Laser printing for organic electronics and sensors applications

PART I

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NATIONAL TECHNICAL UNIVERSITY OF ATHENS

(since 1836)

- 8 engineering schools and 1 applied physics and mathematics school.
- 540 members as academic staff.
- 8500 undergraduate students and 1500 graduate students.

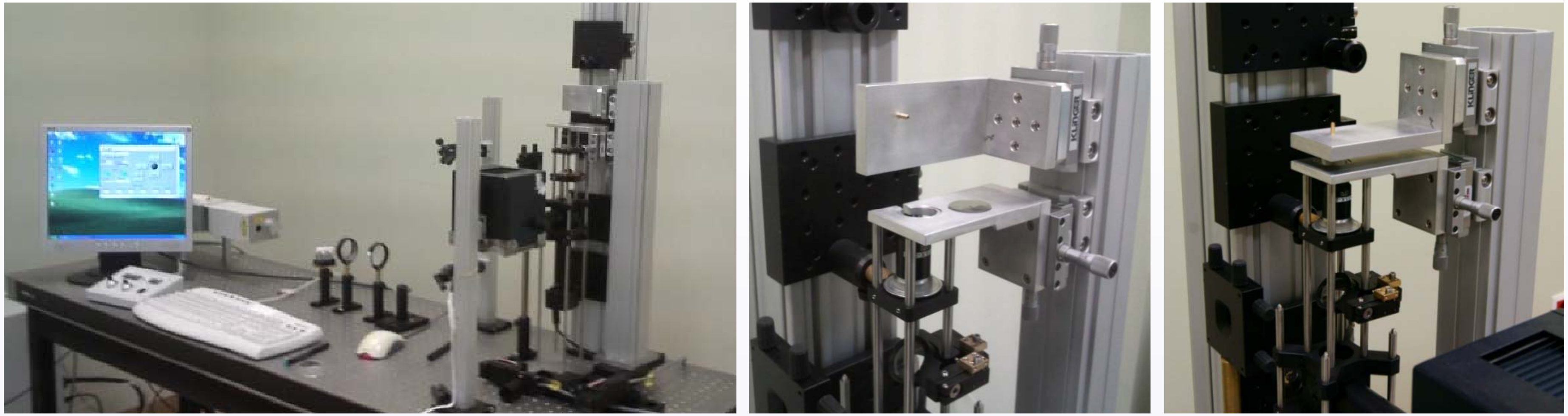
Facilities

Include three different lasers setups and materials characterization facilities. Optical and electrical characterization and simulation laboratory.

- Two Nd:YAG lasers operating at 4 different wavelengths (266, 355, 532 and 1064nm), DPSS ps laser (1064, 532 nm)
- A CO_2 laser irradiation setup for designed for ultra fast thermal processing of semiconductors
- Lab laser micromachining ablation workstation
- Liquid and solid LIFT system
- Micro and Macro RAMAN facilities for structural characterization

Laser printing experimental setup

Solid and Liquid phase LIFT setup @ Physics Department, NTUA



Resolution (266 nm):

✓1 μm – 2 μm (Laser micromachining)
✓5 μm – 10 μm (Printing of liquids)

Translation stages (stepper motors):

✓Resolution 125 nm
✓Travel range 50 mm

Structural Characterization (FESEM –XRD)

- ☐ Thin film attachment XRD characterization in conjunction with TEM measurements, will allow the determination of the obtained nanocrystallization levels in the annealed regions.

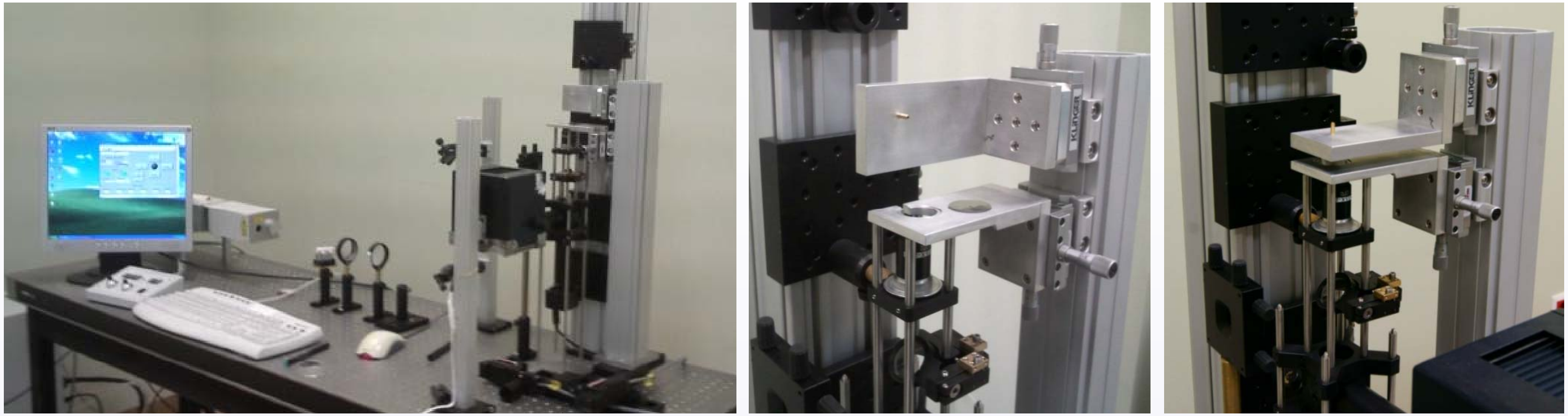
- ☐ FESEM measurements will provide insight in the surface morphology of the nanocrystallized silicon.

FESEM

XRD

Laser printing experimental setup

Solid and Liquid phase LIFT setup @ Physics Department, NTUA



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Translation stages (stepper motors):

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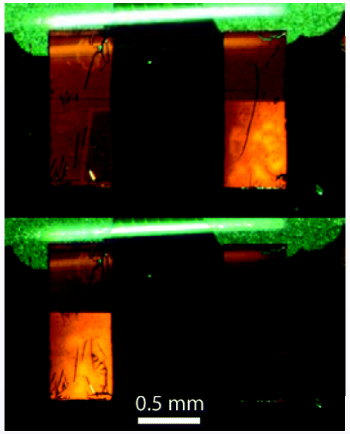
- ✓ Travel range 50 mm

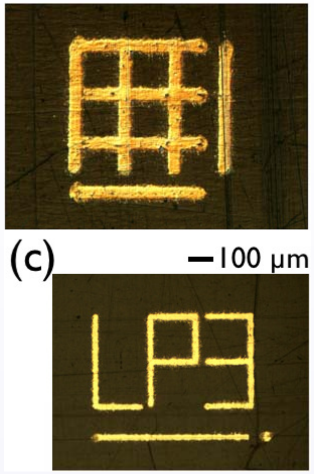
LASER INDUCED FORWARD TRANSFER

Polymer layers

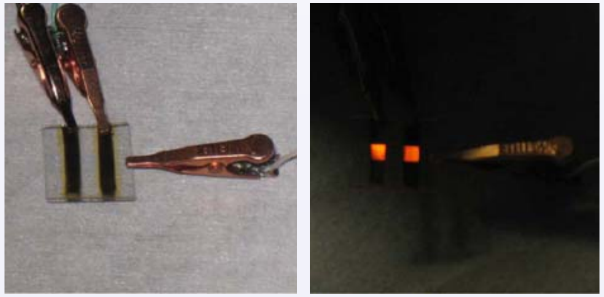


J. Shaw-Stewart *et al.* Appl. Mater. & Interfaces 3, 309 (2011*)*

Ag lines



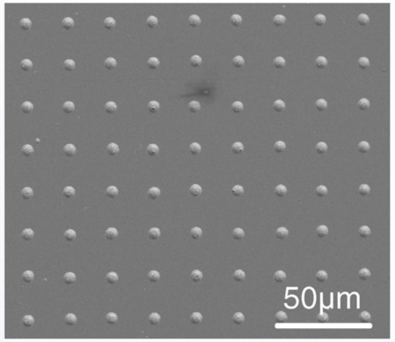
Rapp et al., Optics Express ,19, 22, 21563 (2011)

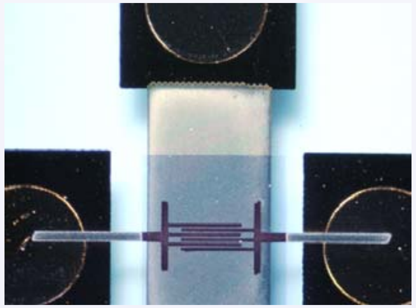


N.T. Kattamis et al. / O. E., **12** 1152–1158, (2011)

Interdigitated Ag electrodes

H Kim *et al* 2010 *J. Phys. D: Appl. Phys.* **43**

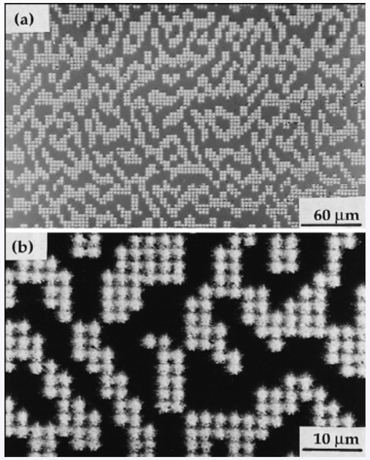




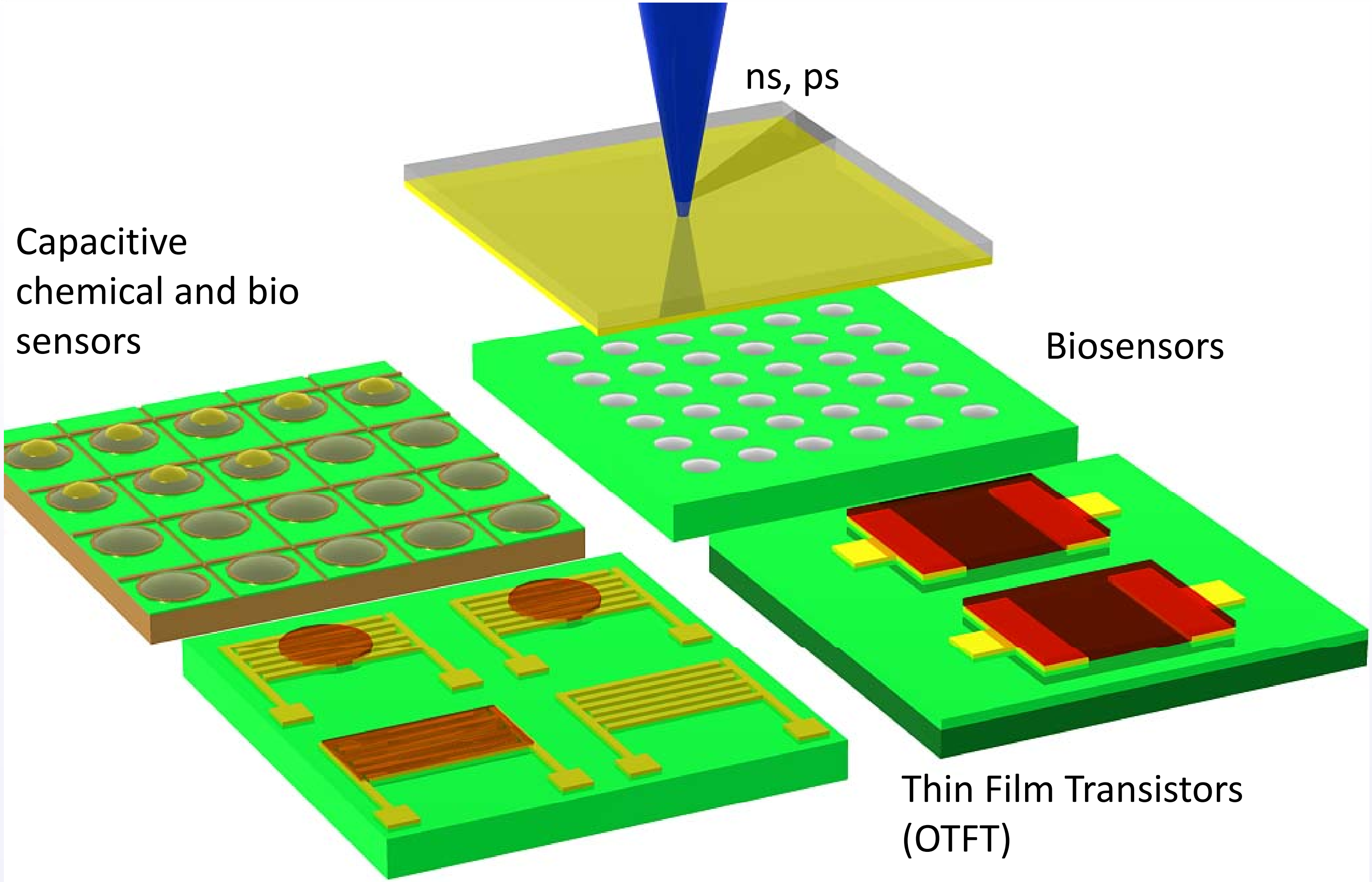
fs LIFT Cr dots,

I. Zergioti *et al.*

Appl. Surf. Sci.,**127-129** 601(1998)



LASER INDUCED FORWARD TRANSFER at NTUA



ns, ps

Capacitive chemical and bio sensors

Biosensors

Thin Film Transistors (OTFT)

Resistivity chemical sensors

Challenge

Materials: Ag, PQT, PBTTT, PEDOT, GRAPHENE, CNTs, polymer composites

Direct Printing Process

Optimization of LIFT process

Single step laser transfer of liquid phase or solid phase multilayer structure

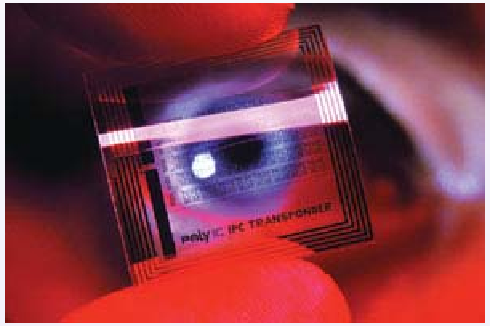
Future prospects

Organic Transistors

Conductive lines

Chemical Sensor FETs

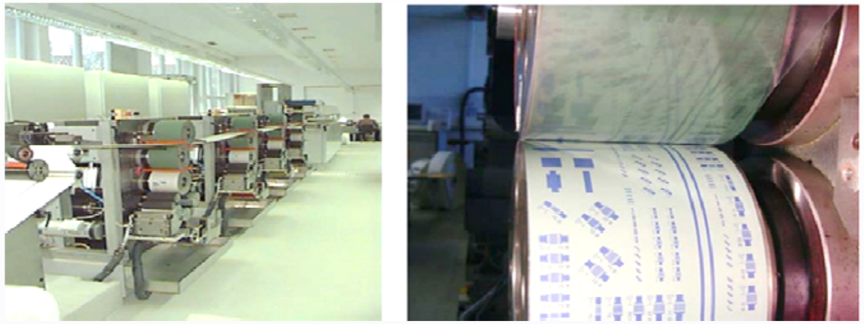
Electronic paper



Polymer organic RFID tag

Nature Materials 4, 581 - 582 (2005)

Printing technologies



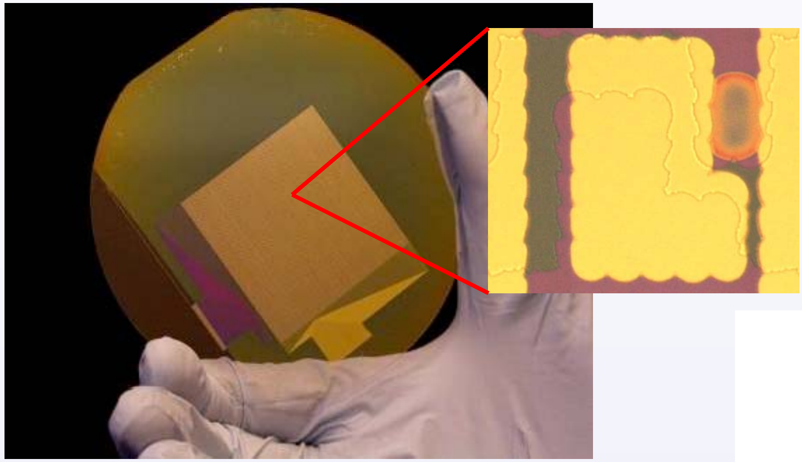
Offset printing machine to produce source/drain structures *(D. Zielke et al., Appl. Phys. Lett. 87 (2005) 123508)*

Roll to roll manufacturing
(flexography, screen printing, …) :

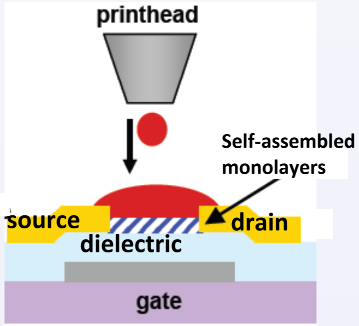
–Fast

–Mass production

–Pre-defined microstructures



All Print-patterned Polymeric TFT Array, *(A. C. Arias et al., Appl. Phys. Lett., Vol. 85, No. 15, 11 October 2004)*



Inkjet printing :

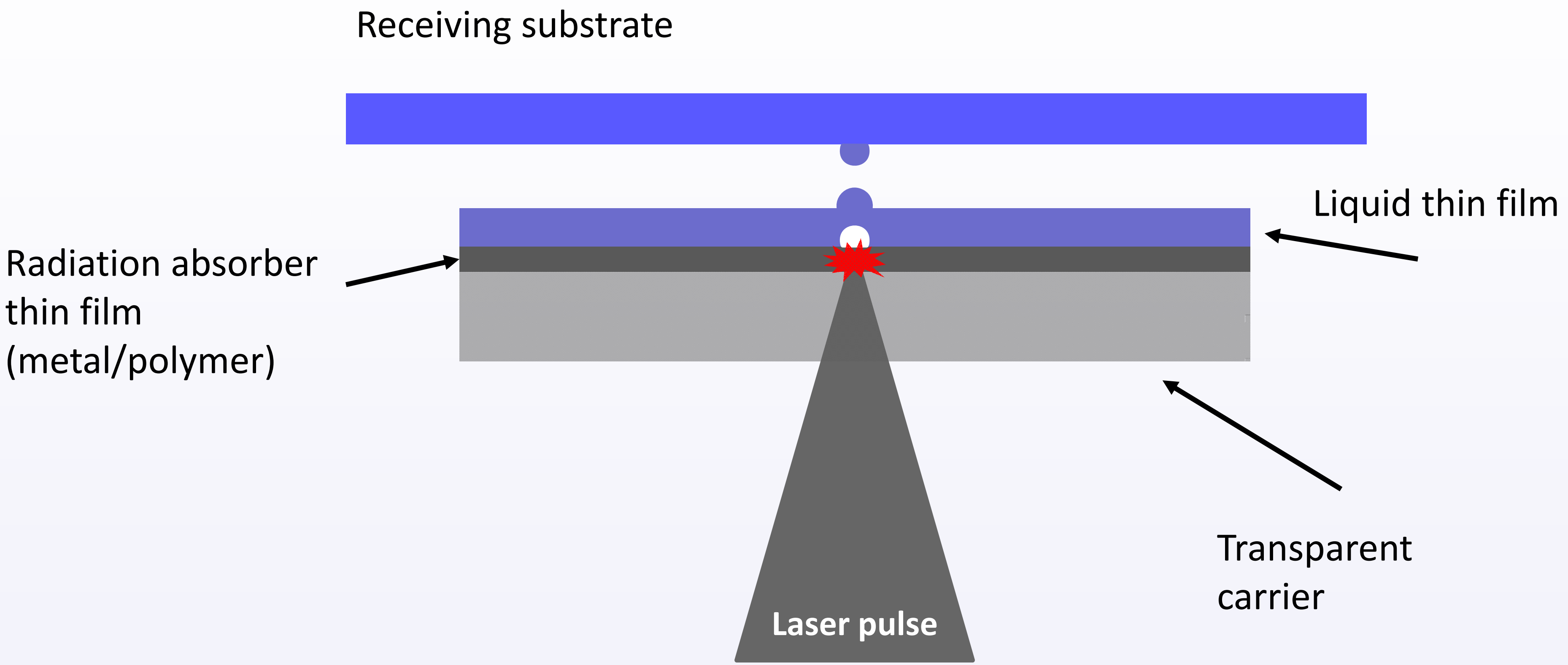
–Computer control design

–Printing in liquid phase

–*Printing limitations:*

- ejection frequency ~ 10-20 kHz
- drop size ~ 40 μm

Liquid Phase Laser Printing or Laser Induced forward Transfer



Receiving substrate

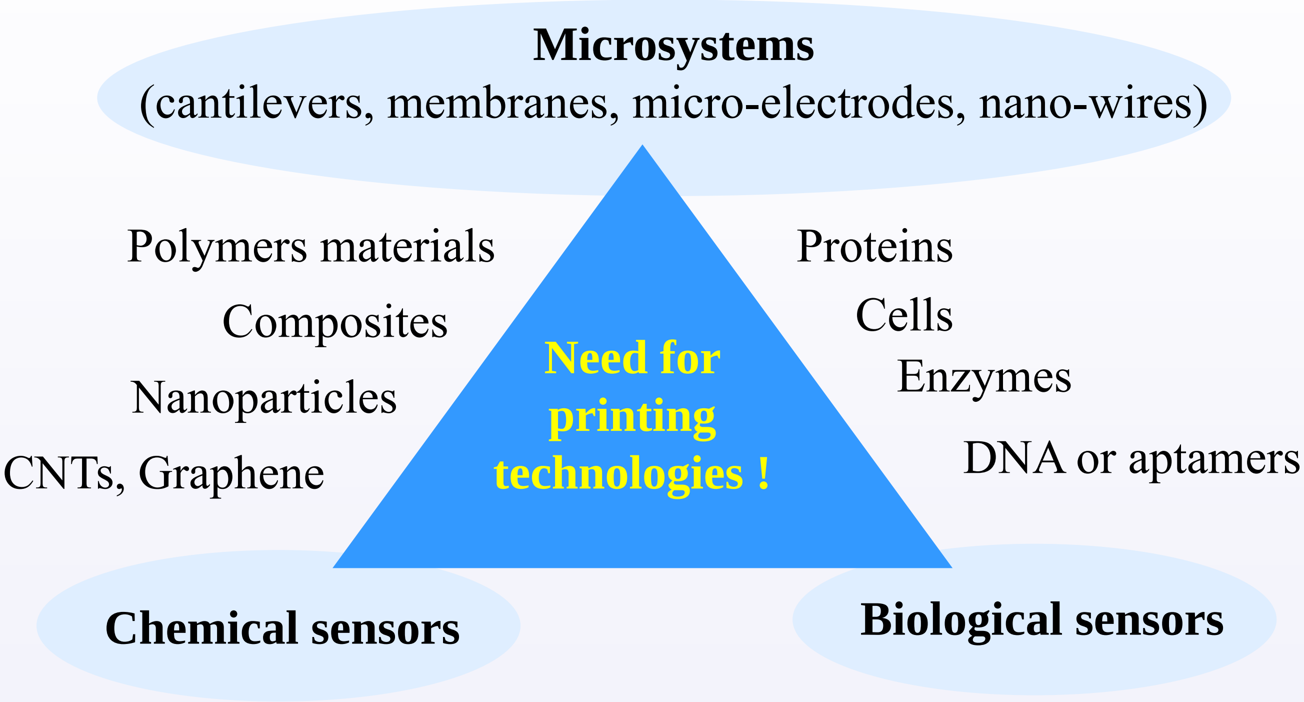
Liquid thin film

Radiation absorber thin film (metal/polymer)

Transparent carrier

Laser pulse

Laser printing for sensors applications



Microsystems
(cantilevers, membranes, micro-electrodes, nano-wires)

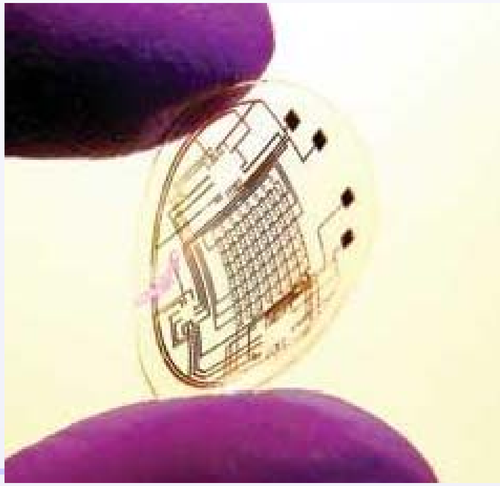
Polymers materials
Composites
Nanoparticles
CNTs, Graphene

Need for printing technologies !

Proteins
Cells
Enzymes
DNA or aptamers

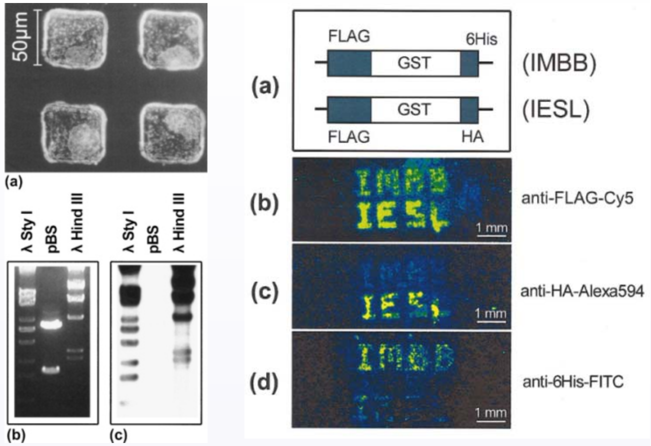
Chemical sensors

Biological sensors



LASER INDUCED FORWARD TRANSFER

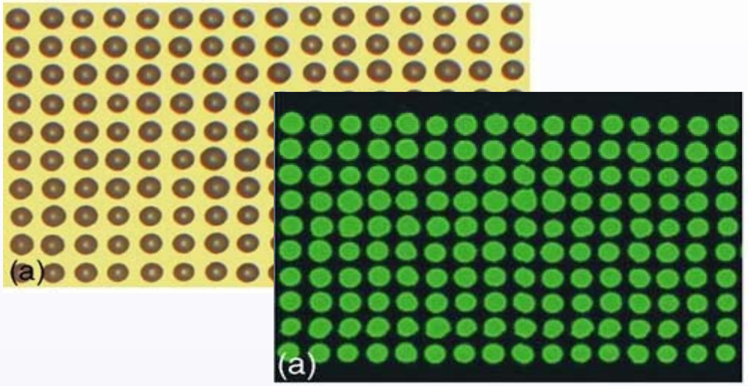
Solid phase bio printing



Zergioti et al. Appl. Phys. Let. **86,** 163902 (2005)
Work at FORTH

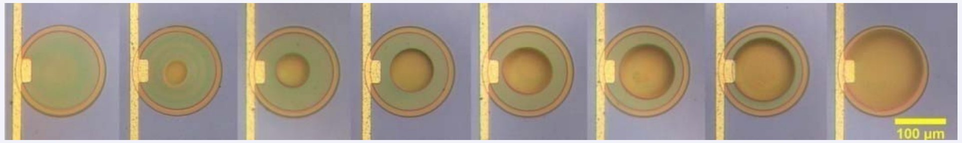
Liquid phase bio printing

DNA microarrays



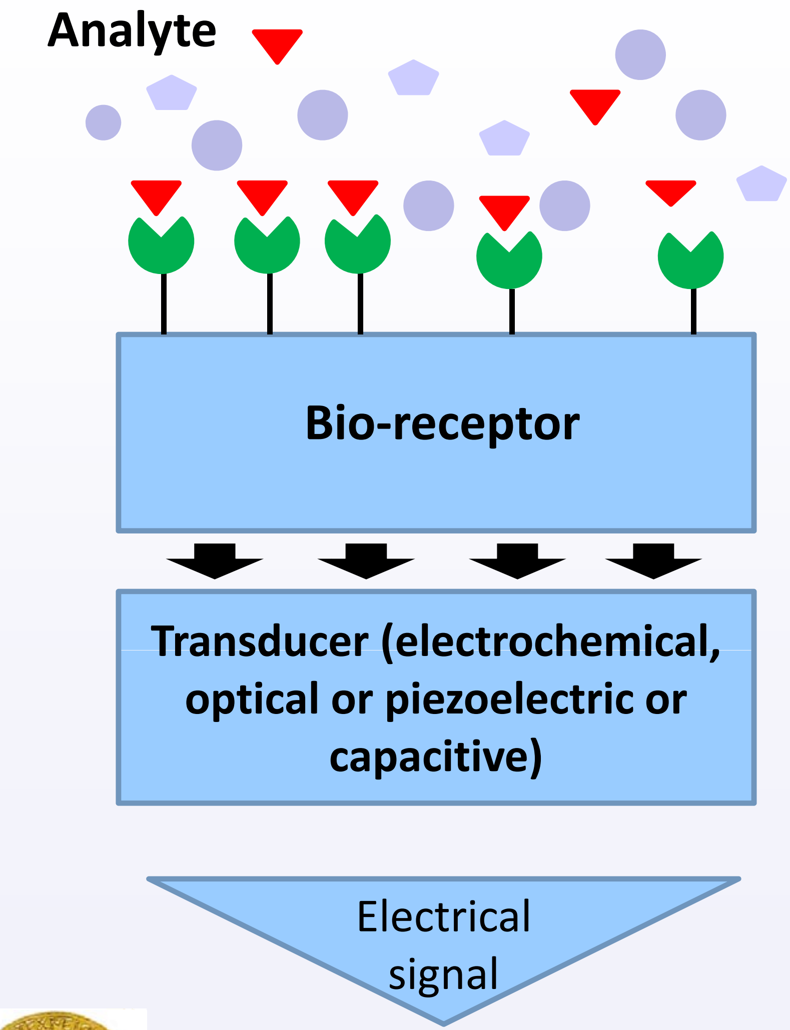
M. Colina et. al., Biosensors and Bioelectronics **20** 1638 (2005)

Polymers for chemical sensors



C. Boutopoulos et al. Appl. Phys. Lett., **19** 191109 (2008)
Work at NTUA

AN OUTLINE



Analyte

Bio-receptor

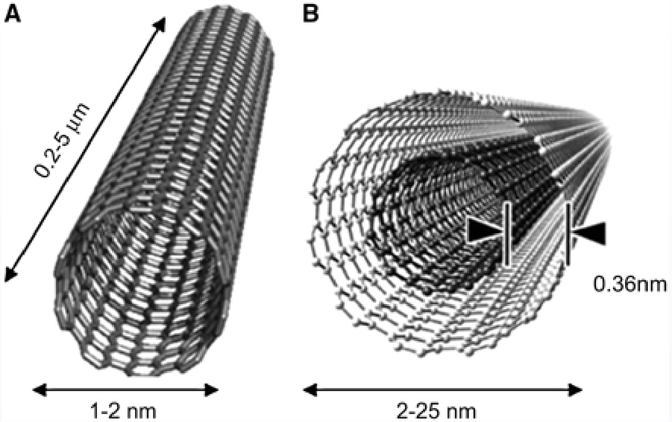
Transducer (electrochemical, optical or piezoelectric or capacitive)

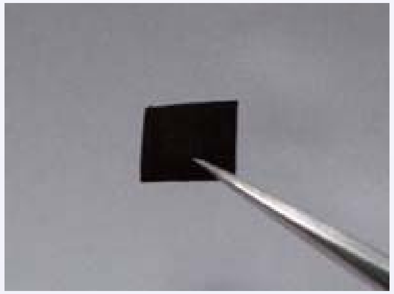
Electrical signal

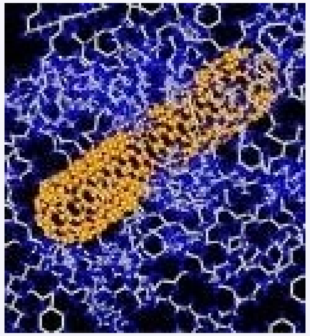
- Polymer/CNT resistivity sensors for humidity monitoring
- PANI resistivity sensors for NH_3 detection
- Photosynthetic amperometric environmental sensors for water monitoring
- Mechanisms study of the laser direct immobilization

Polymer/carbon nanotube (CNT) composites (Properties – Applications)

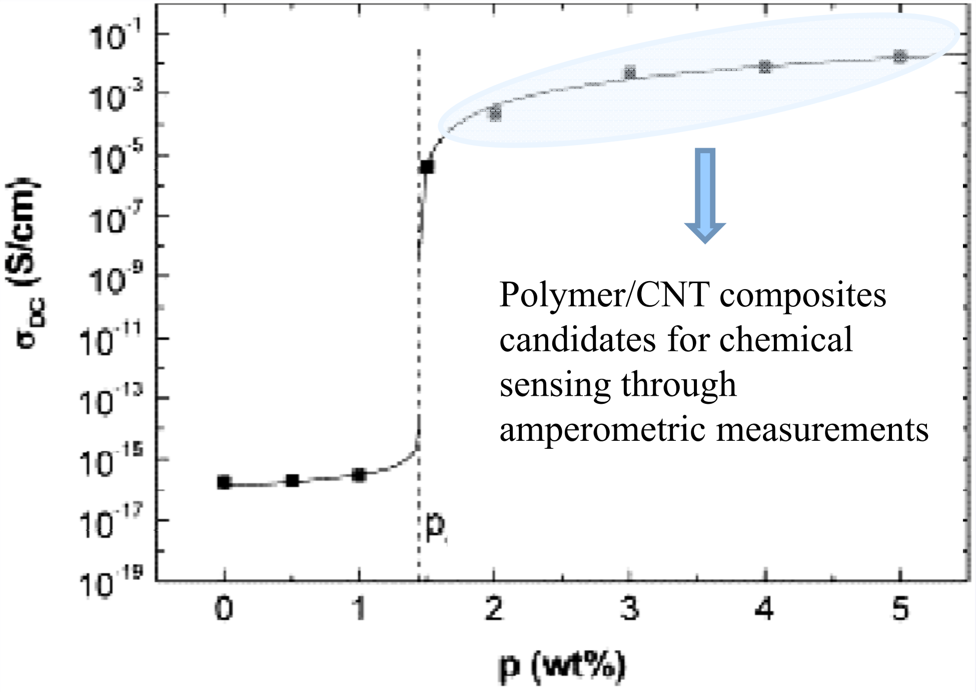
- Mixture of CNT and polymer matrix form **conductive** composite with high electrical conductivity.
- The composite CNT/polymer can be used as chemical sensor.




Polymer/carbon nanotube composite film


Polymer/CNT composites for sensors and electronics

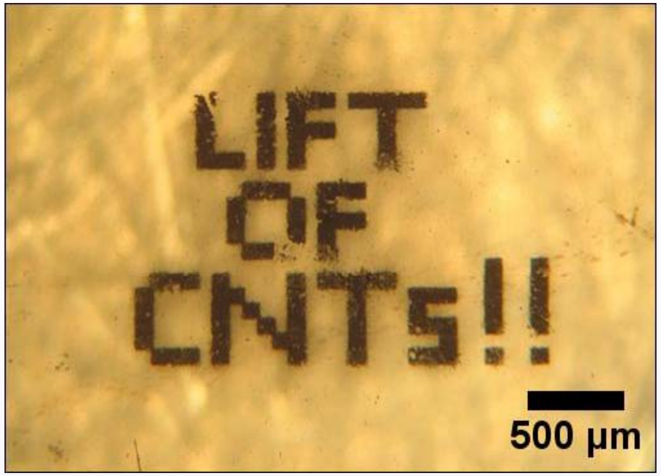
Polymer/carbon nanotube (CNT) composites for chemical sensing

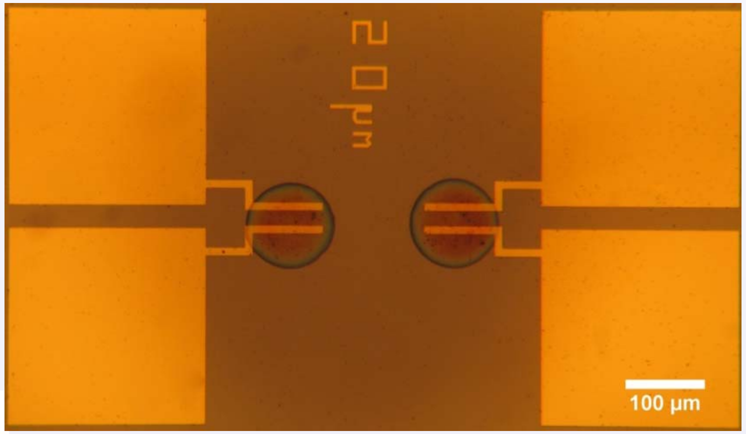


Polymer/CNT composites candidates for chemical sensing through amperometric measurements

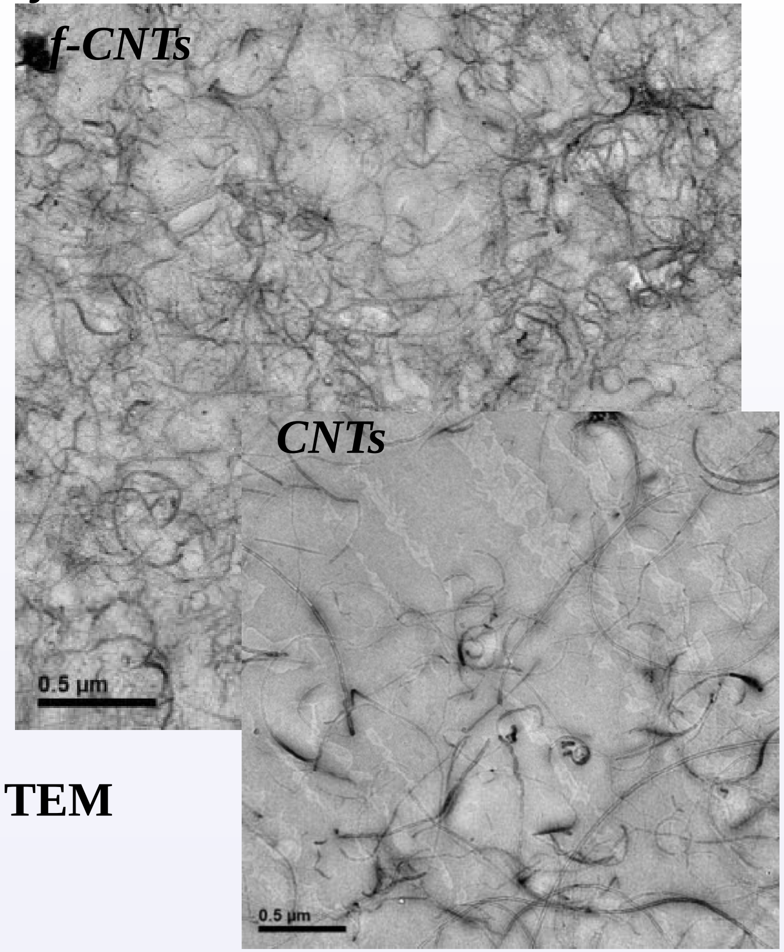
- The electrical conductivity of the polymer/CNT composites depends from the:
  - CNT aspect ratio
  - Dispersion of the CNTs into the polymer matrices
  - Polymer matrix
  - CNT functionalization

Polymer/carbon nanotube (CNT) composites for chemical sensing





Nafion with functionalized and non functionalized CNTs 5% wt.

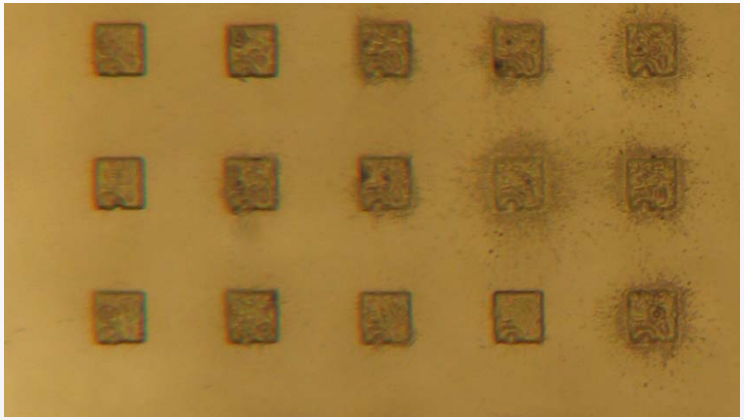


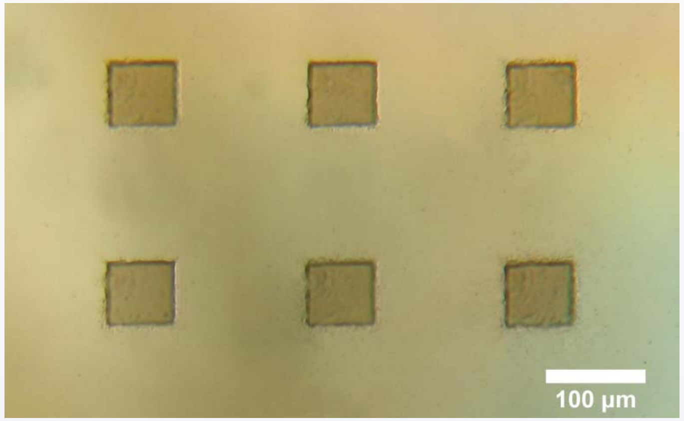
TEM

More uniform distribution of the f-CNTs

Polymer/carbon nanotube (CNT) composites for chemical sensing

Optical microscopy images of **PVP/ 5% f-MWCNT** layers deposited by single laser pulses on glass substrates



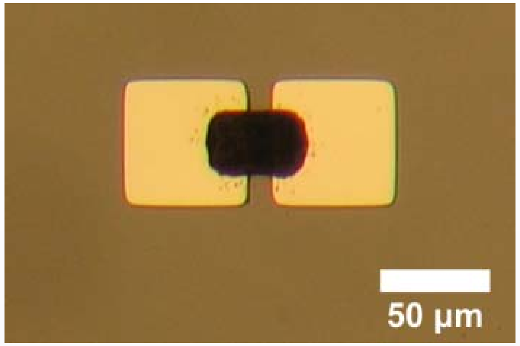


E = 250 mJ/cm^2

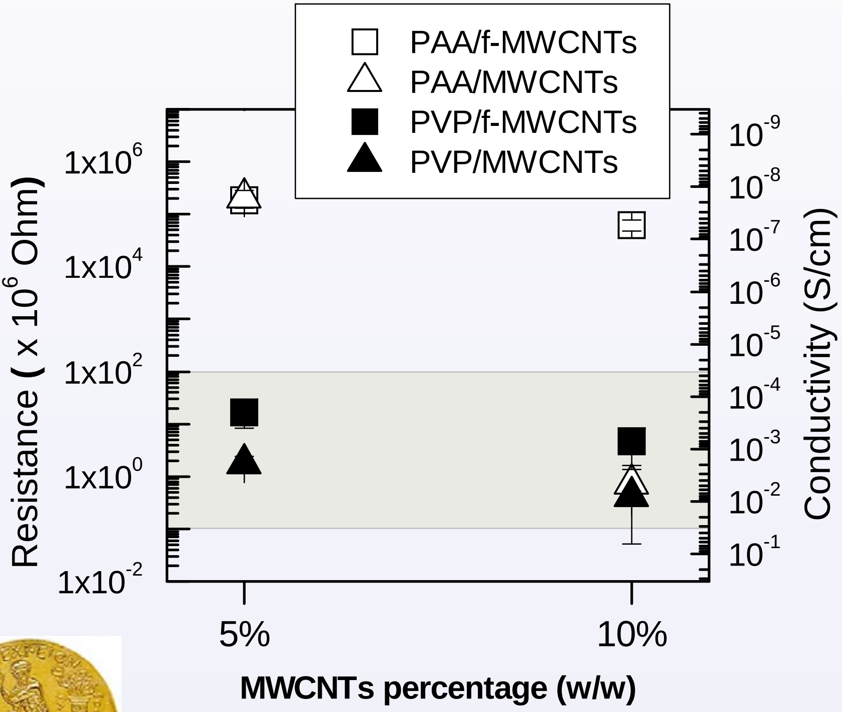
"Polymer/carbon nanotube composite patterns via laser induced forward Transfer", Christos Boutopoulos, Christos Pandis, Konstantinos Giannakopoulos, Polycarpos Pissis, and Ioanna Zergioti, Appl. Phys. Lett., 96, 041104 (2010)

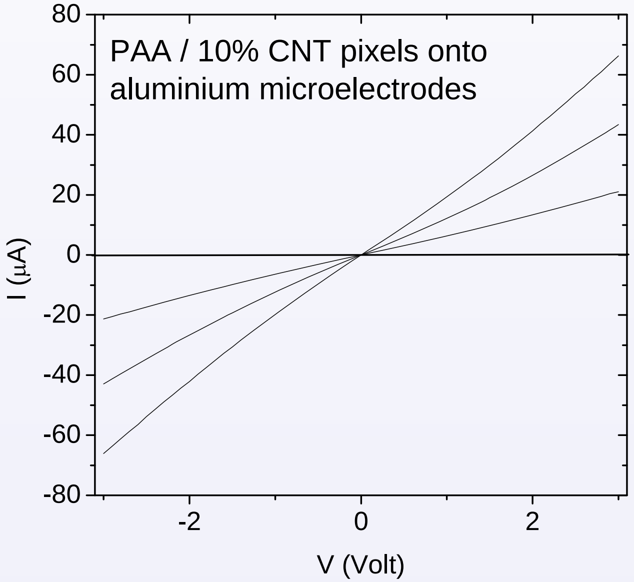
Ioanna Zergioti, NTUA

Electrical characterization of the deposited polymer/carbon nanotube (CNT) composite pixels

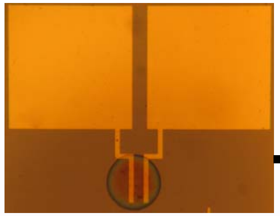


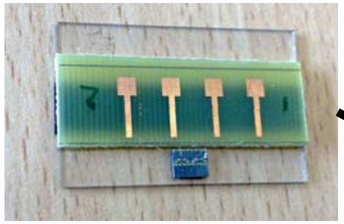
- Printing of Polymer/MWCNT composite pixels on aluminum microelectrodes
- DC electrical conductivity properties of the deposited composite pixels were calculated by current-voltage (I-V) measurements
- 1.9×10^{-3} S/cm and 2×10^{-4} S/cm.
- Above the percolation threshold and thus good candidates for chemical sensing

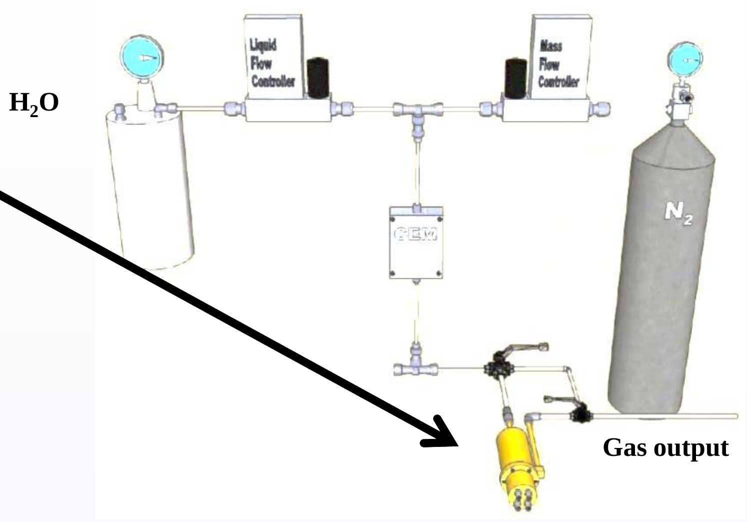


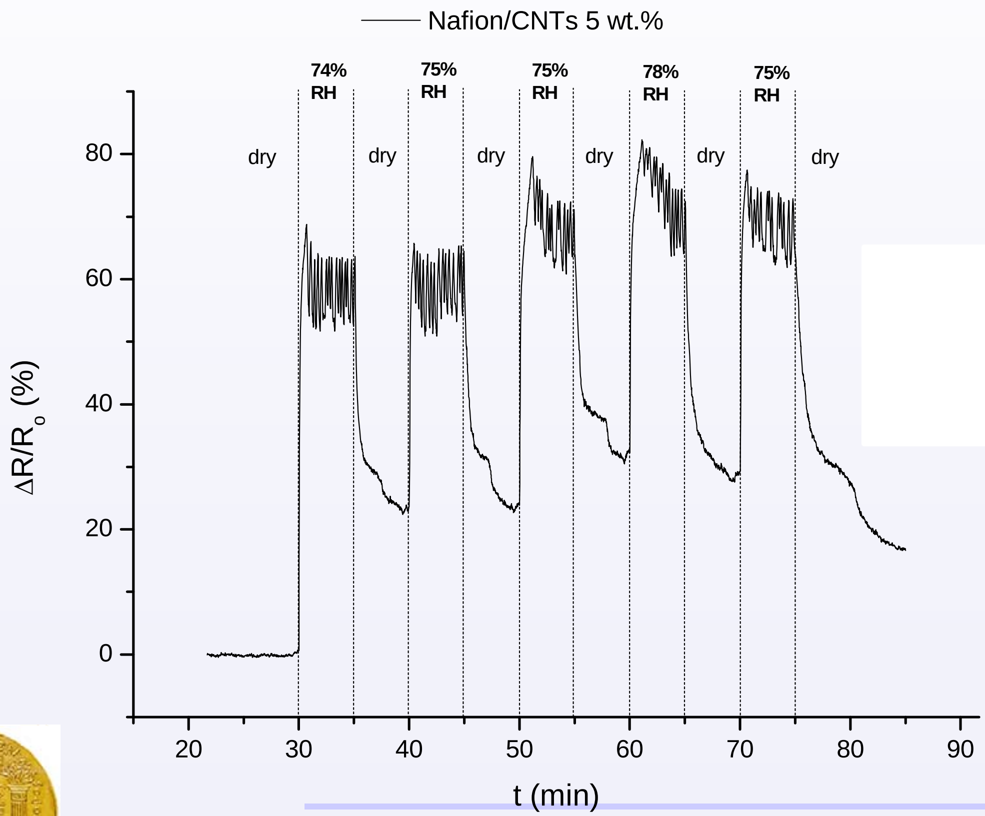


Polymer/carbon nanotube (CNT) composites for chemical sensing









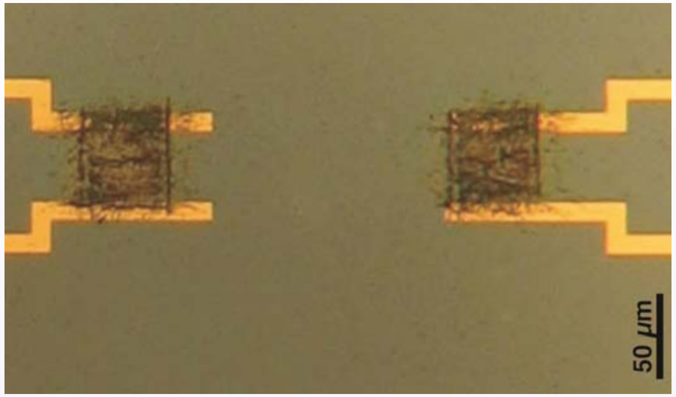
- ✓ Consistent and reproducible change in resistance (70-100%)
- ✓ Quick response time (sec)

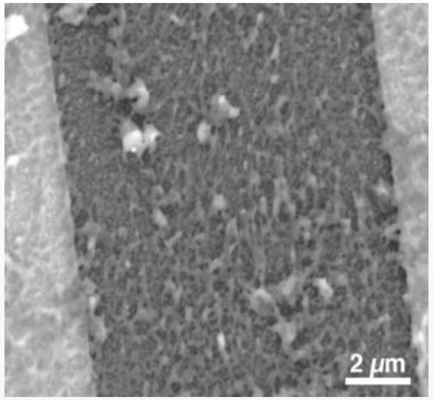
Direct dry-laser printing of thin-film polyaniline devices

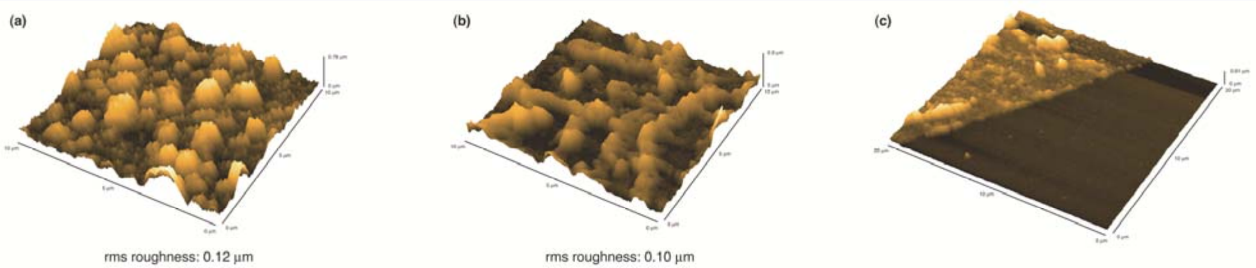
- Polyaniline (PANI) is conductive and is in-situ polymerized on quartz

- Electrical properties change upon biotin-avidin binding

- Electrical properties change upon NH_3 adsorption





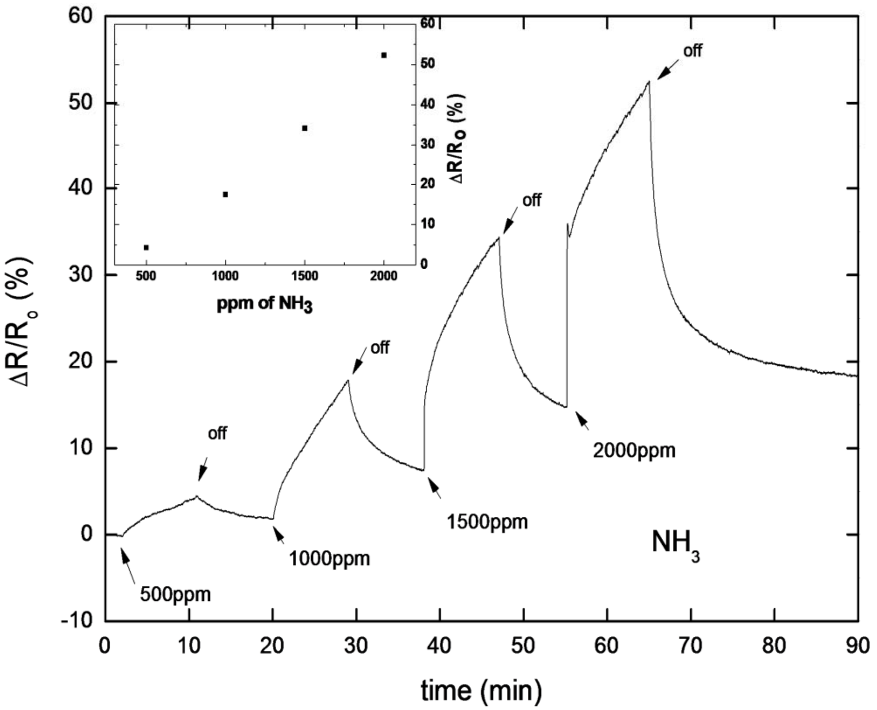


rms roughness: 0.12 µm

rms roughness: 0.10 µm

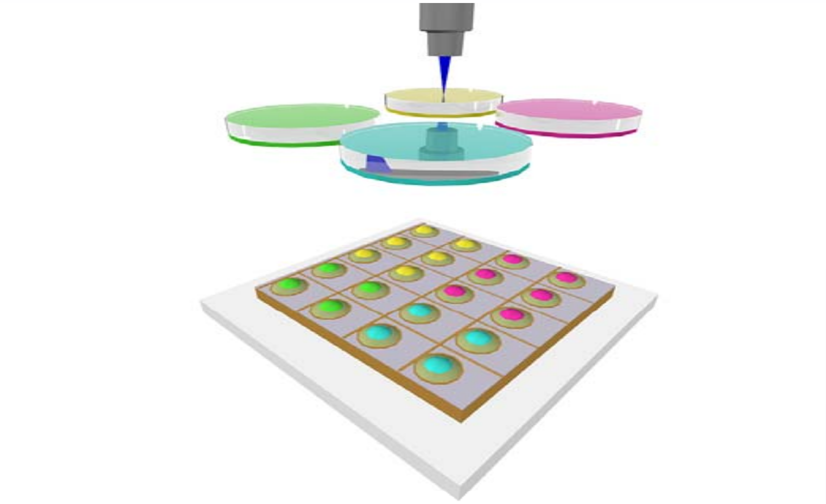
Direct dry-laser printing of thin-film polyaniline devices

- The samples are conductive and present ohmic behavior, which is essential for their use in electroactive applications.
- The resistance is increased when exposed to ammonia, and recovers after the removal of the analyte. This effect is attributed to the deprotonation of PANI due to the interaction with ammonia, leading to an increase of electrical resistance.
- Linear response in the NH_3 concentration range.



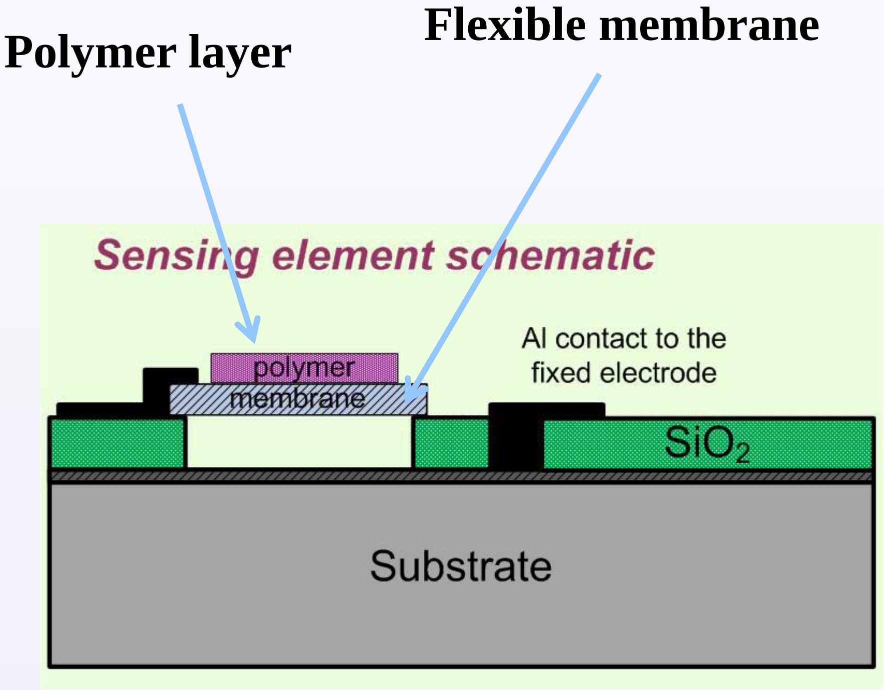
M. Kandyla , C. Pandis, P. Pissis, I. Zergioti, Appl. Phys. A, APA, 2012, DOI:10.1007/s00339-012

The capacitive approach for chemical sensing



Sensors:

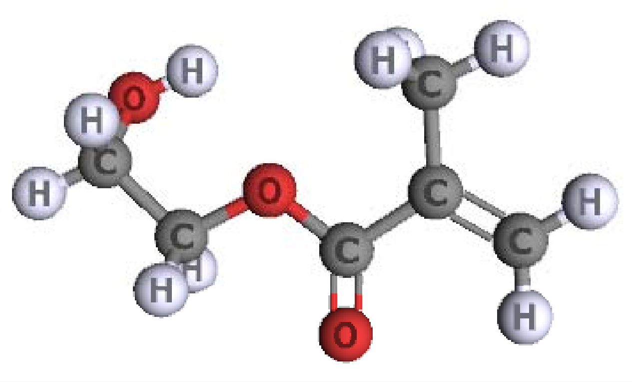
- Diameter : 150, 200, 250 μm
- Thickness : 0.5,1.5 μm
- Gap spacing : 0.5 μm

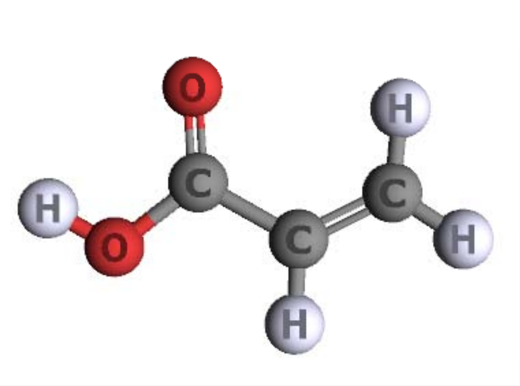


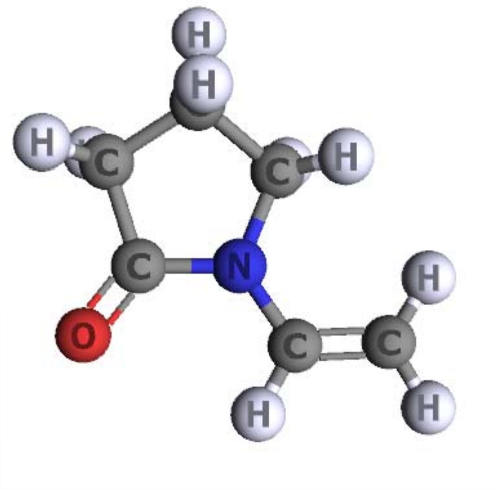
- The sensor is exposed to humidity or Volatile Organic Compounds (VOCs).

- The polymer layer absorbs the corresponding molecules and results in membrane bending and therefore a change in the capacitance value of the device.

Studied polymers







PHEMA : Poly (2-Hydroxyethyl methacrylate)
Solvent : ethyl-actete

PAA : Polyacrylic acid

Solvent: H_20

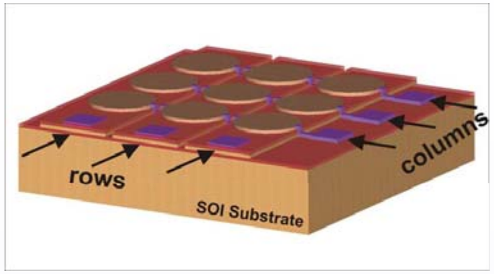
P4VP : Poly (4-vinylpyridine)
Solvent: H_20

Criteria of selection

- High absorption of humidity and Volatile Organic Compounds (VOCs)

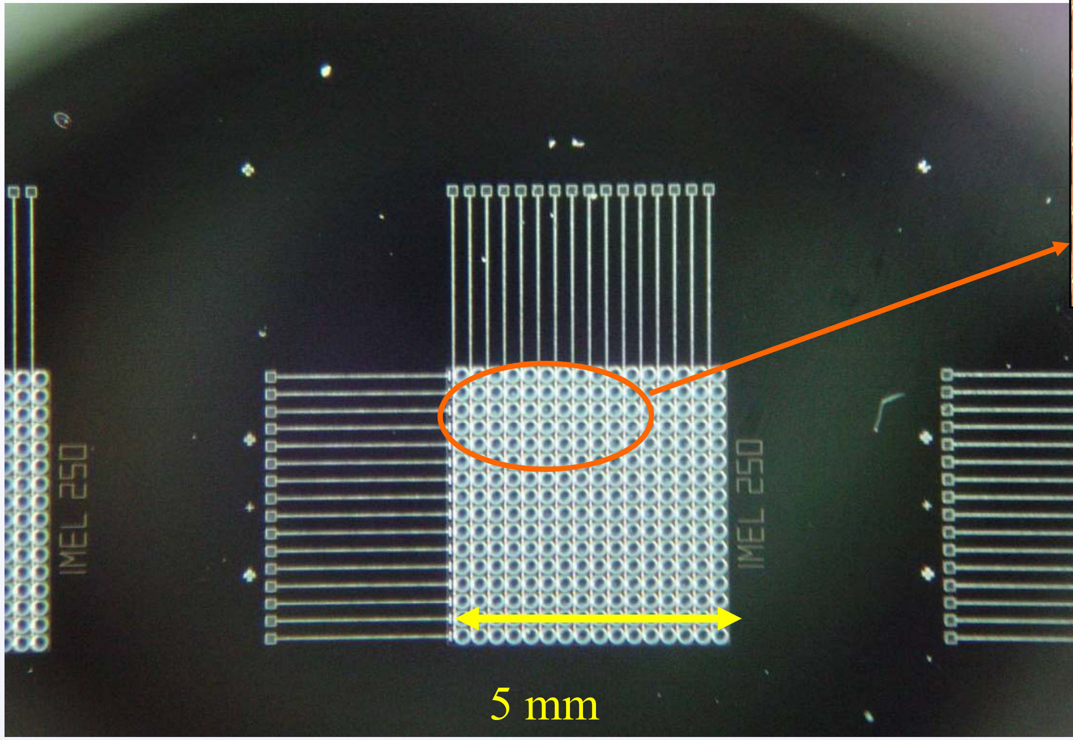
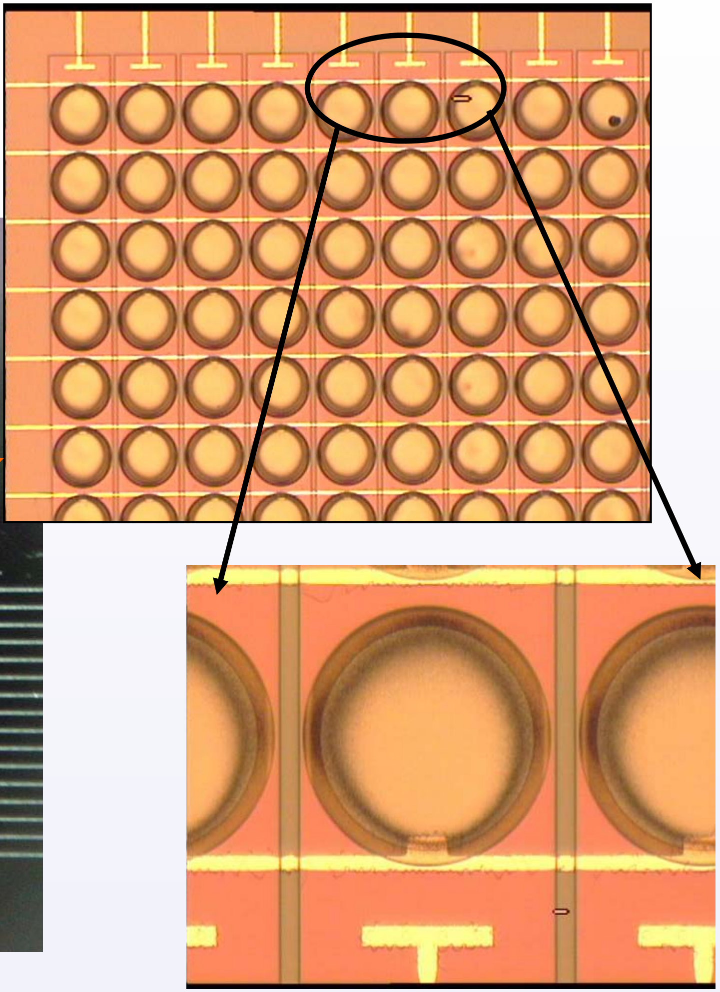
- Selective absorption of analytes for multianalyte detection applications (e-nose)

Capacitive sensors



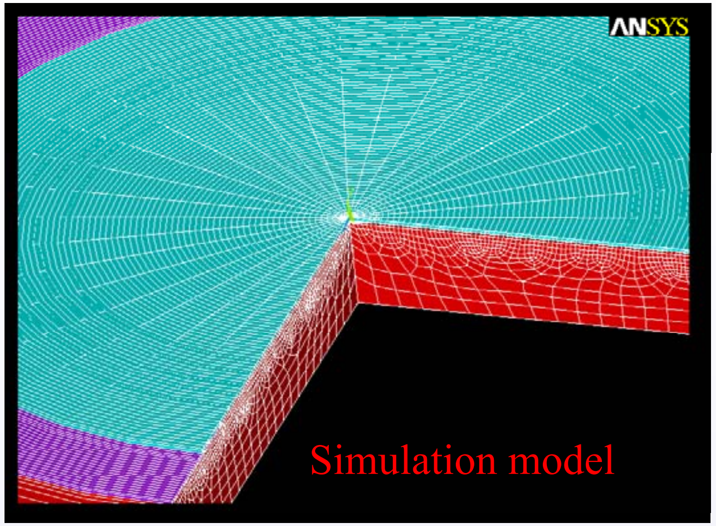
12 x 12 mm^2 die

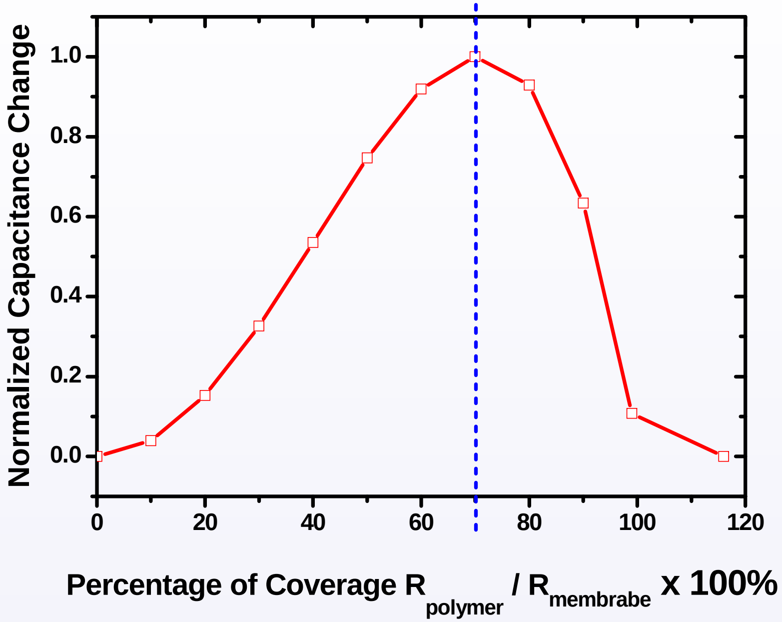
16 x 16 matrix

Sensor simulation

Finite Element Analysis for the estimation of maximum sensitivity





Expanded 2D-axisymmetric Finite Element model of sensor

Optimal polymer coverage of sensor membrane 70%

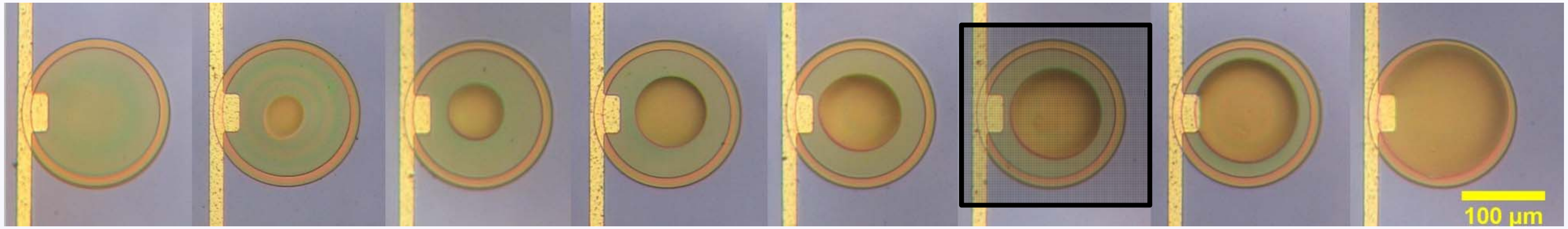
The percentage of coverage expresses the ratio of the polymer spot radius to the sensor membrane radius

V. Tsouti et. al., Microelectron. Eng. ***85****, 1359 (2008)*

Printing process on sensors' membranes

Laser spot size : 20 - 80 μm

Percentage of coverage →



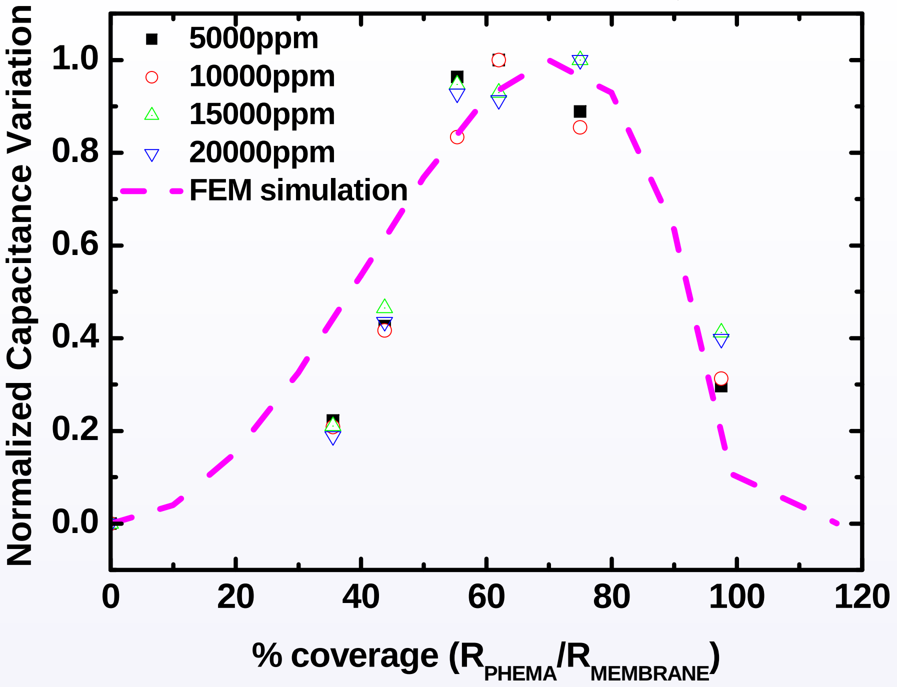
70 % percentage of coverage

Membranes:
- diameter : 150μm
- thickness :1.5μm

"Liquid phase direct laser printing of polymers for chemical sensing applications", C. Boutopoulos, V. Tsouti, D. Goustouridis, S. Chatzandroulis and I. Zergioti, Appl. Phys. Lett., 19 191109 (2008).

Experimental versus simulation results

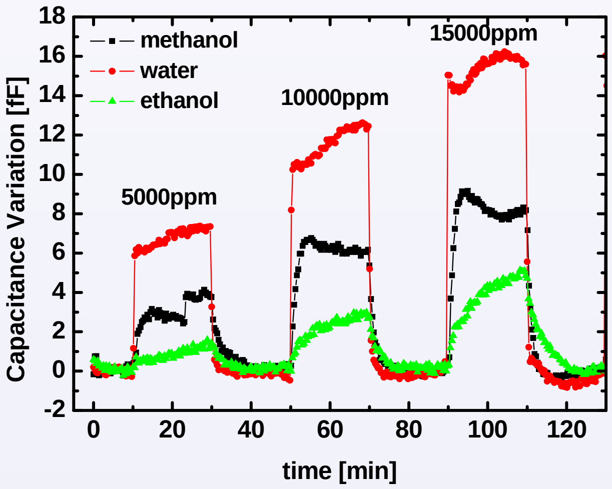
Membrane diameter : 150μm
Membrane thickness : 1.5μm



Normalized sensor capacitance variation plotted as a function of membrane coverage with PHEMA polymer for different concentrations of water analyte

PHEMA 2%, Solvent: ethyl-lactele

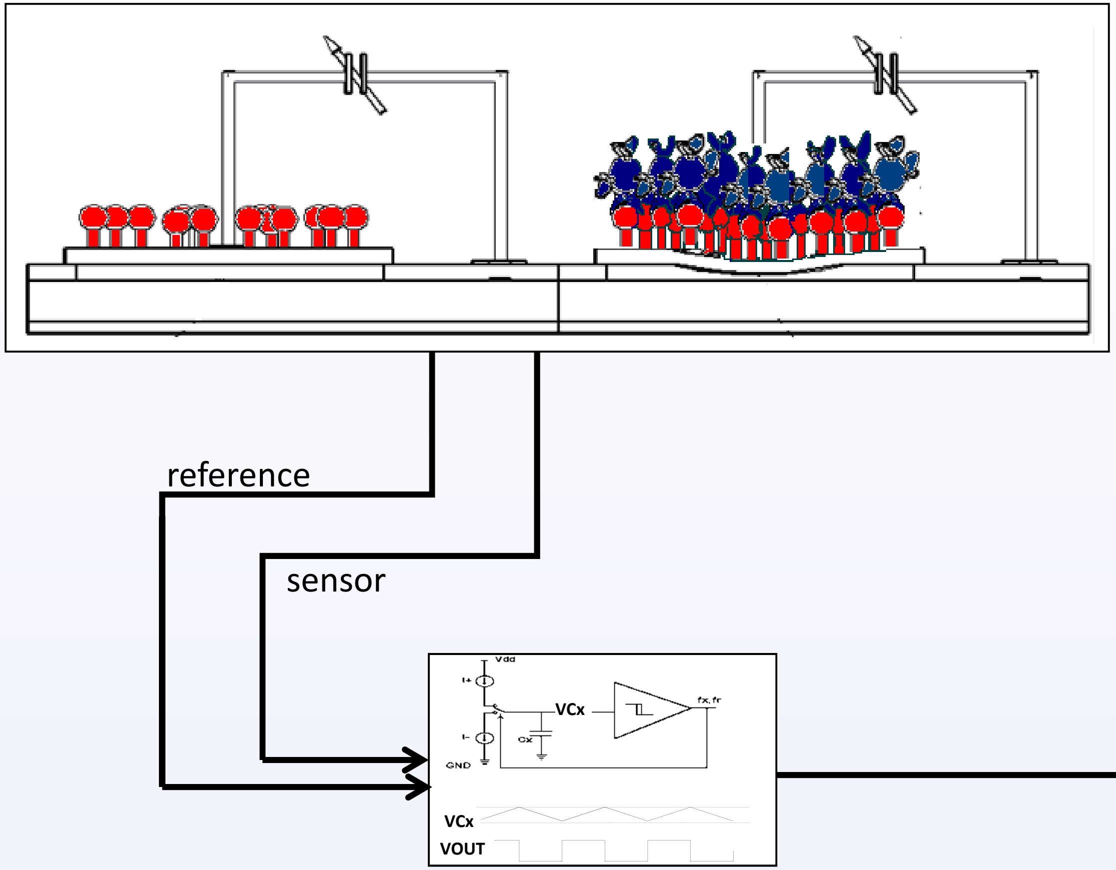
- **The sensor capacitance change is maximized when the sensor membrane coverage is about 70%, regardless of the analyte concentration.**
- **Excellent agreement with the corresponding simulated values the FEM.**

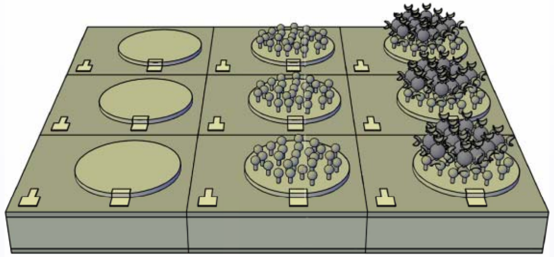


Ioanna Zergioti, NTUA

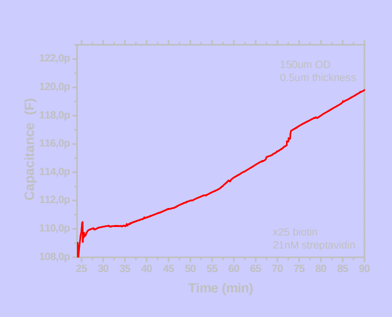
Direct laser printing of biomaterials

THE CAPACITIVE APPROACH FOR SENSOR DEVICES





Change of surface energy due to target binding on receptor molecules results in membrane bending and therefore a change in the capacitance value of the device

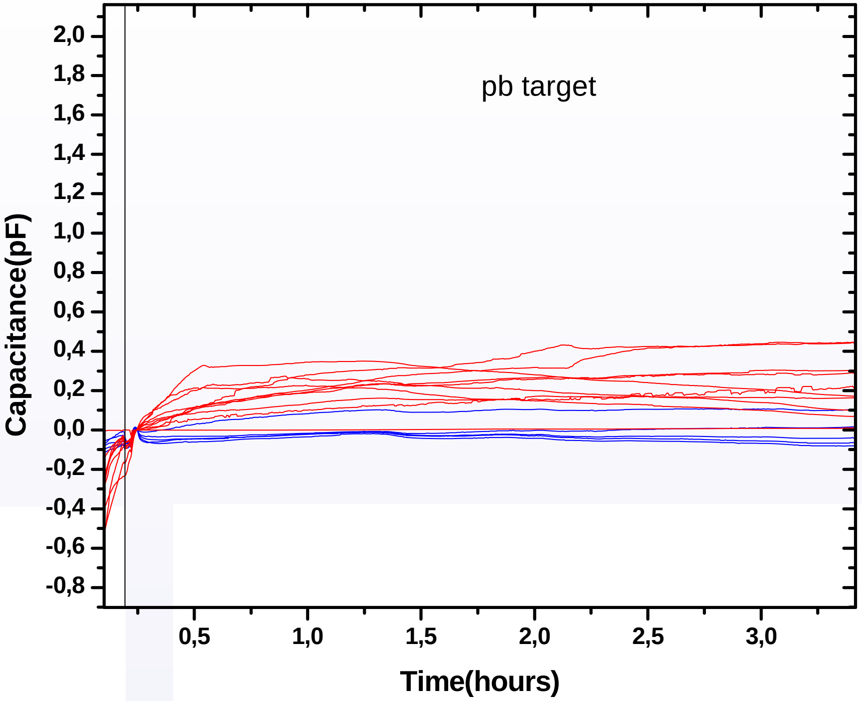


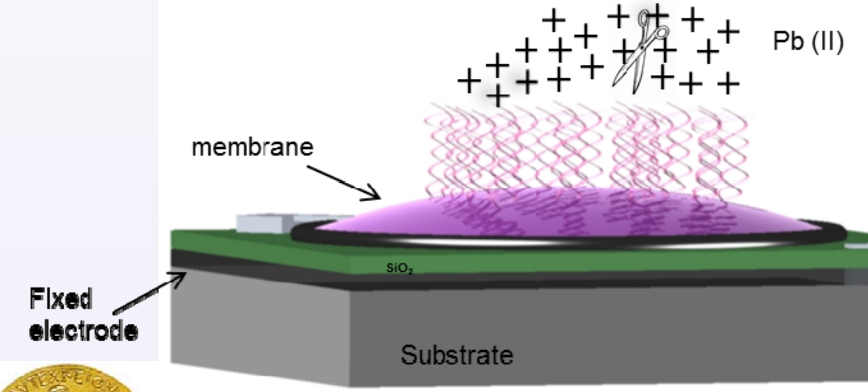
Biosensors by means of the laser induced forward transfer technique, M. Chatzipetrou, G. Tsekenis, V. Tsouti, S. Chatzandroulis, I. Zergioti, Applied Surface Science, **278**, 250–254, 2013.

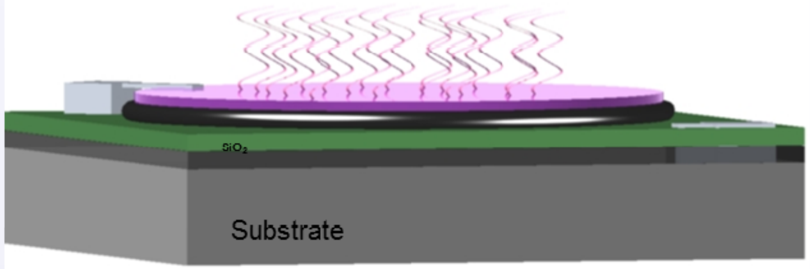
Capacitive sensors

Laser printing of aptamers on capacitive sensors for the detection of Pb ions

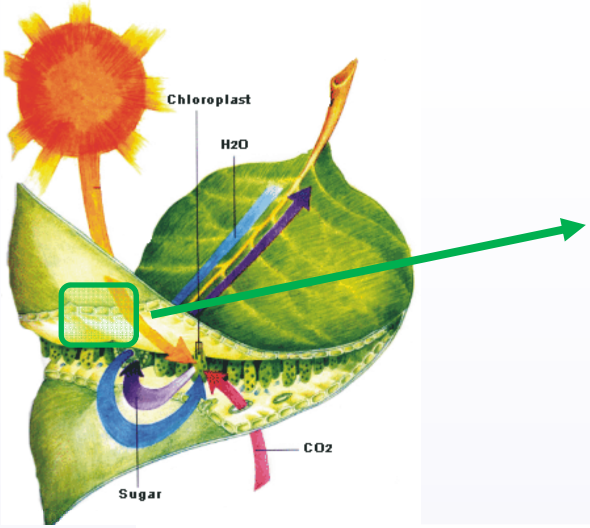
- Reference capacitors: oligomer probes
- Measuring capacitors: hybridized oligomer probes with target

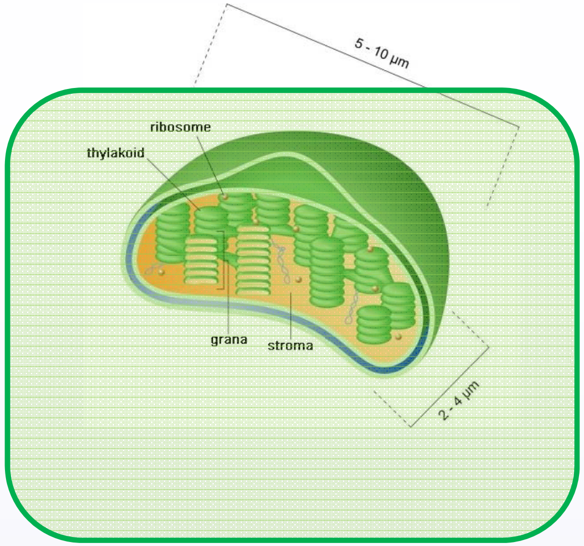


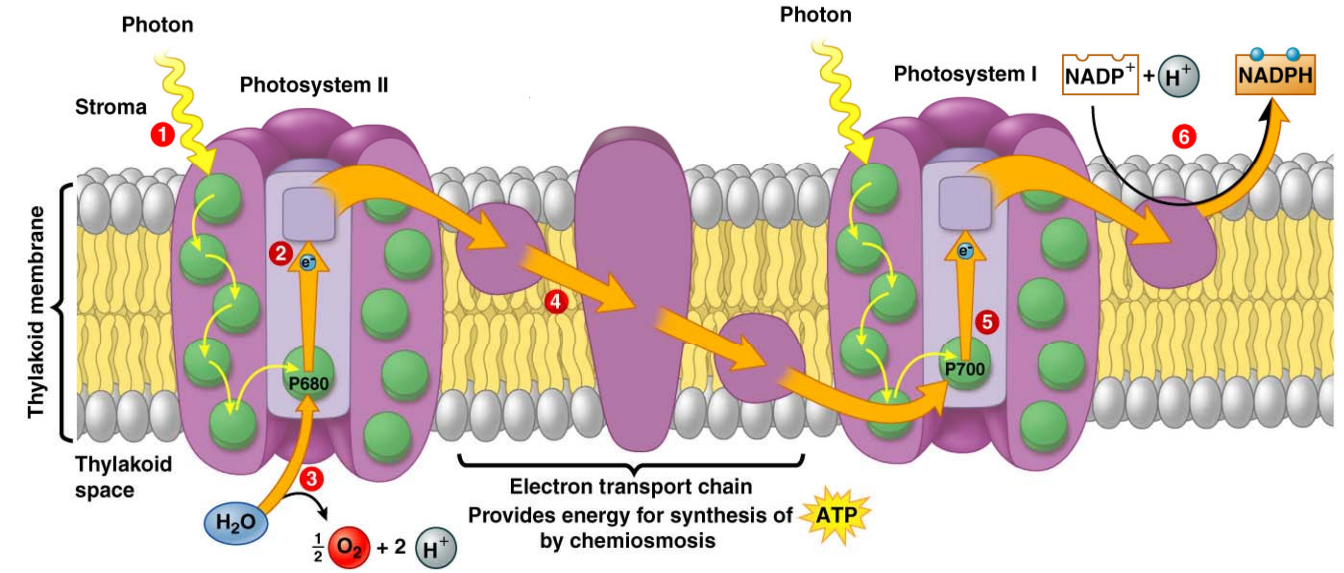




Photosynthetic Biosensors for environmental applications







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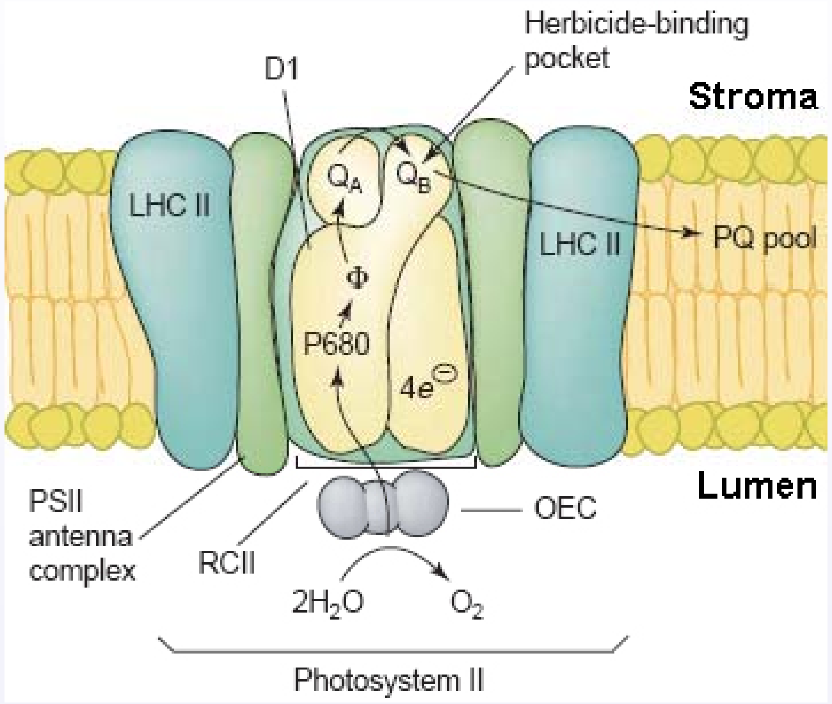
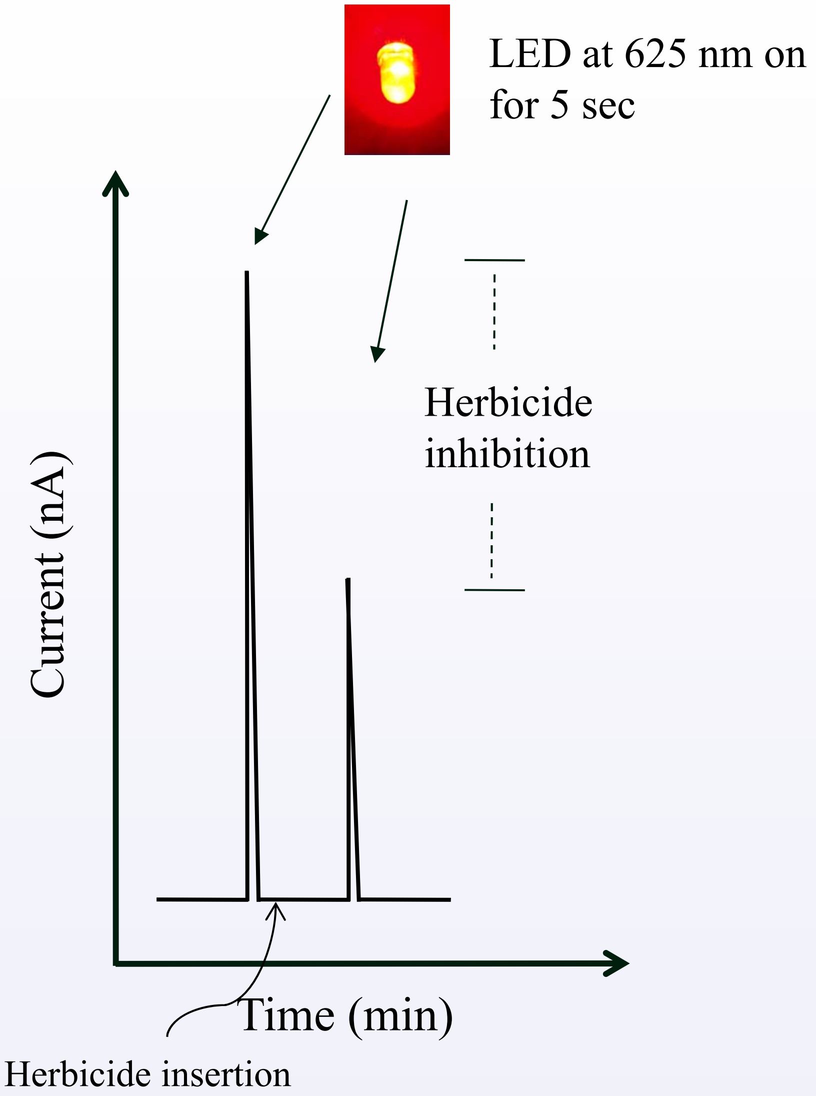
Photosynthetic reaction
Light Harvesting complex II





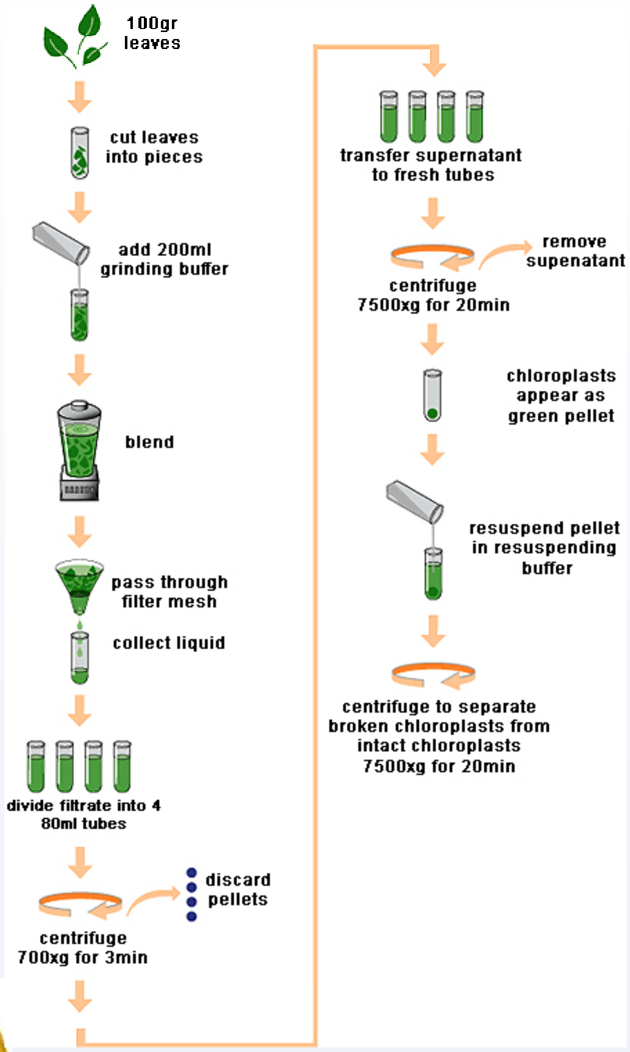
LED at 625 nm on for 5 sec

Herbicide inhibition

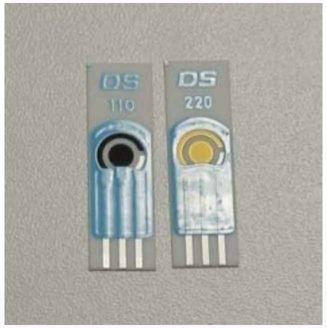
Herbicide insertion

Bio-receptors and Electrodes

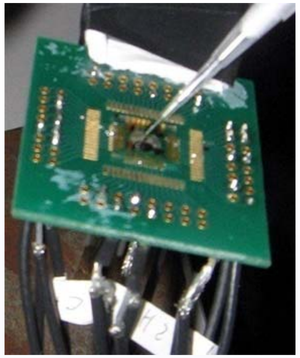
Bio-receptors



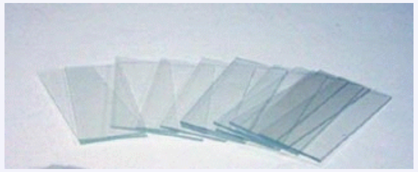
Electrodes



DropSens Screen Printed Electrodes



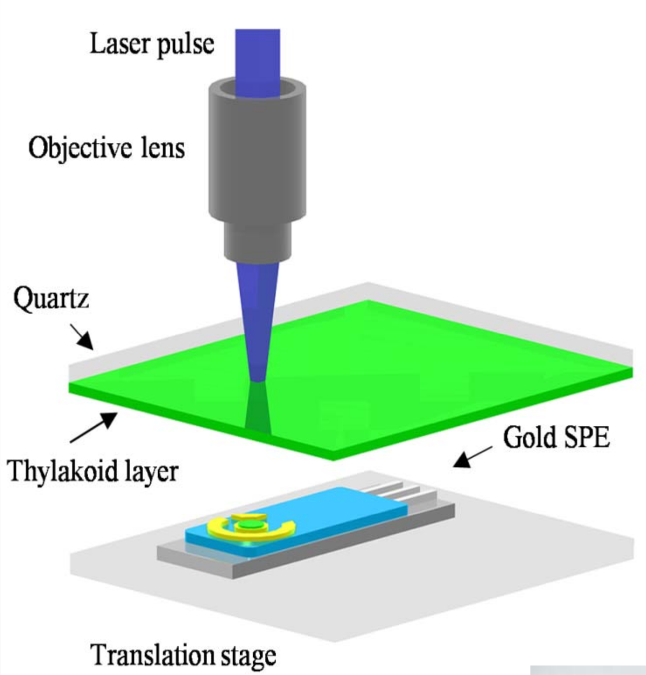
MicroElectrode Arrays

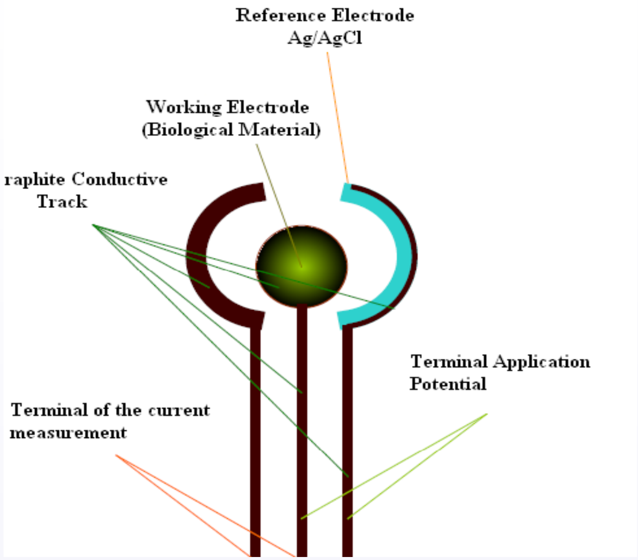


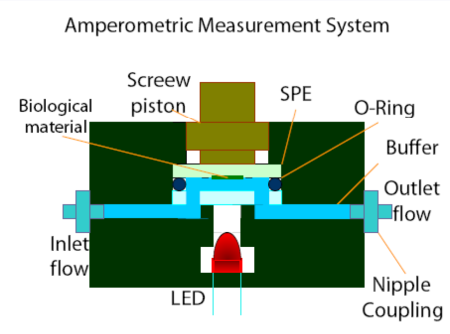
Indium Tin Oxide

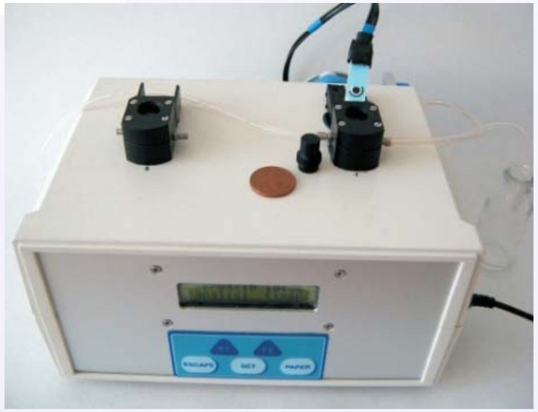
Silicon NanoWires

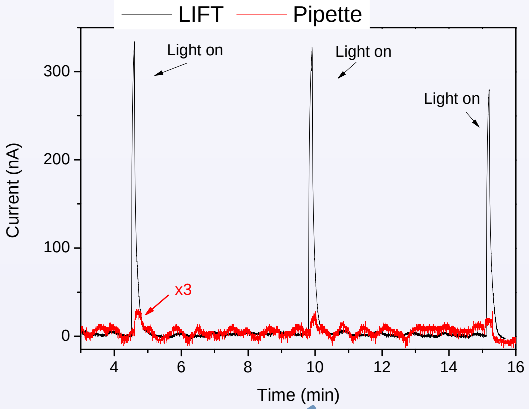
Laser Direct Printing - Immobilisation











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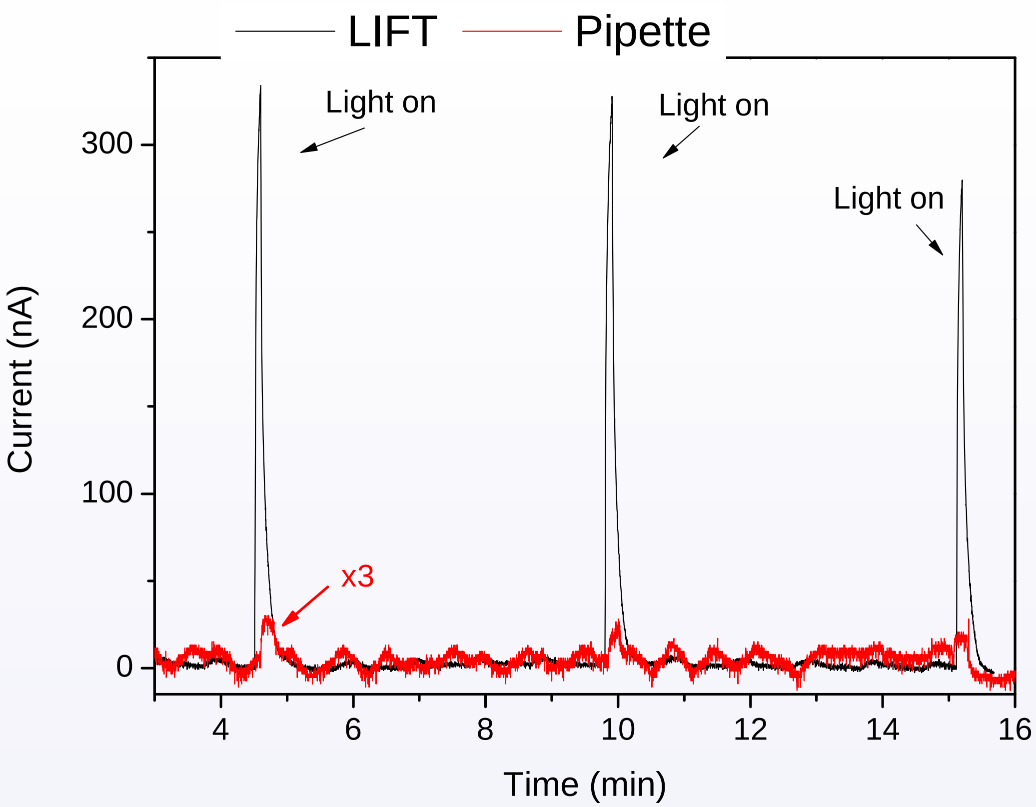
LIFT for Photosynthetic Biosensors : Direct Immobilization



- Direct immobilization of the thylakoid laser printed material without the use of any functionalization layer
- High activity and high signal to noise ratio

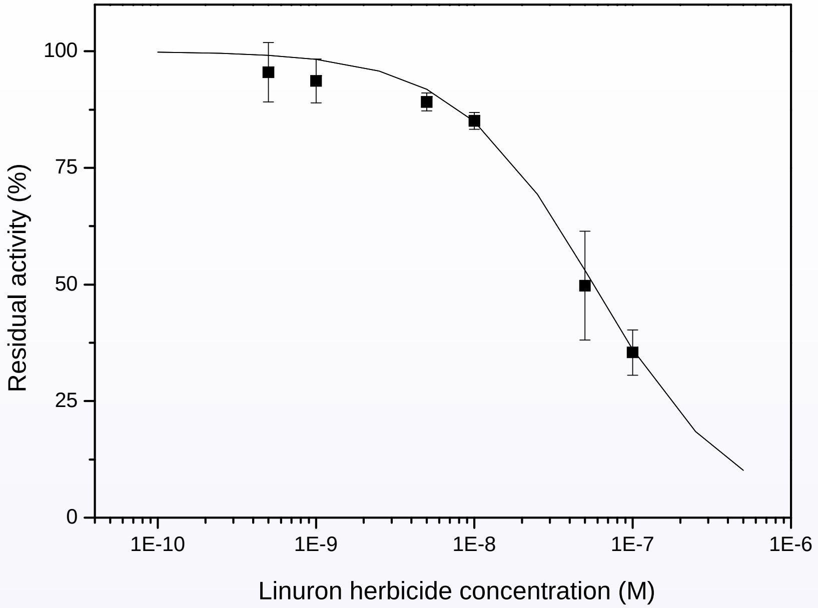
- Conventional technology: Use of chemical linkers and polymer hydrogels as immobilization matrices which harm photosynthetic materials

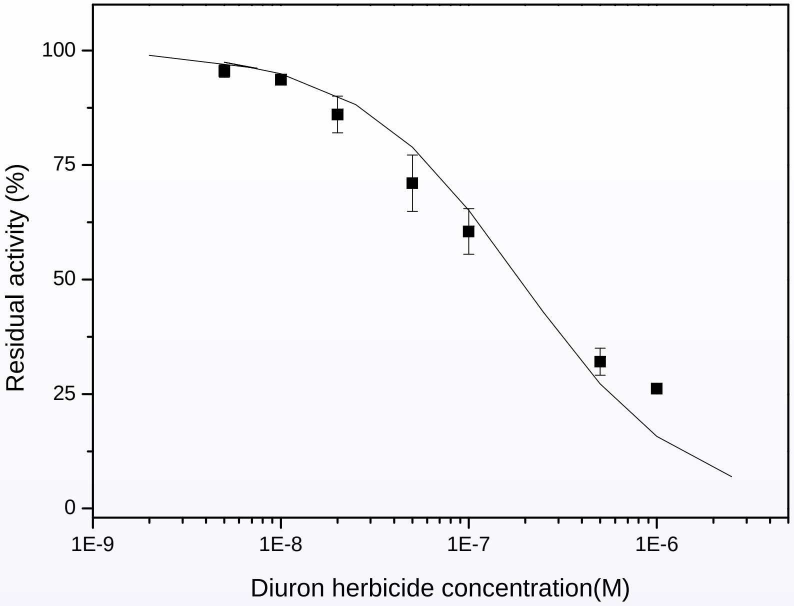
LIFT eliminates the functionalization step of the sensor

-C. Boutopoulos, E. Touloupakis, M. Giardi, I. Zergioti, Appl. Phys. Lett., ***98*** *093703 (2011)*

- C. Boutopoulos, E. Touloupakis, G. Rodio, I. Zergioti, Patent Application number : 20120100368 , 11-07-2012

LIFT for Photosynthetic Biosensors : Calibration Sensitivity curves





Pesticide	LOD (IUPAC]
Linuron	8 x 10^{-9} M
Diuron	4 x 10^{-9} M

E. Touloupakis, C. Boutopoulos, I. Zergioti, M. Giardi, Analytical and Bioanalytical Chemistry, 402 (10), pp. 3237-3244 (2012).

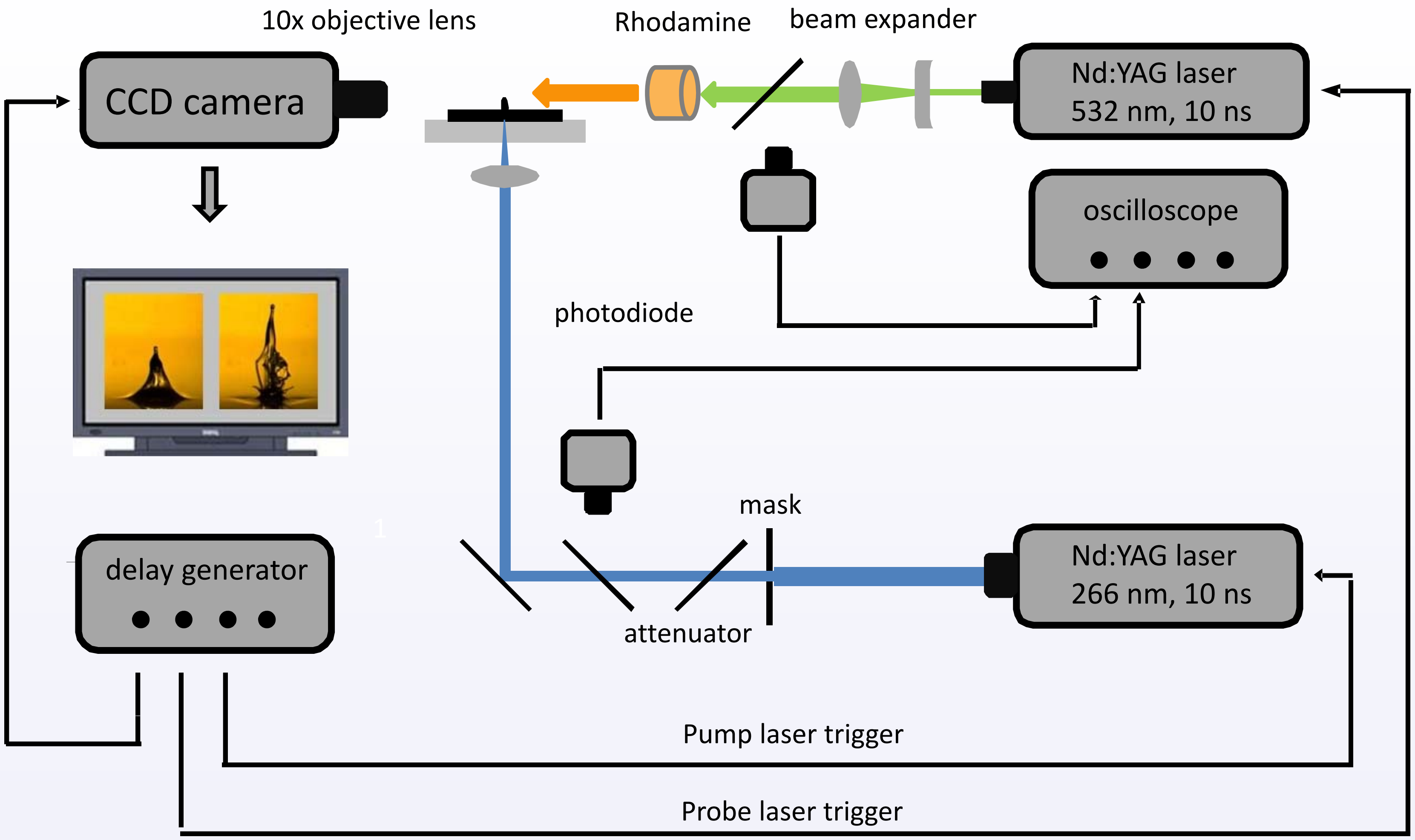
Mechanisms of Direct Laser Immobilization of biomolecules

- Liquid properties (surface tension, viscosity, thickness)

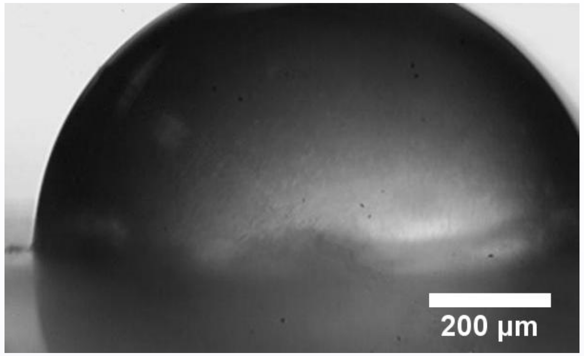
- Wetting and roughness of the sensor surface

- Impact Velocity

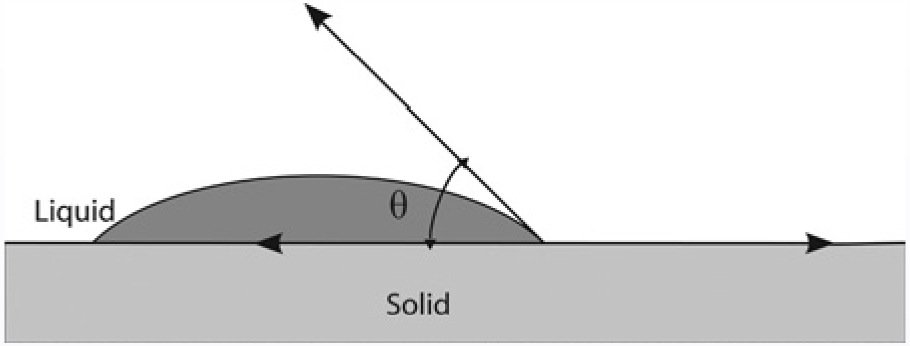
Shadowgraphic imaging setup



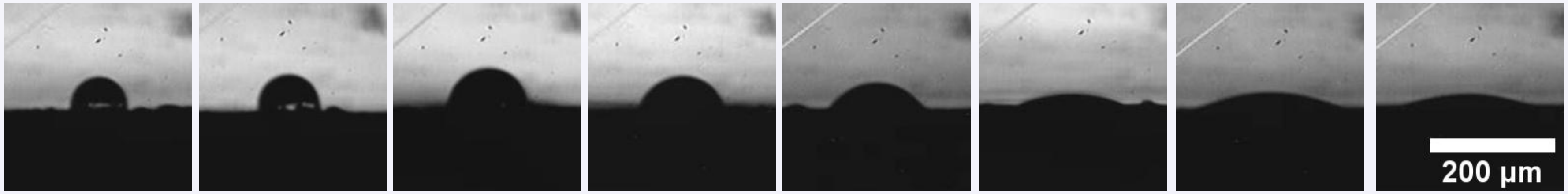
Laccase enzyme direct immobilization on graphite SPE



Reference pipette spotting (θ = 89.4°)



E (mJ/cm²)



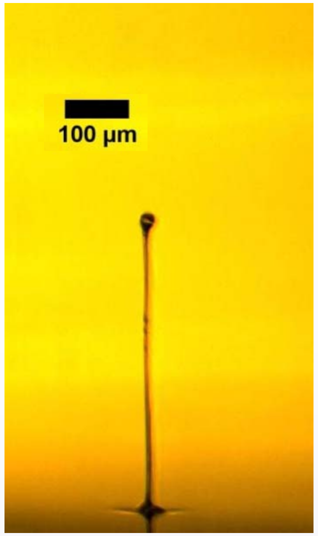
125	150	175	200	225	250	275	300
89.1° ± 2.6°	88.2° ± 8.6°	93.1° ± 5.2°	71.1° ± 11.7°	59.6° ± 7.1°	33.8° ± 5.5°	27.5° ± 12.2°	18.5° ± 3.5°

Contact angle

Laser Induced Forward Transfer Shadowgraphy study

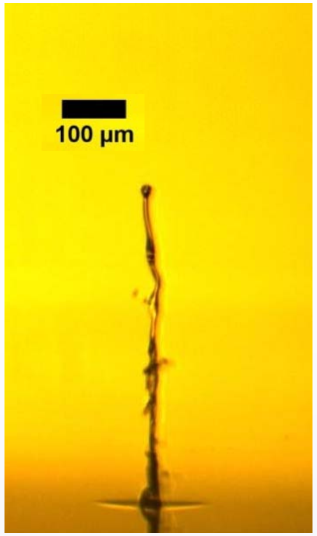
1M phosphate buffer pH8

180 mJ/ cm^2



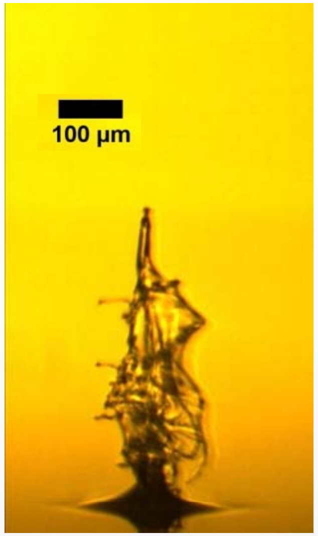
Distance = 467 µm
Time= 14,8 µs

263 mJ/ cm^2



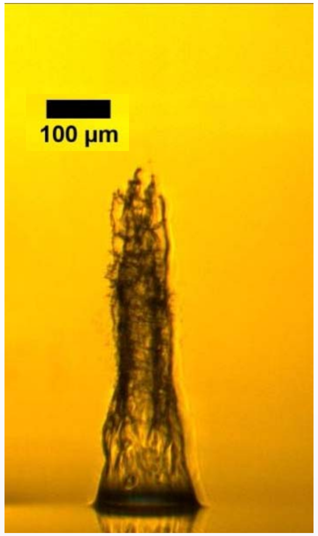
Distance = 506,8 µm
Time= 10,3 µs

454 mJ/ cm^2



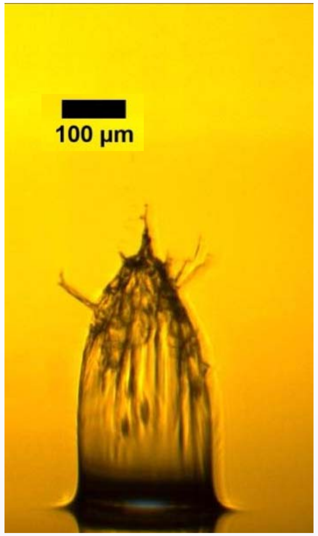
Distance = 412,9 µm
Time= 6,36 µs

890 mJ/ cm^2



Distance = 534 µm
Time= 1,82 µs

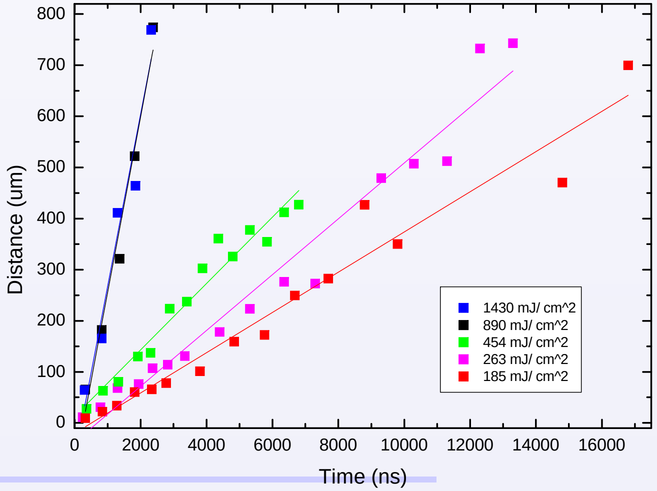
1430 mJ/ cm^2



Distance = 470,3 µm
Time= 1,84 µs

Chosen Laser energy fluence for deposition

180 mJ/ cm^2	**33 m/s**	***Pim= 0,61 MPa***
263 mJ/ cm^2	**47 m/s**	***Pim= 1,17 MPa***
454 mJ/ cm^2	**70 m/s**	***Pim= 2,73 MPa***
890 mJ/ cm^2	**255 m/s**	***Pim= 36,78 MPa***
1430 mJ/ cm^2	**263 m/s**	***Pim= 39,18 MPa***



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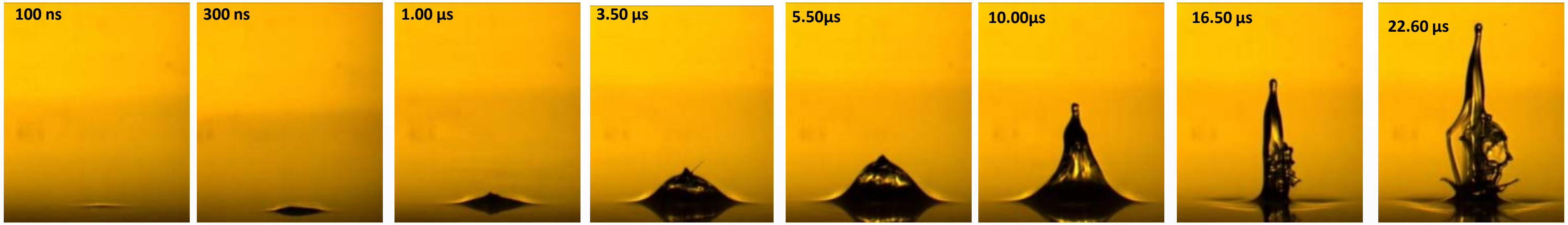
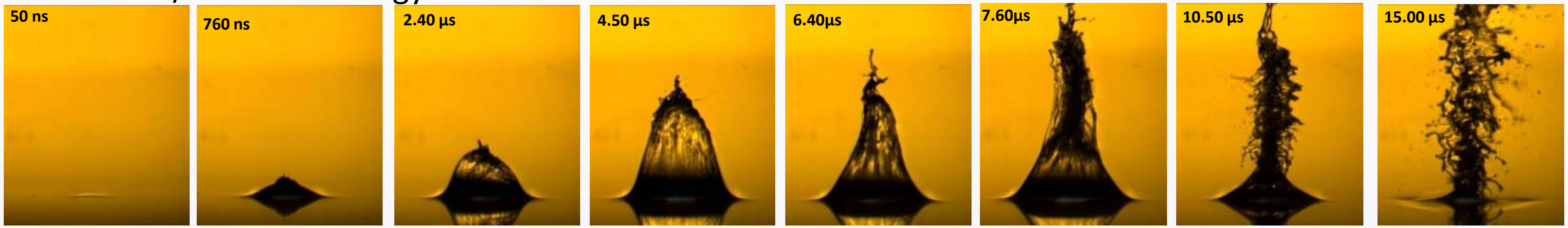
Shadowgraphic time-resolved images of the test liquid ejection under various laser fluences

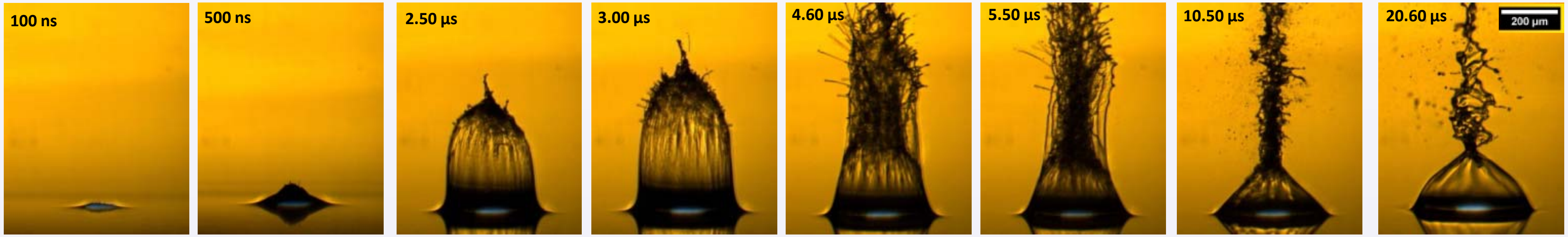
- 430 mJ/cm^2 laser energy fluence



- 600 mJ/cm^2 laser energy fluence



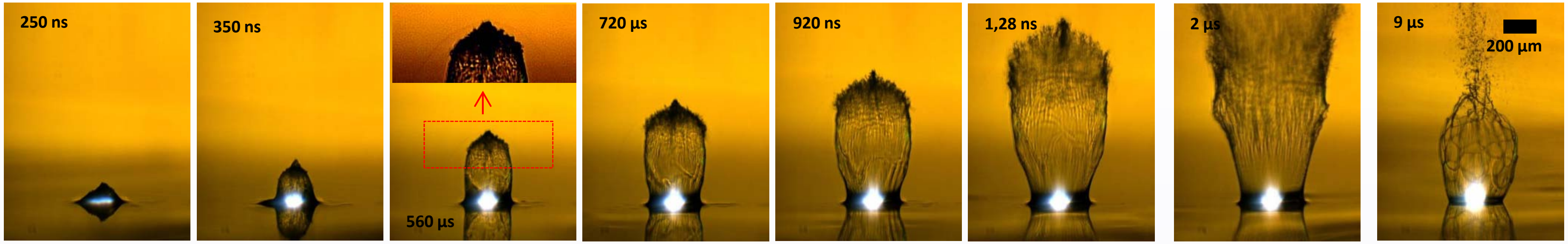
- 930 mJ/cm^2 laser energy fluence

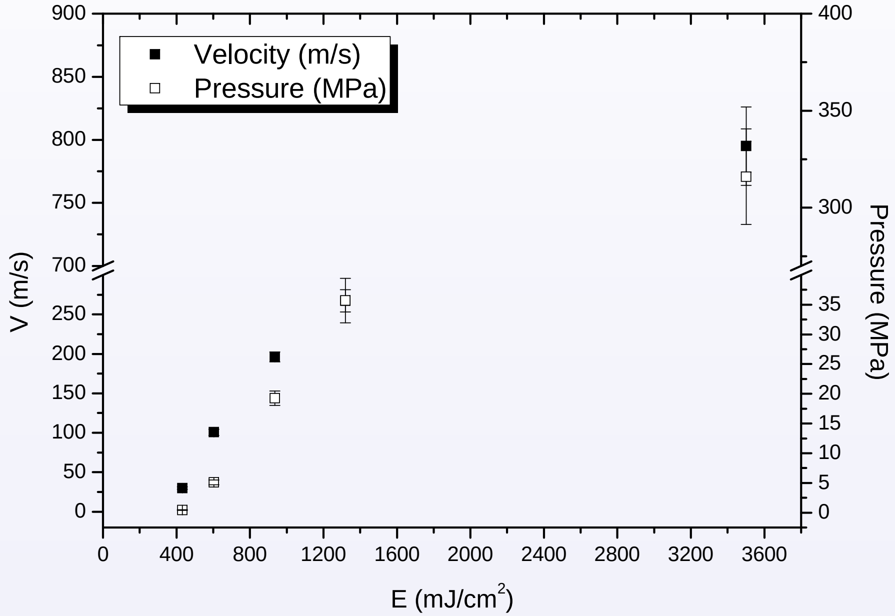


30 μL phosphate buffer on Ti coated quartz target (60 μm thickness), 130 μm spot size

Shadowgraphic time-resolved images of the test liquid ejection under various laser fluences

- 3,50 J/cm^2 laser energy fluence

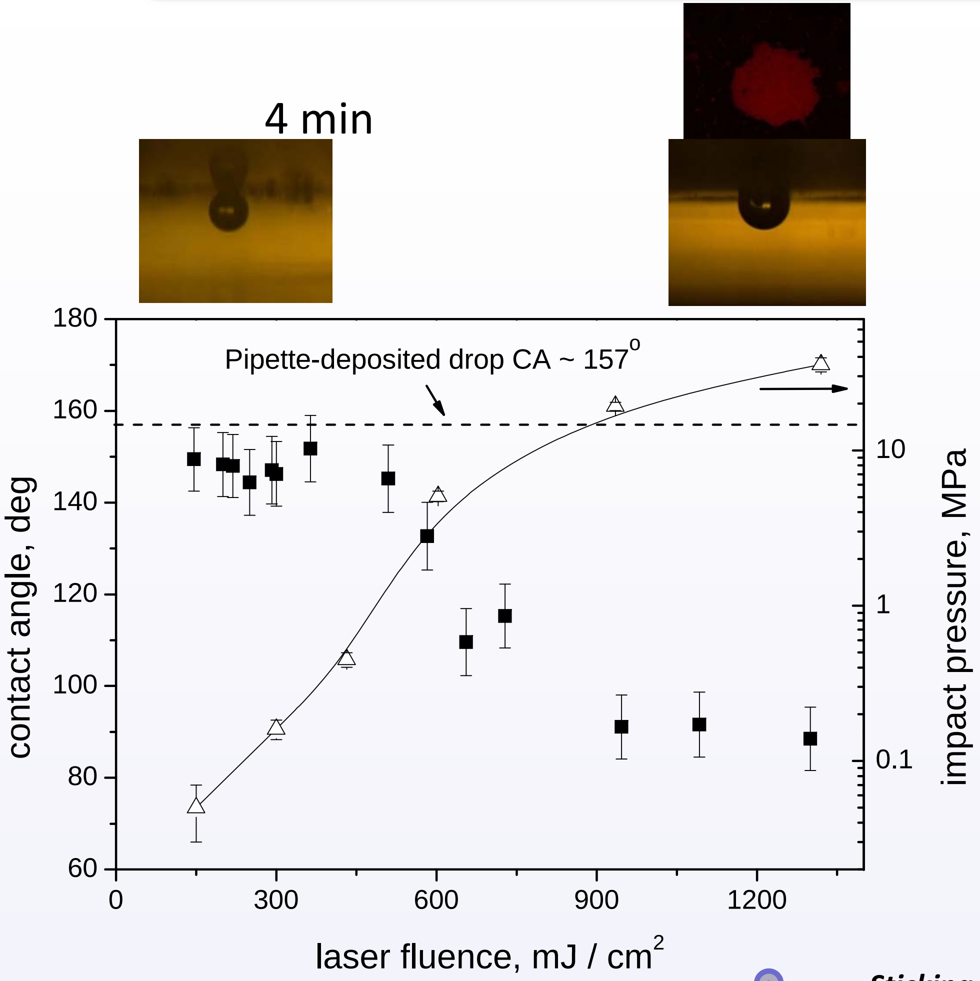




LIFT is a very fast printing technique ⇒ High Impact Pressure ⇒ Direct Laser immobilization of biomaterials on sensor substrates

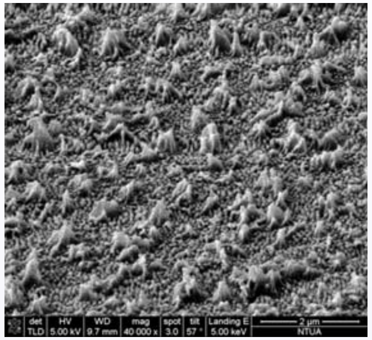
30 µL phosphate buffer on Ti coated quartz target (60 µm thickness), 80 µm spot size

Wetting states transition due to high velocity impact



Transition from partial to complete wetting

$$P_d= \frac{1}{2} \cdot \rho \cdot V_{im}^2$$

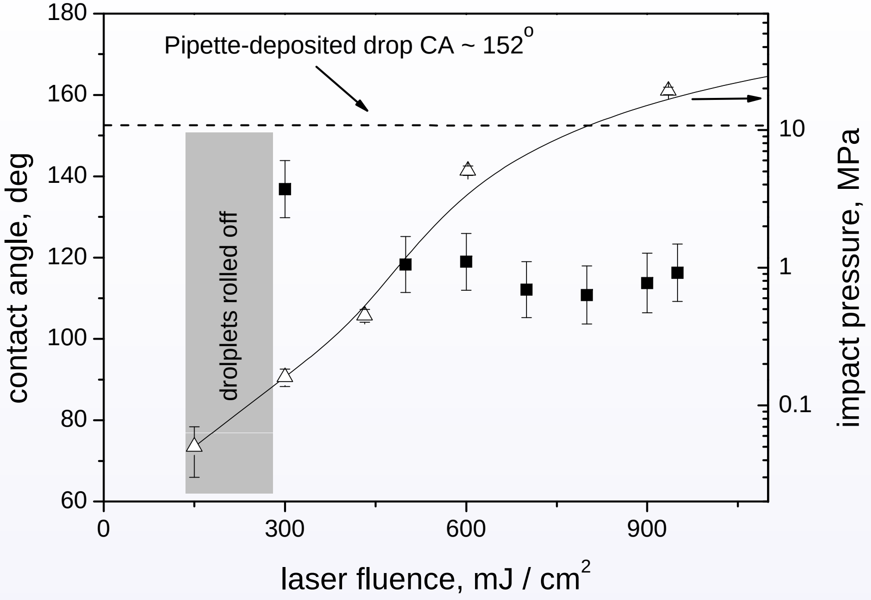


4 min oxygen plasma etched nanotexture PMMA resulting at 600 nm roughness

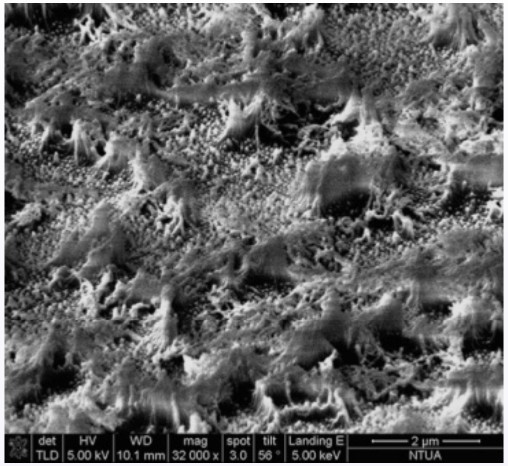
Sticking of droplets on slippery superhydrophobic surfaces by Laser Induced Forward Transfer (LIFT) , *Christos Boutopoulos, Dimitrios P. Papageorgiou, Ioanna Zergioti, Athanasios G. Papathanasiou, accepted in Appl. Phys. Let., 2013.*

30 μL phosphate buffer on Ti coated quartz target (60 μm thickness), 130 μm spot size

Effect of laser energy density on superhydrophobic surfaces



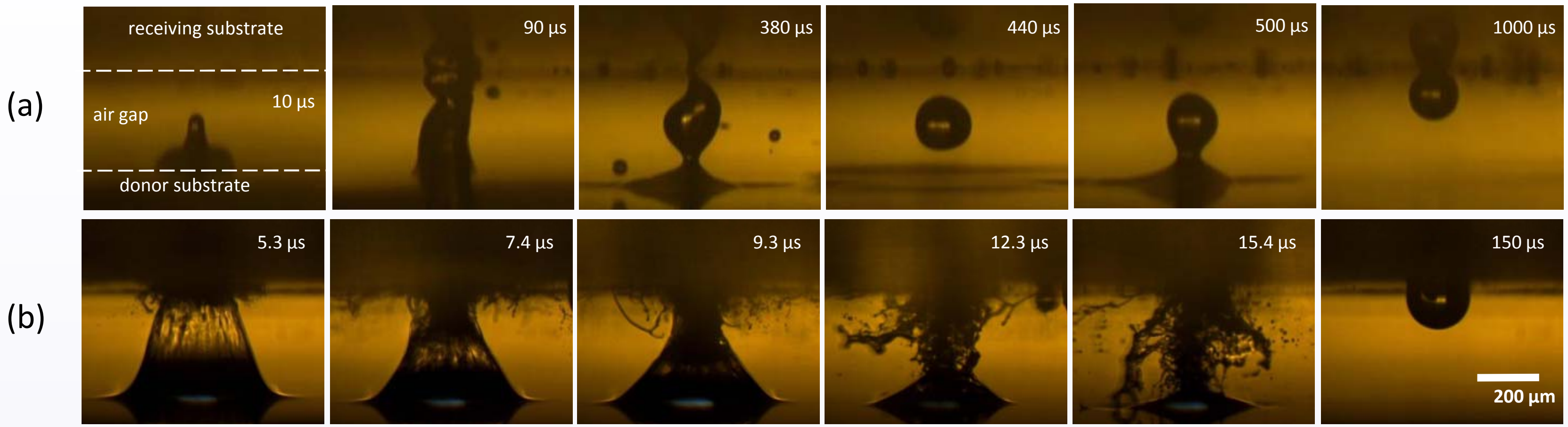
$$P_d = ½·ρ·V_{im}^2$$



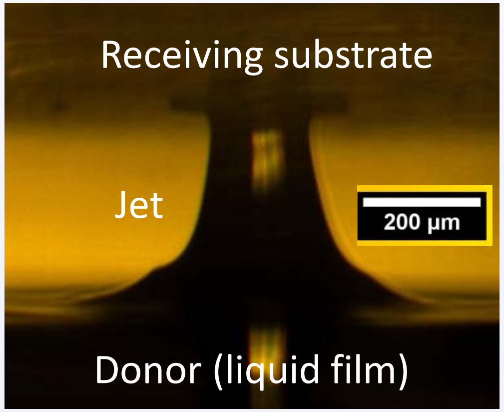
10 min oxygen plasma etched nanotexture PMMA resulting at 2,5 µm roughness

Sticking of droplets on slippery superhydrophobic surfaces by Laser Induced Forward Transfer (LIFT) ,
Christos Boutopoulos, Dimitrios P. Papageorgiou, Ioanna Zergioti, Athanasios G. Papathanasiou, accepted Appl. Phys. Let., 2013.

Effect of superhydrophobic surface on the recoil effect

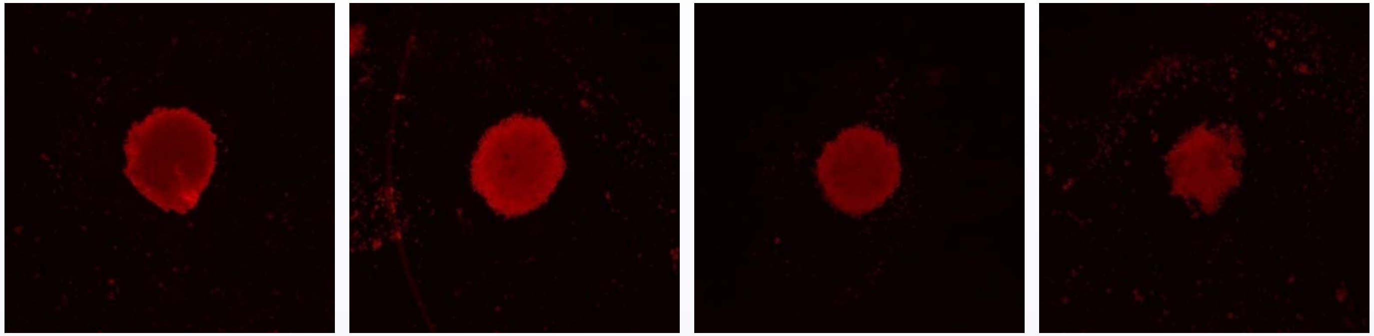


Side view imaging of the evolution of LIFT printing on the superhydrophobic substrate shown in previous slide (a) for low (300 mJ/cm²), and (b) for high (930 mJ/cm²) laser fluence respectively.

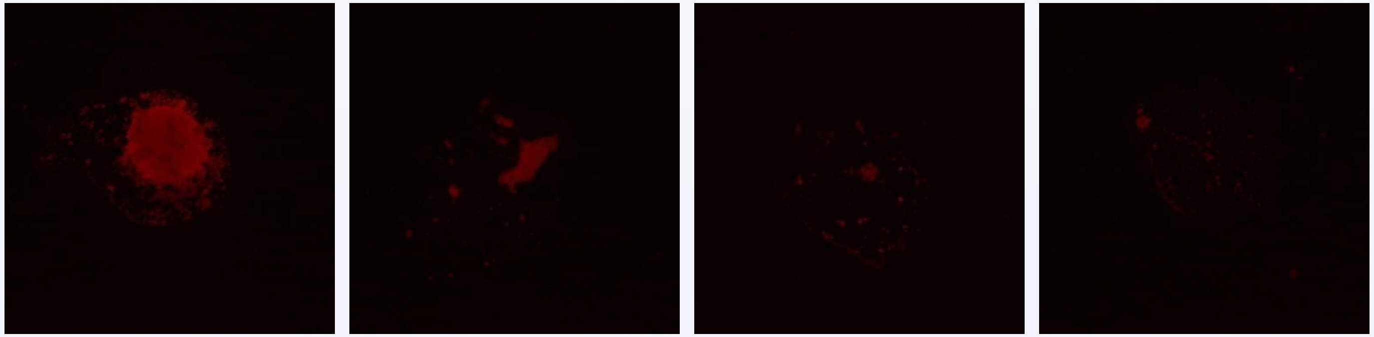


t = 30 µs

LIFT immobilization of thylakoids on various substrates: fluorescence results



1000 mJ/cm^2 800 mJ/cm^2 700 mJ/cm^2 600 mJ/cm^2



500 mJ/cm^2 400 mJ/cm^2 300 mJ/cm^2 200 mJ/cm^2

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BRFAA
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- MARIE CURIE IAPP: FP7-PEOPLE-2012-IAPP-Industry-Academia Partnerships and Pathways (IAPP)
“Laser Digital Micro-Nano fabrication for Organic Electronics and Sensor applications” (2013-2017)

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THANK YOU!