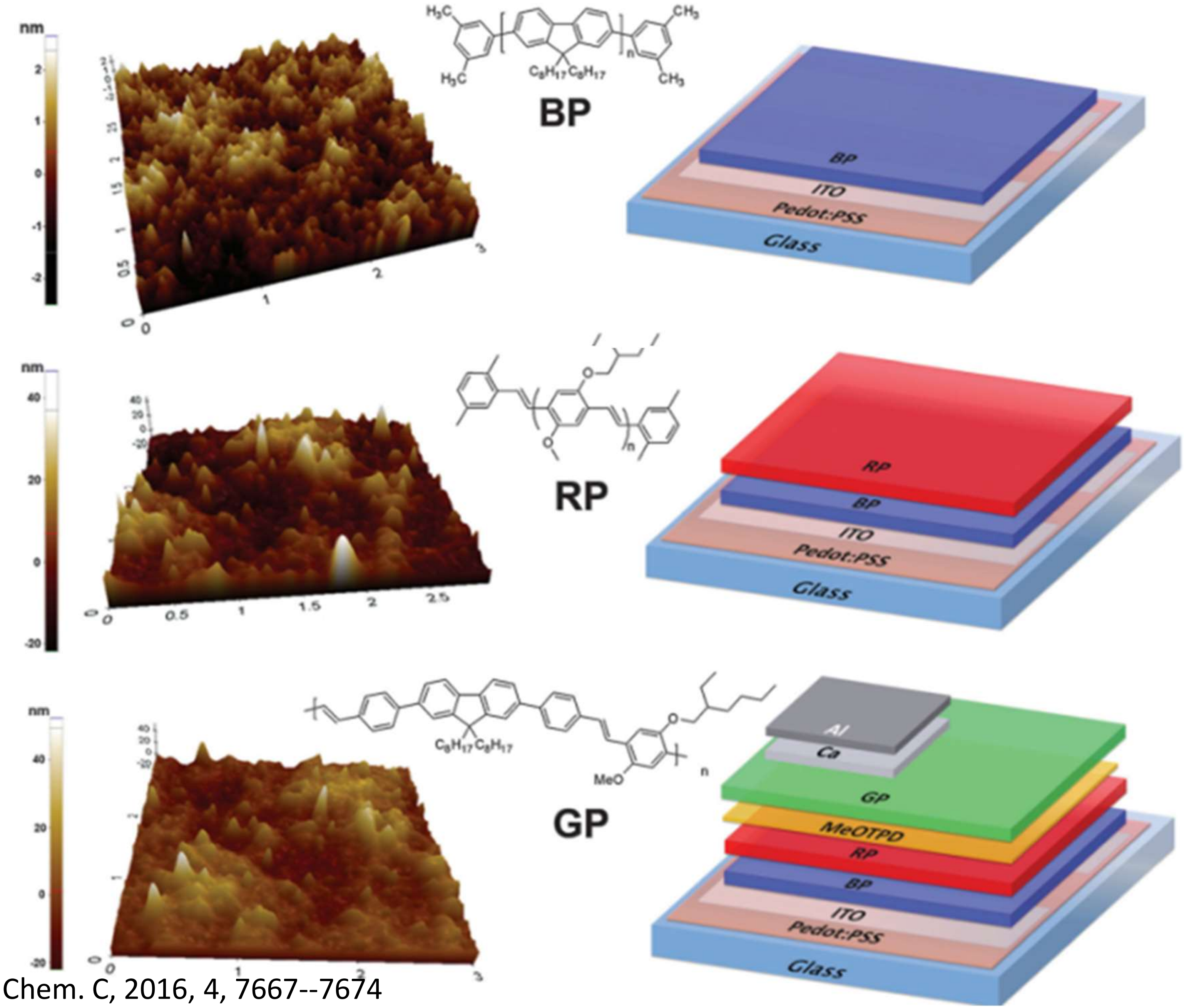
MAPLE: relevant applications/properties

White multi-layered polymer light emitting diode through matrix assisted pulsed laser evaporation

RMS-surface roughness: ~1 nm

RMS-surface roughness: 6.9 ±0.9 nm

RMS-surface roughness: 10.3 ±1.6 nm

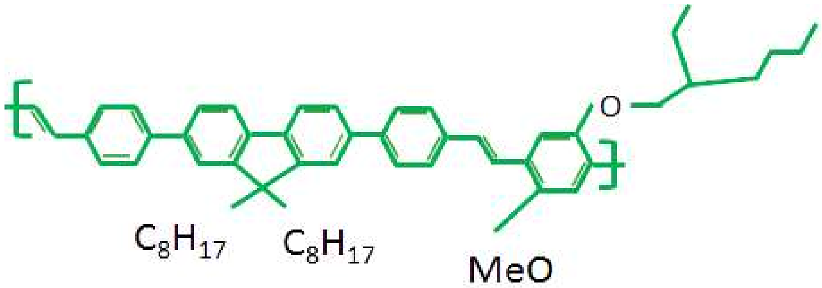


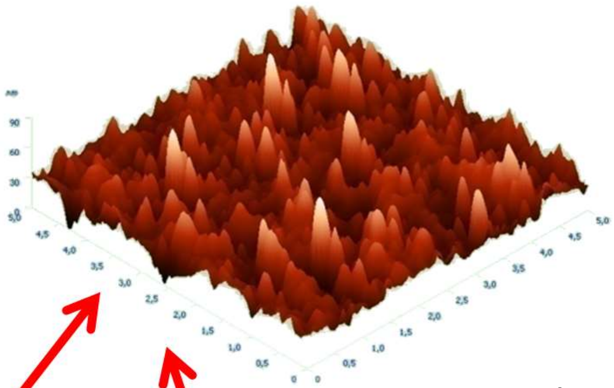
F. Mariano et al., J. Mater. Chem. C, 2016, 4, 7667--7674

MAPLE: influence of deposition parameters

White multi-layered polymer light emitting diode through matrix assisted pulsed laser evaporation

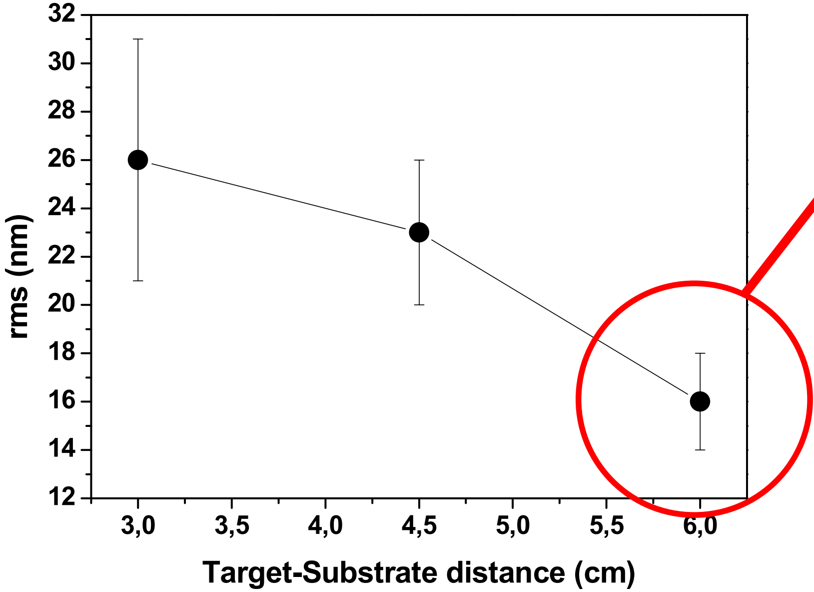
Polymer concentration

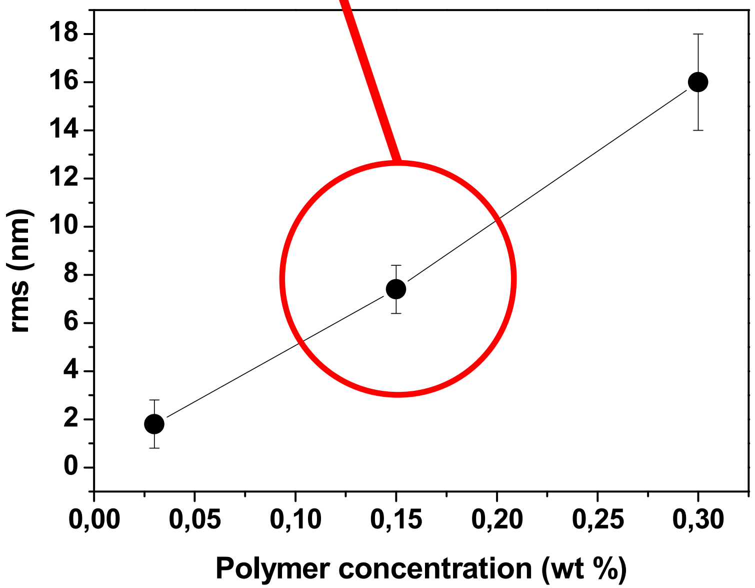




~ 7 nm (film thickness 40 nm)

poly[9,9-dioctylfluorenylene-2,7-diyl)co-(1,4-diphenylene-vinylene-2-methoxy-5-2{-ethylhexyloxy}-benzene)] in toluene



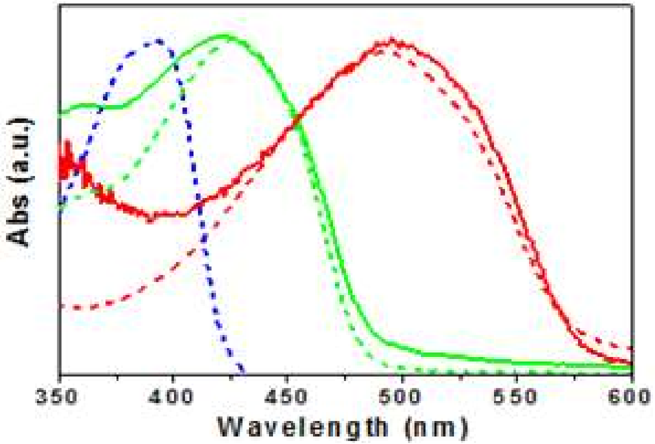


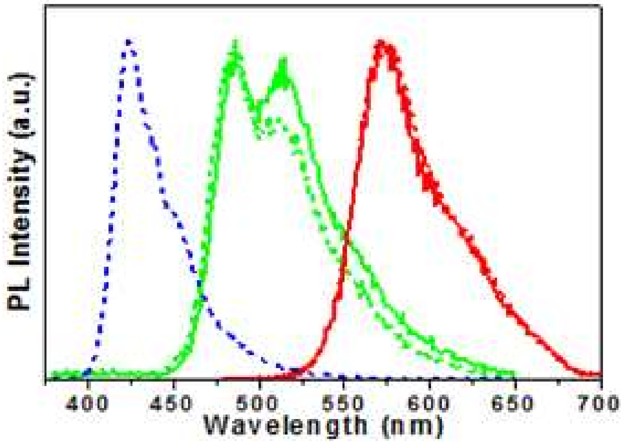
A.P. Caricato et. al. J. Phys. D: Appl. Phys. **48** 135501 (2015)

MAPLE: relevant applications/properties

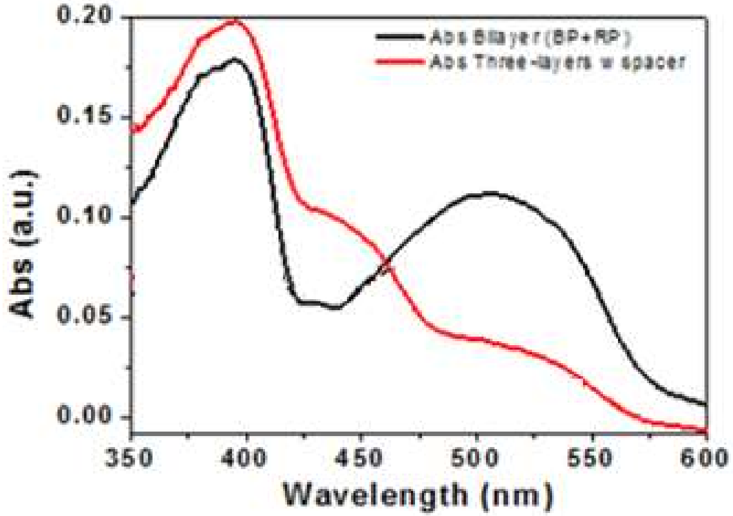
MAPLE deposition of trylayer structure and device realization

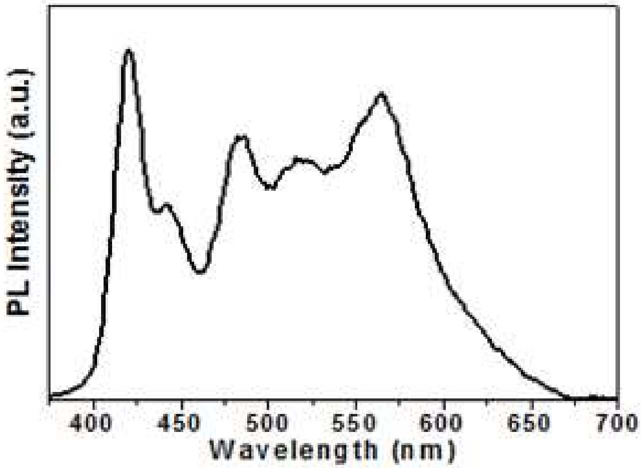
Single layers: spin coating (dot line) and MAPLE (full line) comparison





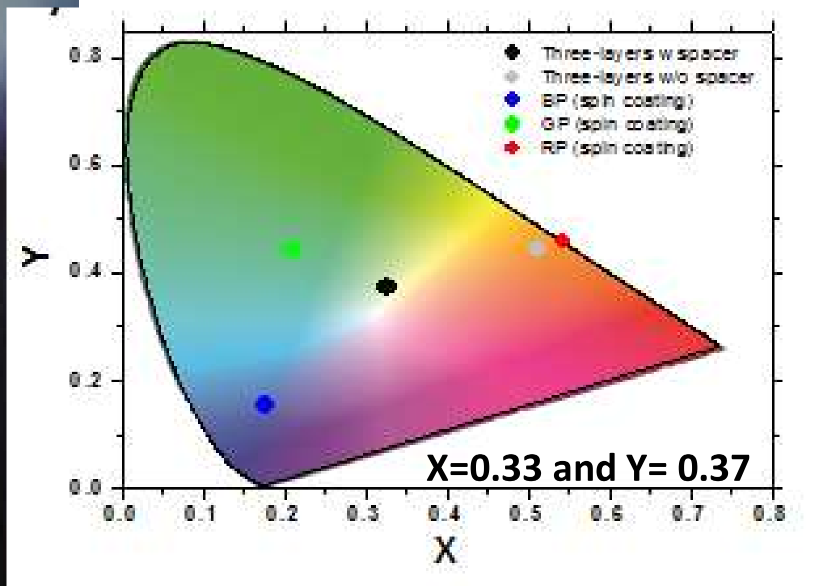
Multilayers





The contribution by all the layers is present!

Luminancece 200 cd/cm^2; CRI=70



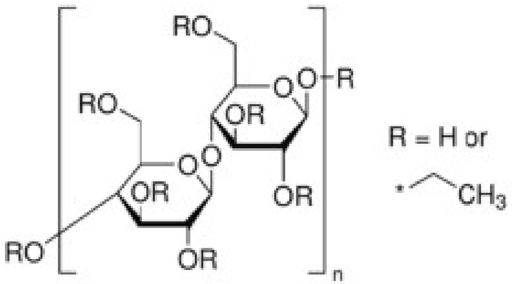
F. Mariano, A. P. Caricato, J. Mater. Chem. C, 2016, 4, 7667

MAPLE: relevant applications/properties

MAPLE deposition of polymer blends

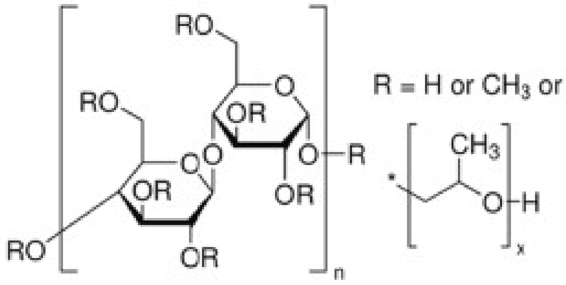
Laser engineered polymer thin flms as drug delivery systems

Transdermal patches are alternative drug delivery systems, which are applied on the skin and are able to provide the controlled release of a drug, for the systemic treatment of the disease



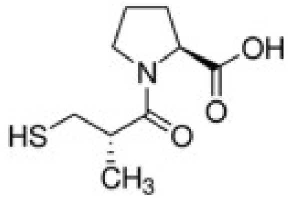
EC

ethylcellulose

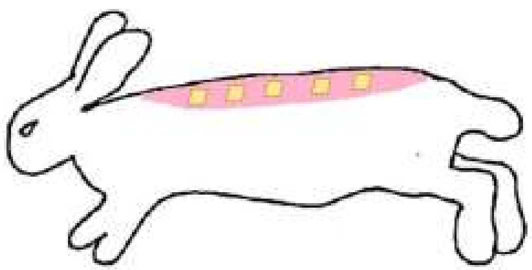


HPMC

Hydroxypropyl methylcellulose (HPMC)



Captopril

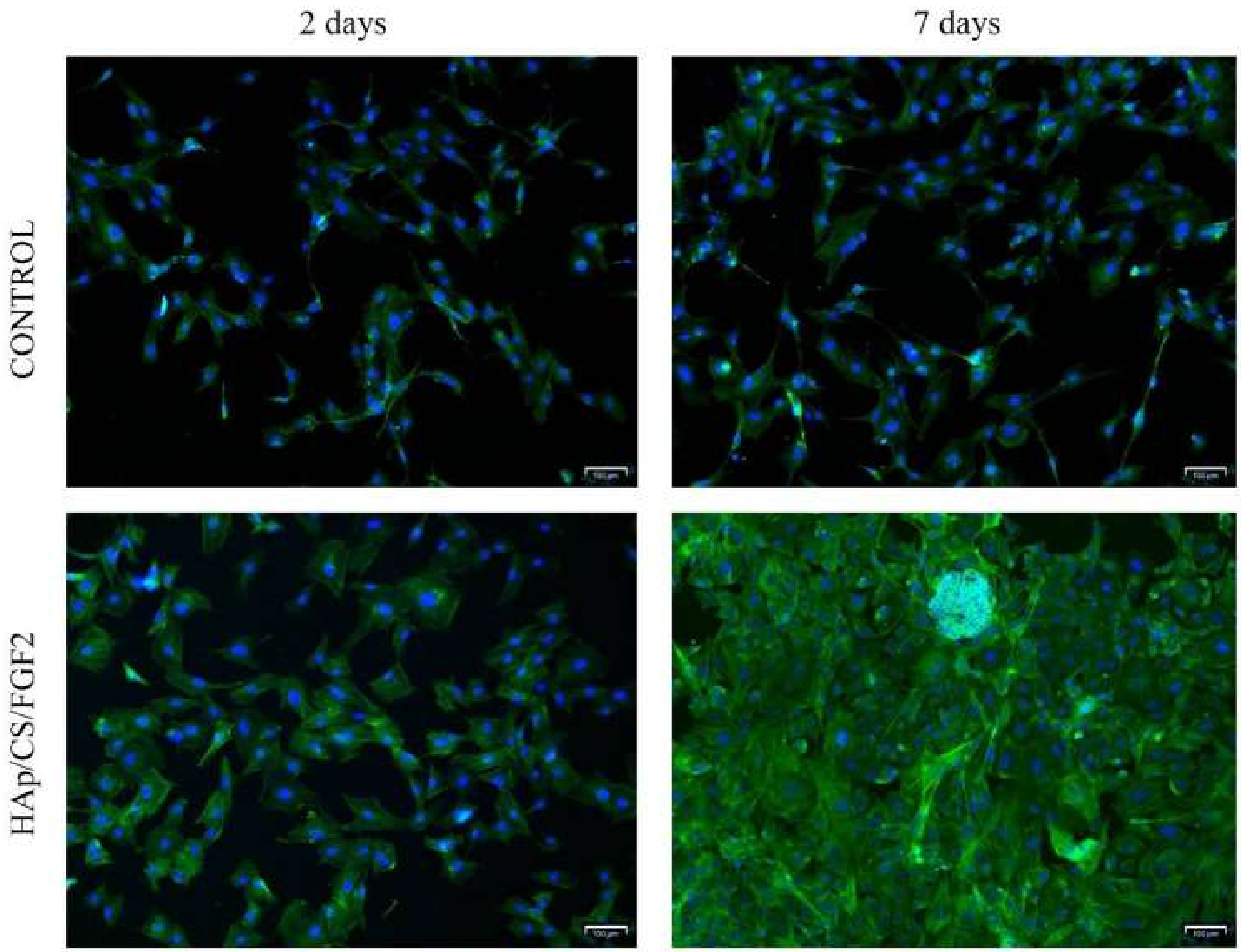


A. Bonciu et al, Applied Physics A (2023) 129:327

MAPLE: relevant applications/properties

MAPLE deposition of polymer blends

Laser engineered polymer thin flms for bone tissue engineering



Polymers 2022, 14, 2934

MAPLE variant: deposition of colloidal nano-particles/rods

The MAPLE technique can be used to deposit only polymers and biomaterials?

MAPLE variant: deposition of colloidal nano-particles/rods

The MAPLE technique can be used to deposit nanoparticles and nanonorods films starting from solution of colloidal nanoparticles (nanorods) which are relatively easy and cheap to fabricate.

Colloidal nanoparticles of very different materials are fabricated by laser ablation and chemical routes with very small sizes and low size dispersion.

The nanoparticle solution, once frozen to liquid nitrogen temperature, can be used as target to be laser-irradiated.

MAPLE variant: deposition of colloidal nano-particles/rods

What new and/or different?

The nanofluids present high thermal diffusivity*: no thermal confinement

The solute generally highly absorbs the laser radiation and contributes to the heating of the target

Nanomaterials are characterized by low metling temperature**: possible modification of the size and shape of the nanostructures to be transferred for this reason.

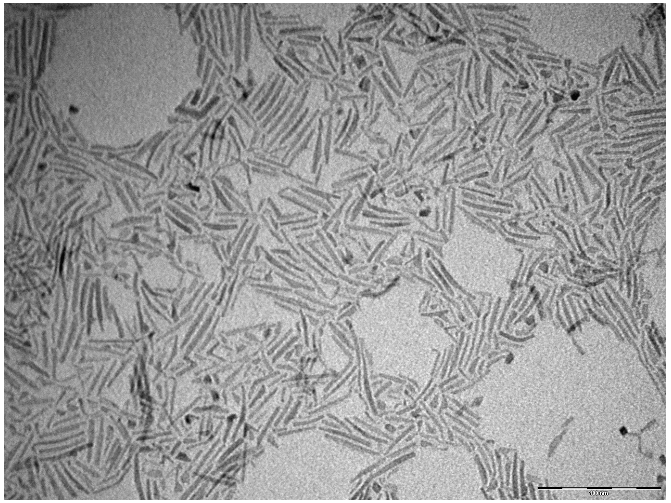
Attention to the choice of laser fluence!

*P. Keblinski et al. materialstoday June 2005, p. 36

** C. Pan, PHYSICAL REVIEW B 70, 233404 (2004), **M.W. Cross,** Nanotechnology **19** (2008) 435705 (5pp)

MAPLE variant: deposition of colloidal nano-particles/rods

MAPLE deposition of **TiO_2 nanorods** in brookite phase for gas sensing applications*



TiO_2 concentration: 0.016 wt %

Solvent: toluene

KrF excimer laser (λ=248 nm, τ=20 ns)

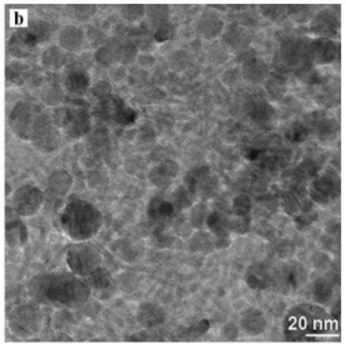
f= 10 Hz

F= 350 - 25 mJ/cm^2

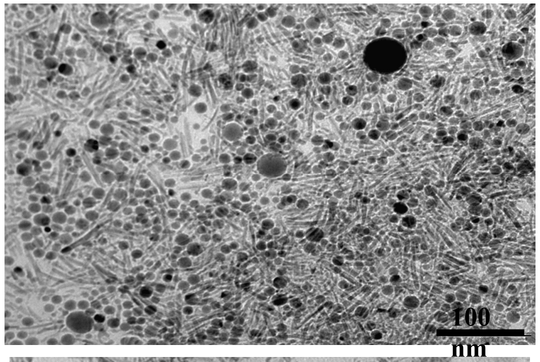
Mean dimensions: 3 - 4 nm × 20 – 40 nm

*A.P. Caricato et al., Appl. Phys. A 104, 963-968 (2011)

MAPLE variant: deposition of colloidal nano-particles/rods

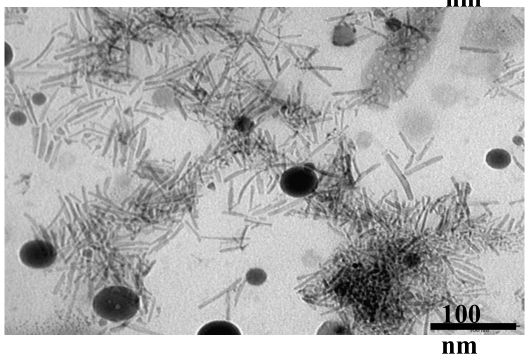


F = 350 mJ/cm^{2*}



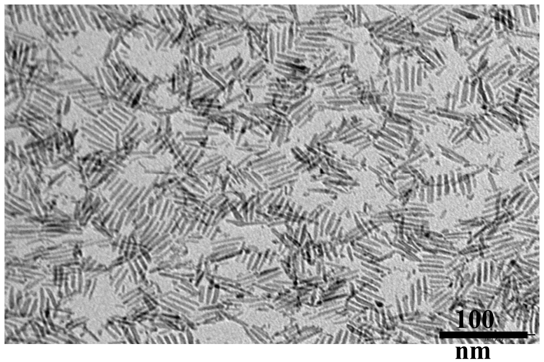
F = 100 mJ/cm^{2*}

Except for very low fluence values changes of the initial shape of the nanorods due, very probably, to fusion processes



F = 50 mJ/cm^2

A decrease of the effective melting temperature is reported when low-dimensional systems are compared to their corresponding bulk materials (~ 1800°C).

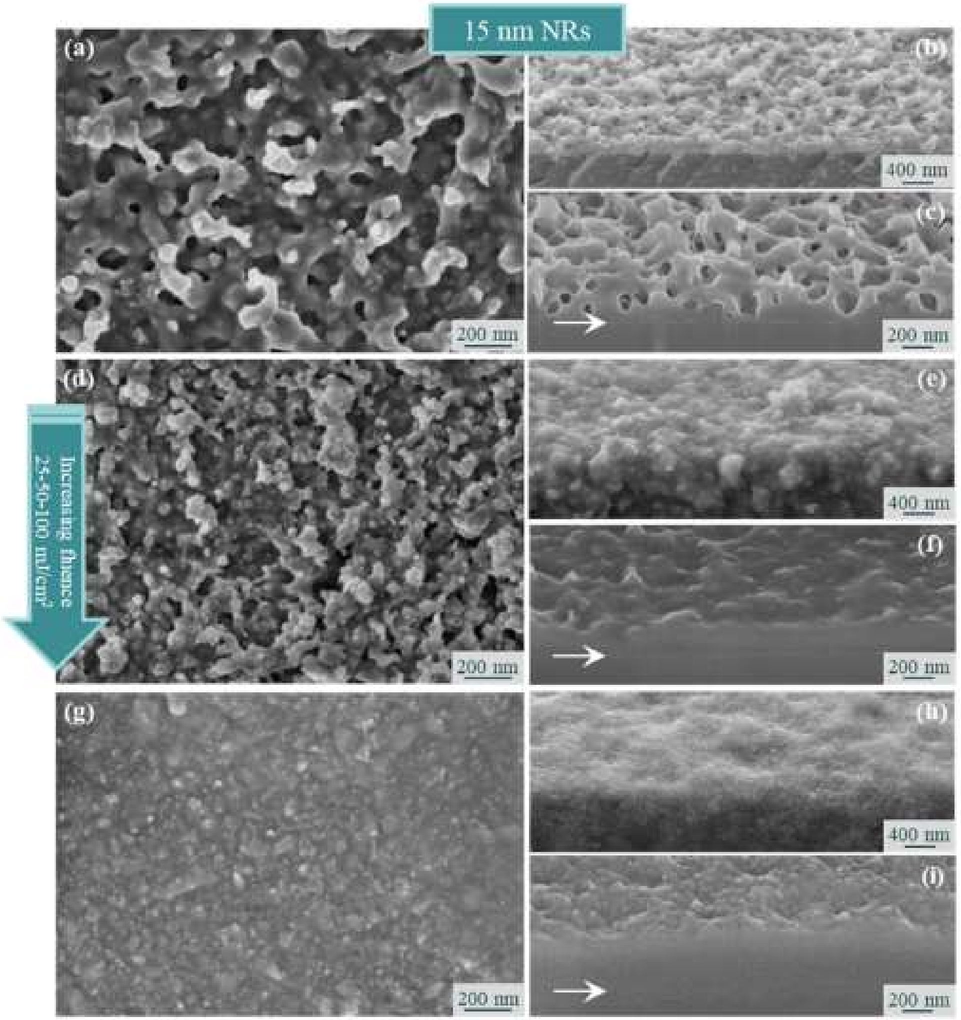


F = 25 mJ/cm^2

*A.P. Caricato et al., Appl. Phys. A 105, 65-582 (2011)

MAPLE variant: deposition of colloidal nano-particles/rods

Nanoparticles capping layer can contribute to film formation

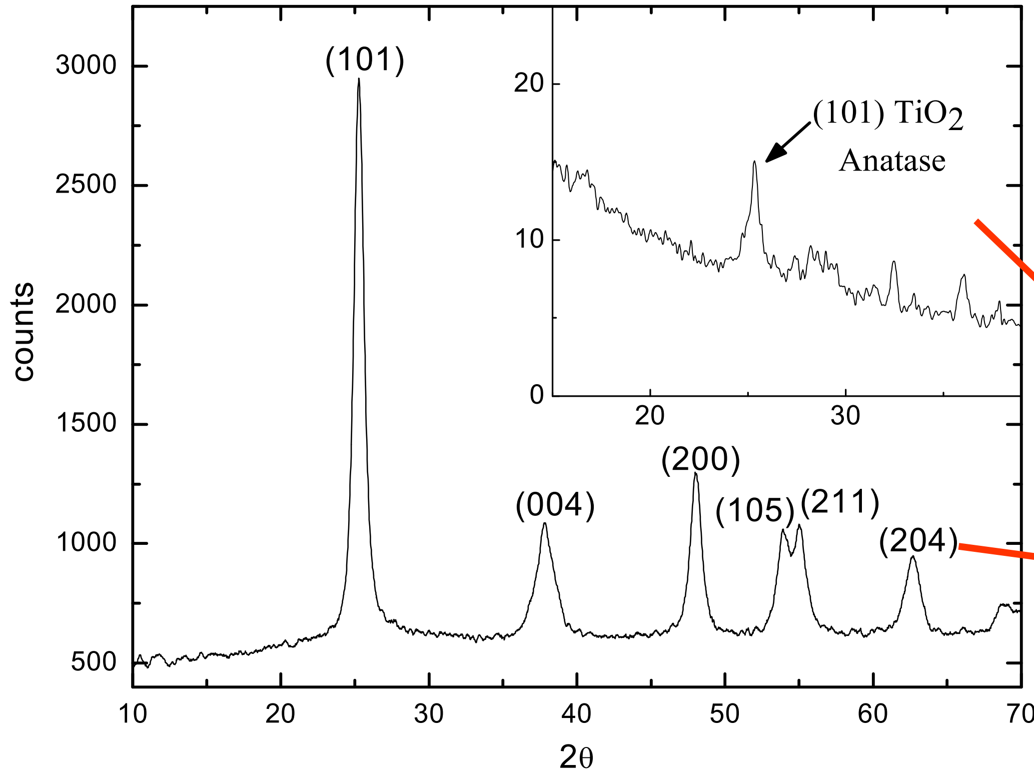


M. Cesaria, A.P. Caricato et al., Processes 2023, 11, 2591

MAPLE variant: deposition of colloidal nano-particles/rods

MAPLE deposition of **TiO_2 nanoparticles** in anatase phase for gas sensing applications*

XRD



Target MAPLE: TiO_2 in deionized water (0.2 wt.%)
Laser parameters: ArF; 20 ns, F=550 mJ/cm^2, f=10 Hz, 6500 pulses)
Substrate: Si, silica, Al_2O_3

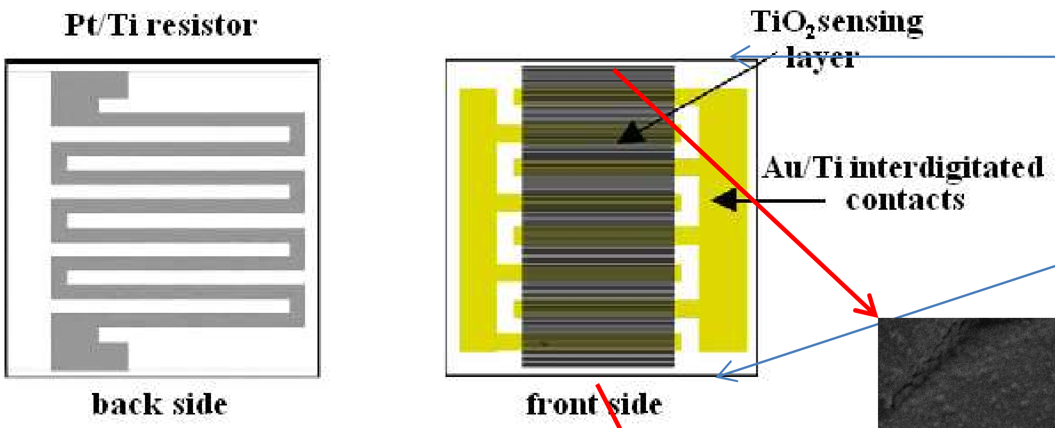
Starting material: TiO_2 nanoparticle (size 10 nm) in the anatase phase

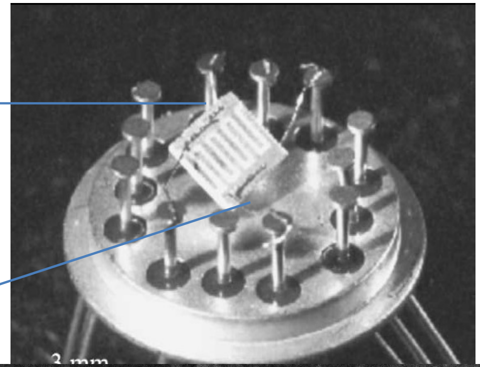
The nanoparticle anatase phase is preserved

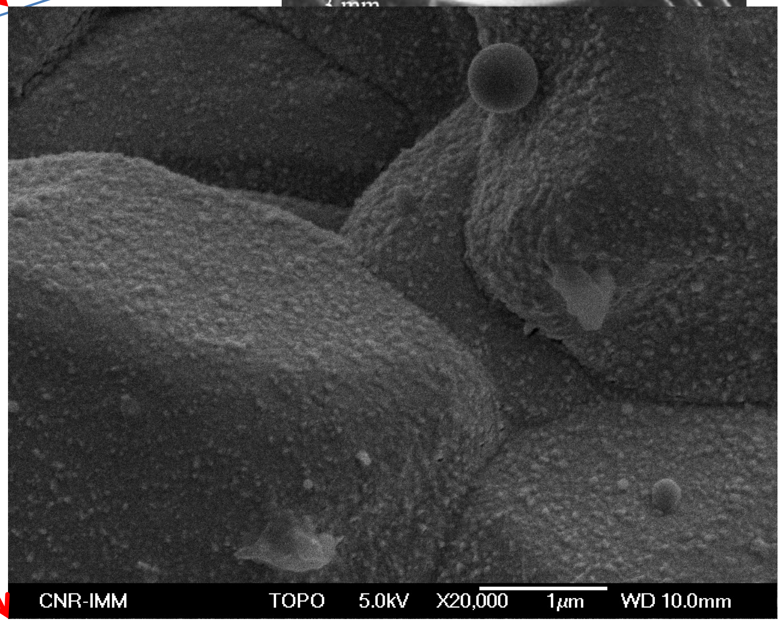
*A.P. Caricato et.al, Appl. Surf. Sci. 253, 7937-7941 (2007)

MAPLE variant: deposition of colloidal nano-particles/rods

MAPLE deposition of **TiO_2 nanoparticles** in anatase phase for gas sensing applications





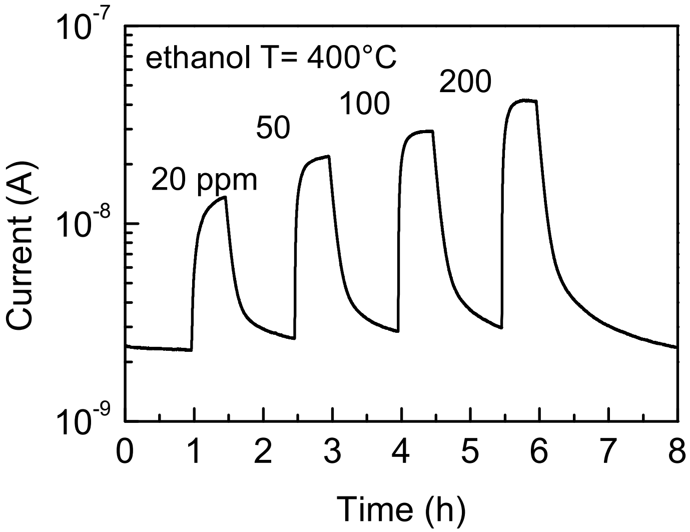


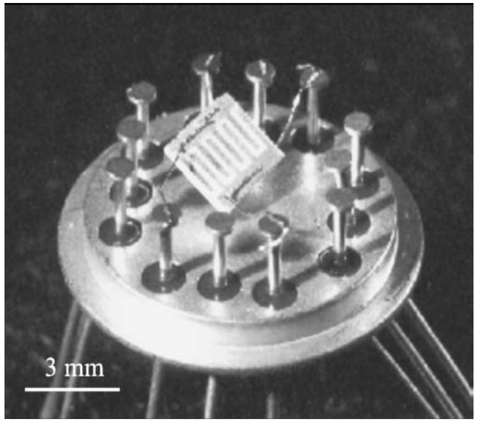
R. Rella et al. Sensors and Actuators B 127, 426-431 (2007)

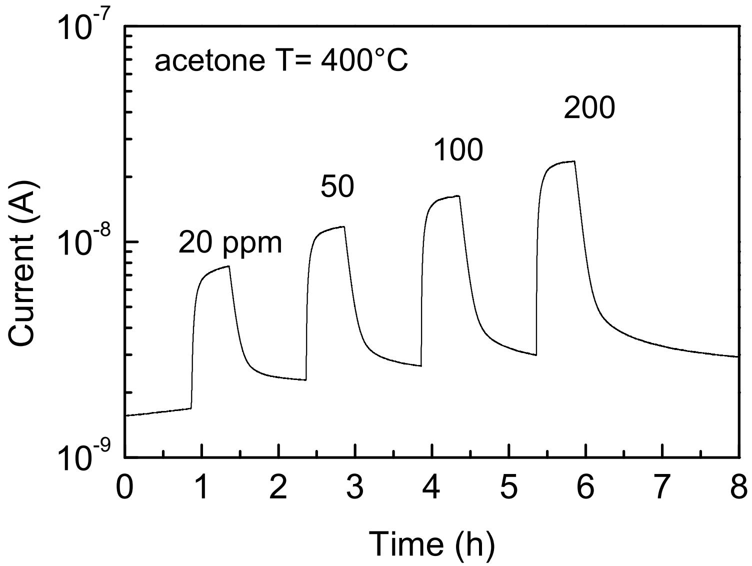
Good substrate coverage on rough substrates

MAPLE variant: deposition of colloidal nano-particles/rods

The films were deposited on the upper part of an interdigitated electrode and were used as gas sensor with very good results

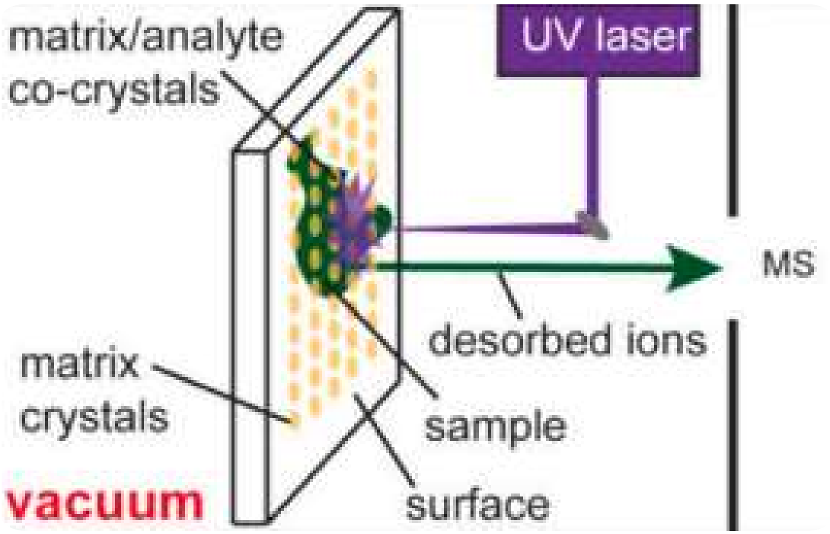






Good electrical response to acetone and ethanol vapors

*R. Rella et al. Sensors and Actuators B 127, 426-431 (2007)



MALDI

Matrix-assisted laser desorption ionization

MALDI: Principle

MALDI is a soft ionization technique that allows the desorption and ionization of large molecular species

~ 10 – 1000 kDa

MALDI is based on the discovery that dissolving a biomolecule (like enzyme, proteins, DNA, e.t.c.) within a great excess of a particular matrix (usually 2,5-DHB-dihydroxybenzoic acid) specifically chosen to absorb at the irradiation wavelength can lead to its ejection into the gas phase and ionization with

MINIMUM DEGRADATION

1987 Matrix-assisted desorption ionization (MALDI) at Universitat Munster, Germany.

M. Karas, et al and F. Hillenkamp ***Int. J. Mass Spectrom. Ion Process*, 1987, 78, p53**

Karas M, Hillenkamp F, ***Anal. Chem.* 1988, 60, 2299-2301.**

MALDI: Principle

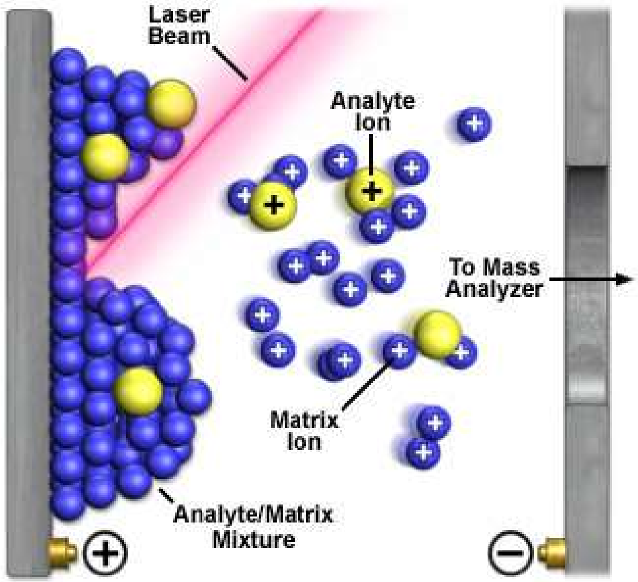
When used in combination with mass spectrometry (MALDI-MS) it allows the analysis of biomolecules and large organic molecules increasing the sensitivity of conventional mass spectrometry instruments (100 /240 Da).

1988 Application of MALDI mass spectrometric analysis to biological macromolecules

K. Tanaka, et al; ***Rapid Commun. Mass Spectrom.* *1988*, 2, p151**

Koichi Tanaka at Shimadzu Corp.

2002 Nobel Prize for Chemistry

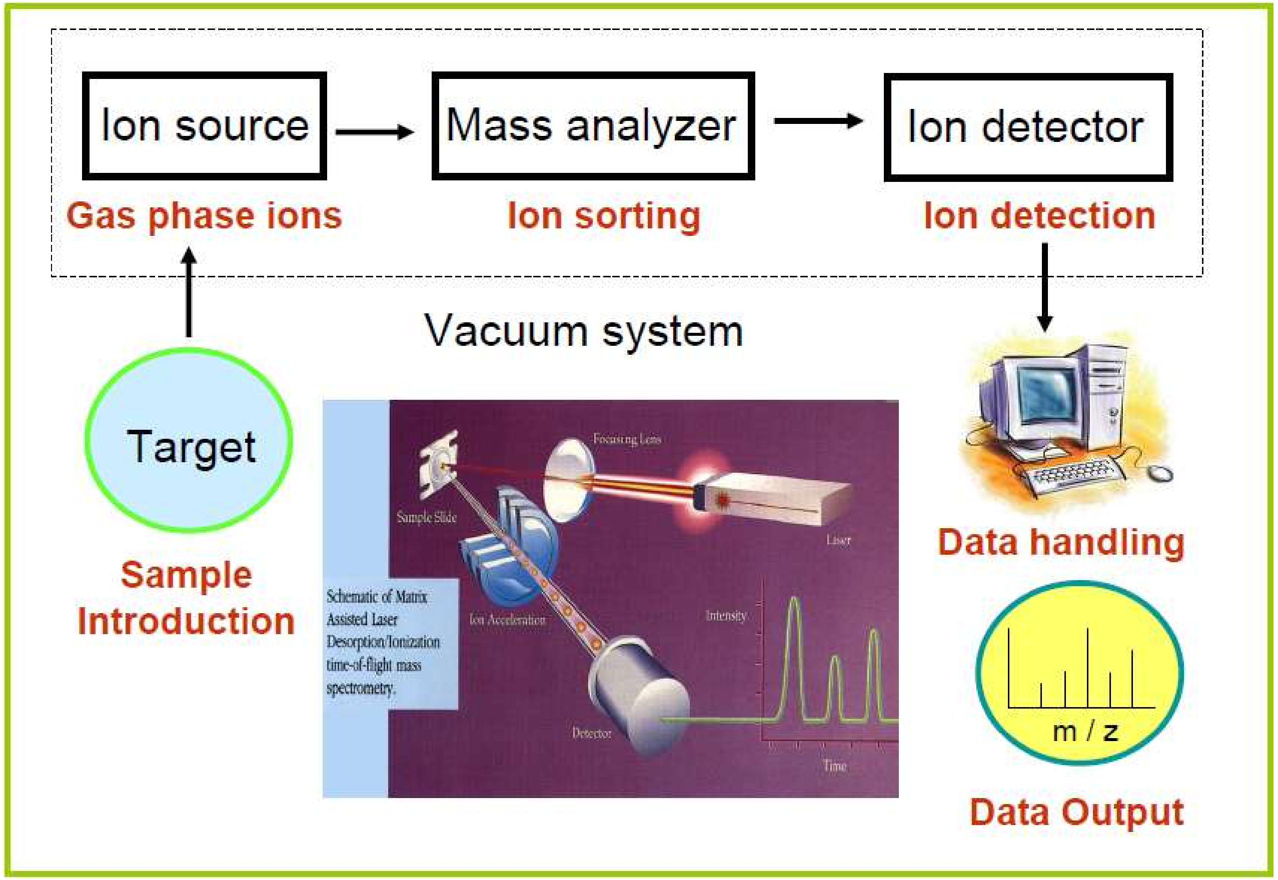


MALDI: Principle

1999 MALDI QqTOF mass spectrometer
at University of Manitoba, K. G. Standing

Anal. Chem. **1999, 71, 452A-461A**

Rapid. Commun. Mass Spectrom. **2000, 14, 1047-1057.**

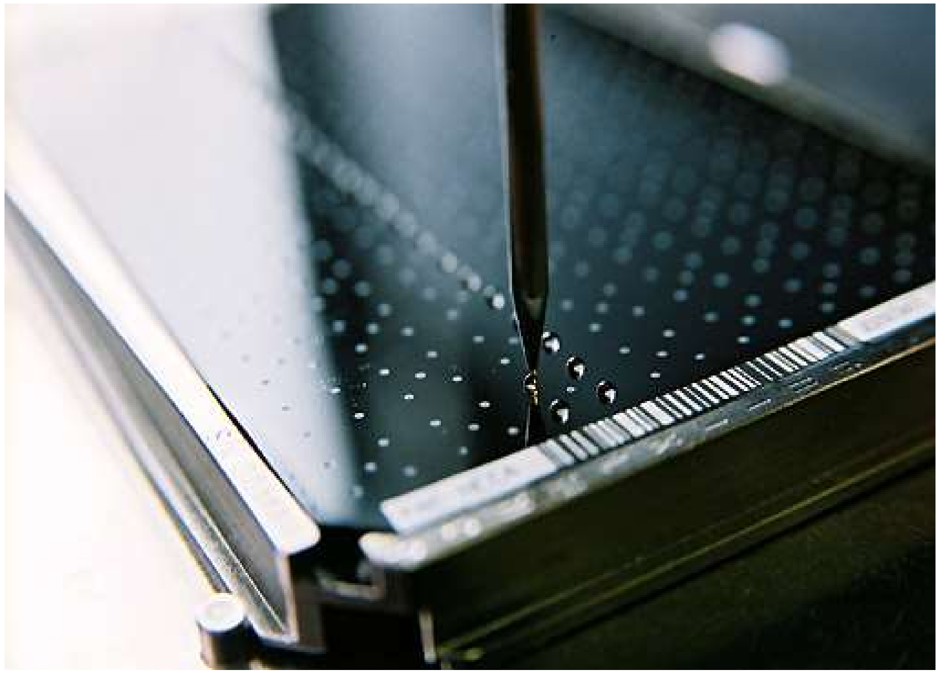


MALDI: Principle

1. Sample preparation: dilution of the analyte (A) molecules in a matrix with particular properties);

2. This solution is spotted onto a MALDI plate (usually a metal plate designed for this purpose). The solvent vaporizes, leaving only the recrystallized matrix, but now with analyte molecules embedded into MALDI crystals. The matrix and the analyte are said to be co-crystallized.

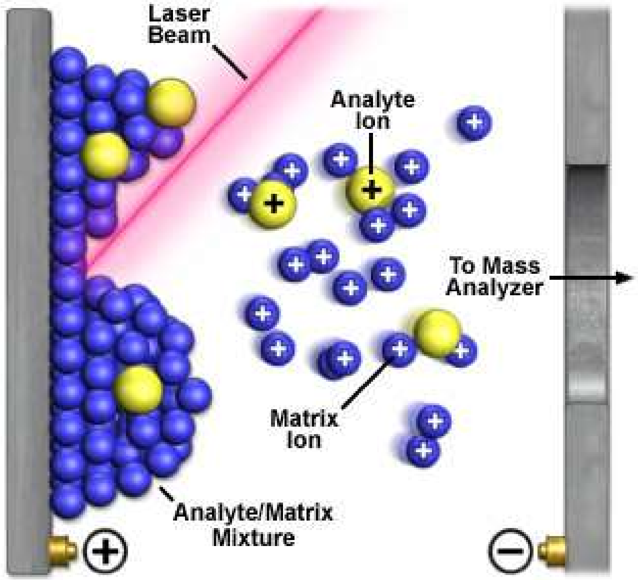
8x12 pattern, 6 mm spacing, reusable sample card compatible with microtitre plates



The MAPLE technique is analogous to the MALDI-MS analytical technique but in MAPLE the target is generally refrigerated while in MALDI the matrix is usually solid at room temperature

MALDI: Principle

3. Excitation, by means of a UV (or IR) laser beam, of the sample and disintegration of the condensed phase;

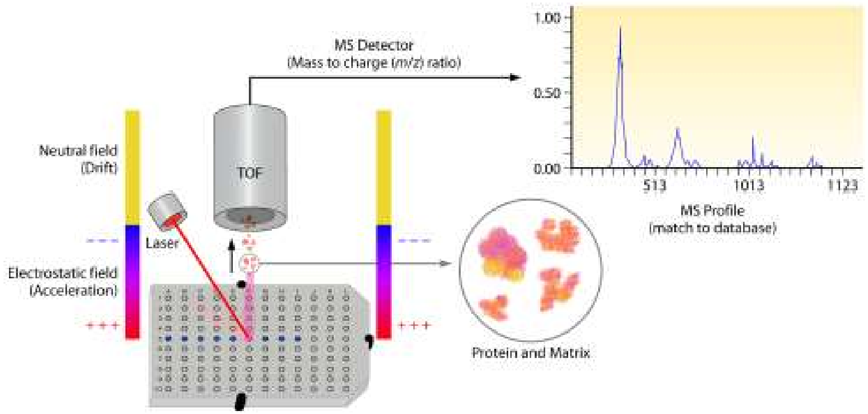


4. Generation and separation of charges and ionization (protonation or deprotonation) of analyte molecules

$$MH^+ + A \rightarrow M + AH^+;$$

MALDI: Principle

6. Detection.



Different software are available for spectra analysis

Database Searching for Protein Identification

Major Proteomics search engines

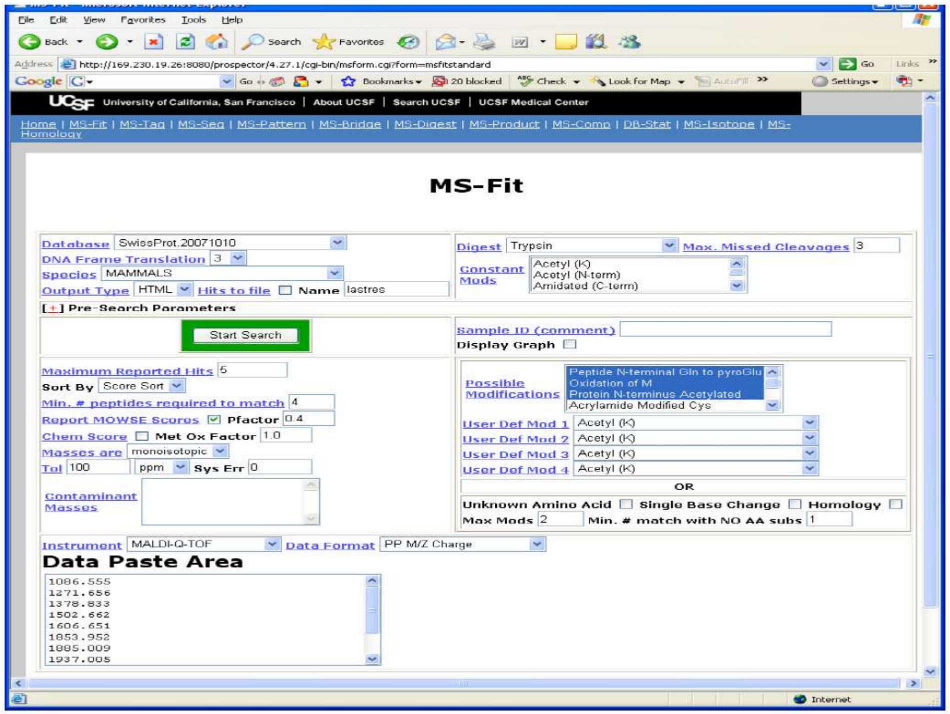
ProteinProspector
http://prospector.ucsf.edu/

Matrixscience: Mascot
http://www.matrixscience.com/

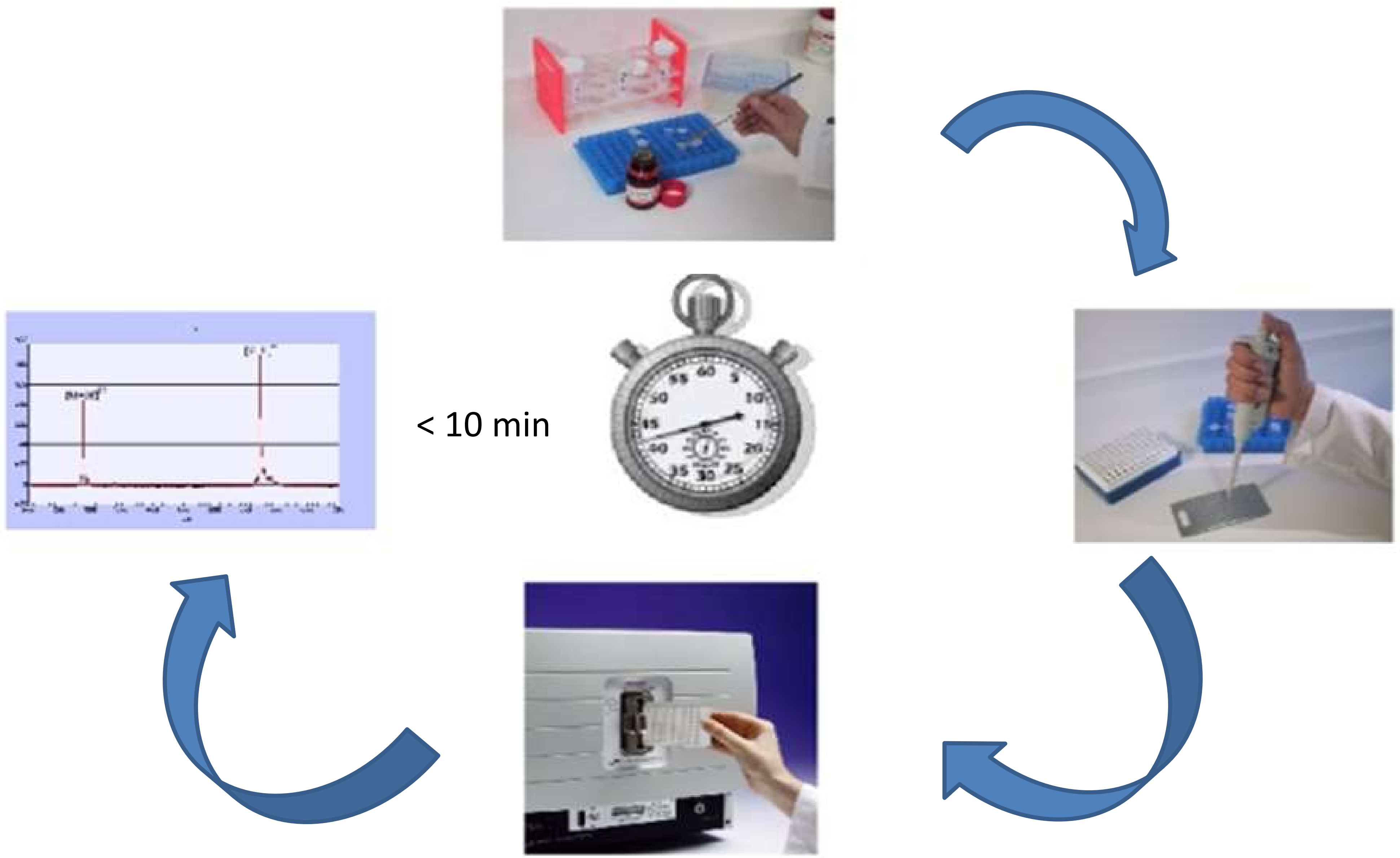
ProFound
http://prowl.rockefeller.edu/

- ➢EMBL http://www.narrador.embl-heidelberg.de/
- ➢ X! Tandem (GPM) http://www.thegpm.org/
- ➢Pepsea http://195.41.108.38/
- ➢BLAST http://www.ncbi.nlm.nih.gov/
- ➢FASTA http://www.ebi.ac.uk/

http://prospector.ucsf.edu/prospector/cgi-bin/msform.cgi?form=msfitstandard



MALDI: Principle



MALDI: Principle

A successful matrix should exhibit the following criteria:

It has to isolate analyte molecules by dilution within the preparation, to prevent analyte aggregation. Moreover the "exact" dilution of the analyte is such that to reduce its thermal degradation. Tipycal analyte/matrix ratio are in the range of about $(1\text{-}5)\times10^{-2}$)

It has to absorb the laser energy* via electronic (UV-MALDI) or vibrational excitation (IR-MALDI) in order to have disintegration of the condensed phase without excessive destructive heating of the embedded analyte molecules.

It has to be acidic in order to act as a proton source to encourage ionization of the analyte.

MALDI: Principle

Fast excitation is necessary in order to avoid destructive thermal excitation of the analyte: laser pulse duration 0.5 ns – 10 ns (maximum 25 ns)

MALDI: Principle

There are many different matrices that can be used for MALDI - TOF. Some of the most common include:

Matrices for 337 nm (UV) laser	**applications**
2,5-dihydroxybenoic acid (DHB)	1,2,3,4,5
α-cyano-4-hydroxycinnamic acid (CHCA)	1,2
Sinapinic acid (SA)	2
3-hydroxypicolinic acid (3 HPA)	4
6-Aza-2-thiothymine (not acidic)	1,4
2,4,6-trihydroacetophenone (THAP) (not acidic)	3,4
Dithranol (not acidic)	5

(1=peptides; 2=proteins; 3=carbohydrates; 4=nucleic acids; 5=polymers)

Matrices for 2.94 μm (IR) laser

Succinic acid
Malic acid
Glycerol (not acidic)
5-(trifluoromethyl)uracil (not acidic)
Urea (not acidic)
TRIS (not acidic)

MALDI: some characteristics of the process

Presence of a threshold fluence for ion detection

Strong dependence of the threshold fluence by the laser spot dimension

The ion signal increases with the laser fluence (depending on the kind of matrix)

Mean ion velocity: 200 – 1000 m/s

Mean neutral velocity: ~ 500 m/s

Ion/neutral ratio ~ 10^{-5} – 10^{-3}

MALDI: Principle

For the desorption “mechanism” using UV laser (which means excitation of samples, the subsequent phase change, and the dynamics of the material plume expansion) look at the reference:

K. Dreisewerd, *Chem. Rev. 103,* 395-425 (2003)

Primary (matrix) and secondary (analyte) excitation and ionization mechanisms are reviewed in the two closely related articles by Karas and Kru¨ger** and Knochenmuss and Zenobi***

** M. Karas, R. Kru¨ ger, *Chem. Rev*. 103 (2003)

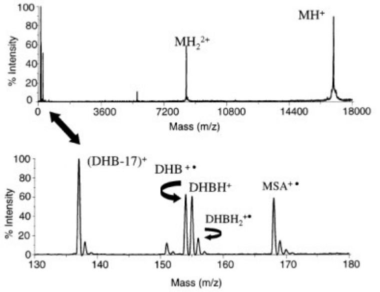
*****R.** Knochenmuss, R. Zenobi, *Chem. Rev*. 103 (2003)

MALDI: Principle

A review about IR-MALDI

K. Dreisewerd, S. Berenkamp, A. Leisner, A. Rohlfing, C. Menzel,
Int. J. Mass Spetrom. (2003)

MALDI: Principle



DISADVANTAGES: the analysis of small molecules is still a problem

ADVANTAGES:

1. The necessary sample preparation is simple and fast;

2. Tolerance to the impurity presence as salt or buffer contaminations;

3. Presence of nearly exclusive singly charged ions;

4. Minimum time of acquisition;

5. Extreme sensitivity: even single cells may be analyzed and it has also been demonstrated that already 10 molecules (ca. 700 yoctomoles) of an analyte are sufficient to give a detectable signal limits of modern MS detectors.

MALDI: Applications

- Molecular Weight Screening
- Protein Identification
- Peptide Mapping
- Identification of Post-Translational Modifications
- Real-Time Monitoring and Optimization of Enzymatic Reactions
- Ligand/Binding Studies
- Proteomics Projects
- DNA and RNA Sequencing and Analysis
- In-Source, Fast Fragmentation
- Forensic Investigations
- Pharmaceutical and Biotech QC/QA
- Characterization of Oligosaccharides
- Analysis of Polymers and Polymer Blends

and more...

Clinical Microbiology;
Clinical chemistry;
....

CONCLUSIONS

Matrix plays an important role in defining laser-matrix interaction dealing with complex and large molecules

Controlling the process is fundamental of successful applications

Thank you for the attention!