UNIVERSITÀ DEGLI STUDI DI PADOVA

A novel plasma jet with RF and HF coupled electrodes

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Why a novel device?

Aims

Efficient
Low temperature

Examples

Requirements

Clean
Homogeneous coatings
Preserve precursors functionalities

Applications

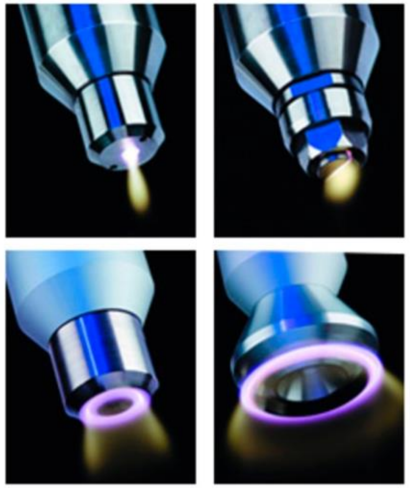
Manufacturing
Medical devices
Electronics
Sensors

Target surface charging

In the market

Acxys

Plasmatreat ®

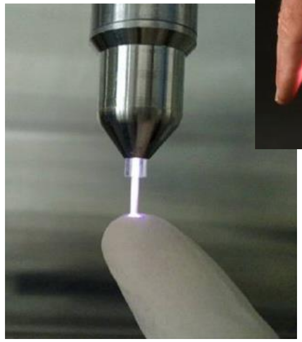


Maan

Vito

Plasmawerk

Kinpen



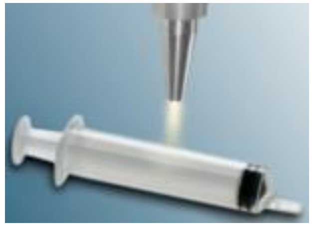
SurfX

Innophysics

Applications

Energy
- Membrane treatment before coil bonding
- Activation before screen printing
- Metal treatment before polymer spraying

Automotive
- Windscreen / frame adhesion enhancement
- Paint / composite or plastic parts adhesion enhancement
- EPDM profiles treatment
- Bonding path activation before glue dispensing and pressing



Healthcare
- Syringes
- Catheters
- ophtalmic lenses
- microfluidics chips
- implants

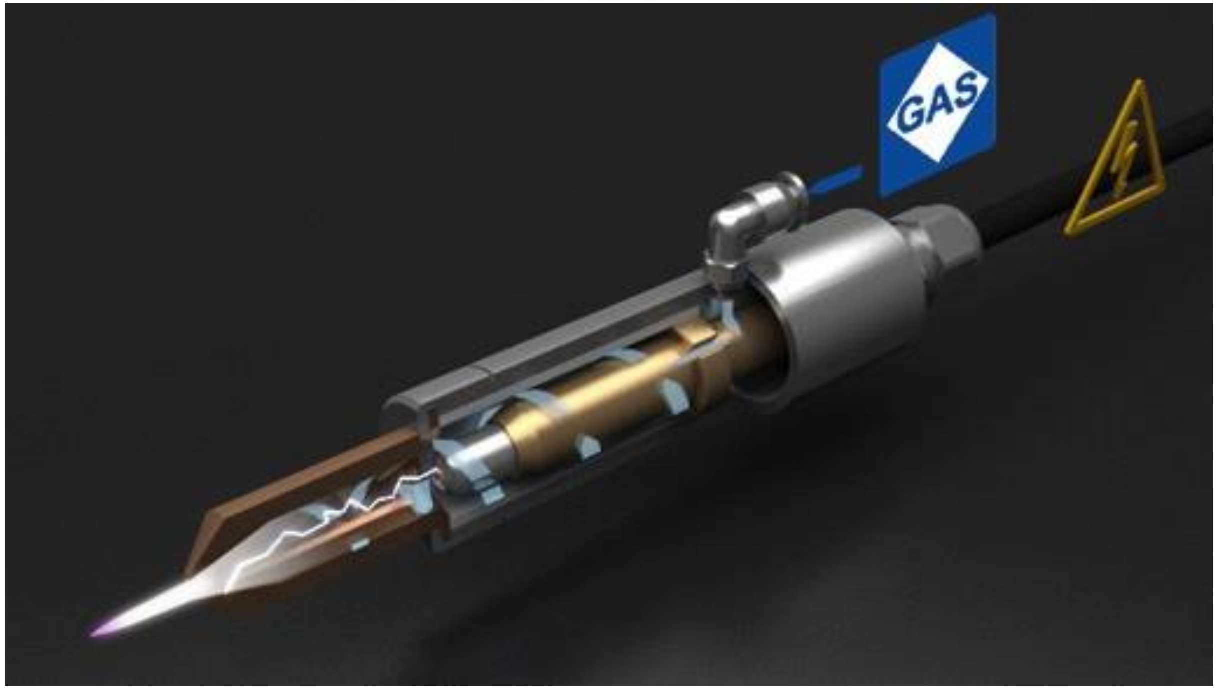
Micro-technologies
- Surface treatment before bonding or marking
- Silicon wafers bonding
- Oxyde removal on electrical circuits
- Encapsulation layers
- Watch manufacturing (preparation of dials before pad printing or varnishing)

Packaging, textiles, aerospace
- Surface treatment for improving bonding, printing, varnishing, dyeing etc…

Choices

Non transferred arc discharges

Relyon / Plasmatreat / Diener

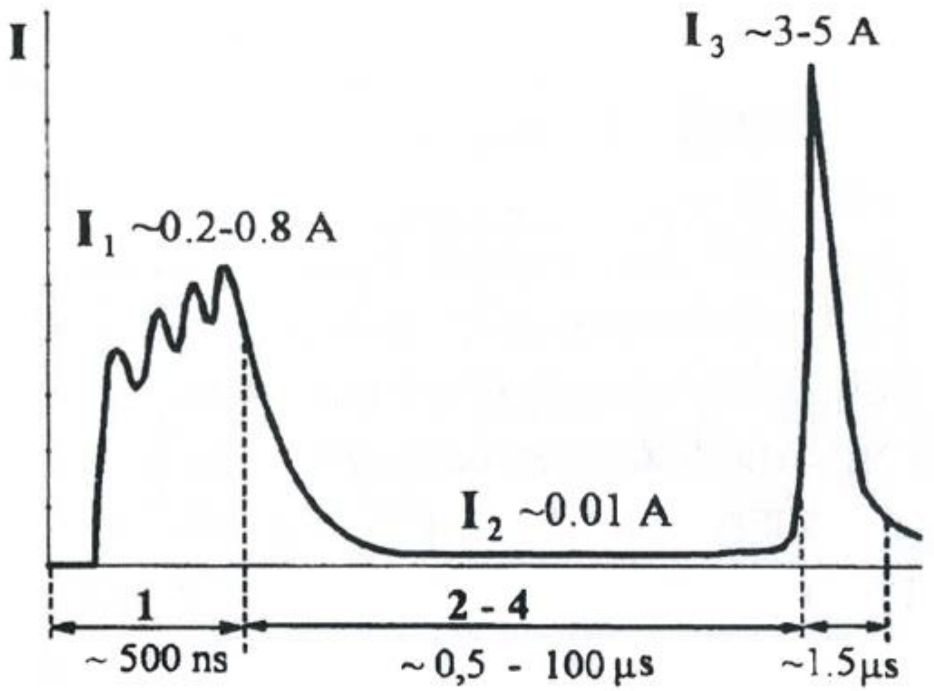


Through the use of a unipolar pulsed high voltage source and a vortex flow in the nozzle, the arc is prevented from stabilising at a "hot spot".

µArc discharges → High temperature
Metal electrodes in view of the plasma → electrodes erosion and particles deposition

High Frequency effect

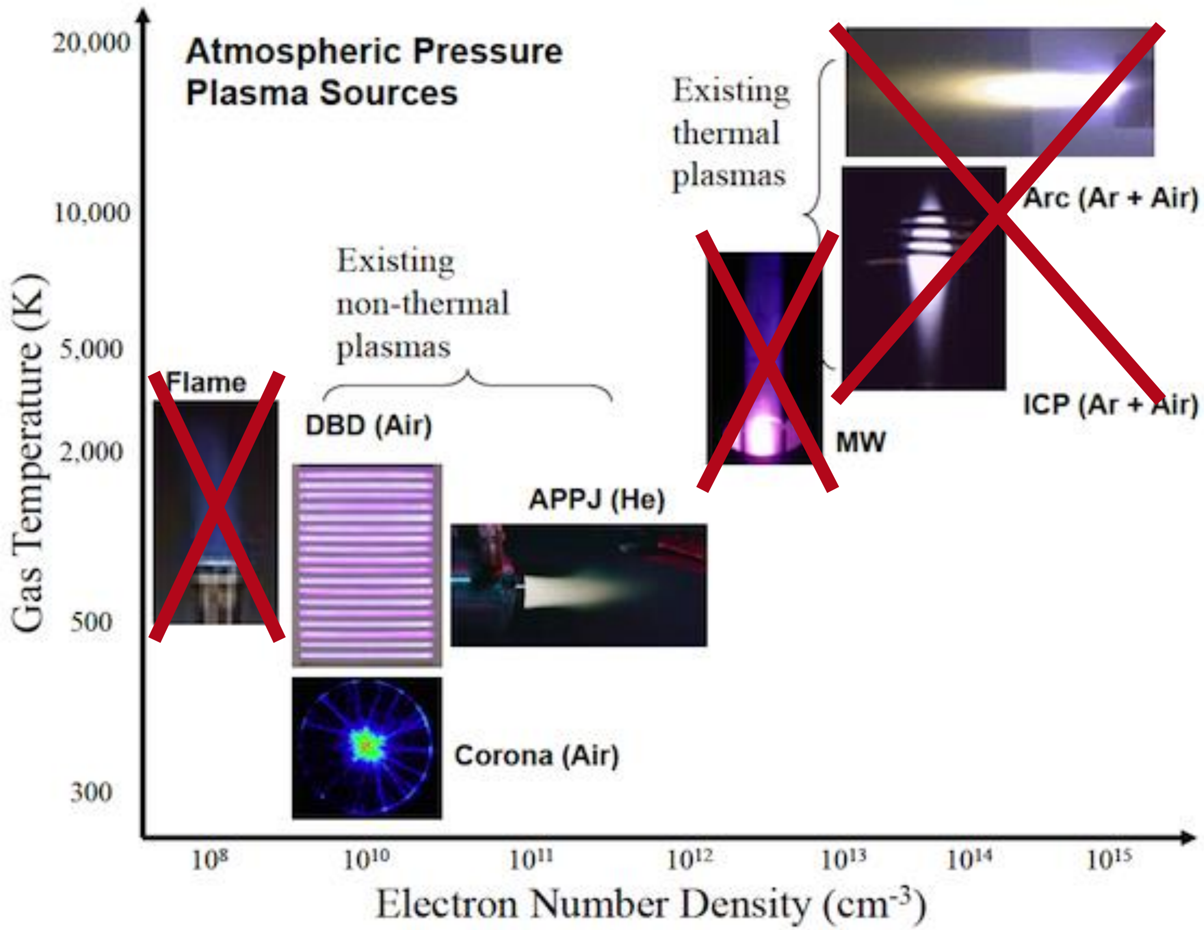
Non-Equilibrium Air Plasmas at Atmospheric Pressure
K.H. Becker, et al., CRC Press



Streamers propagation is fast of the order of 10 ns but channel evolution is slower

Streamers channels have a memory effect only within a cycle

Choices



Los Alamos National Laboratory—Yongho Kim

µArc discharges → High temperature, electrodes erosion

ICP design → Too high plasma density, high temperature, size linked to frequency, coil cooling needed

MW design → Too high plasma density, high temperature

Air as feeding gas → high temperature

More energy is dissipated in vibrational/rotational motion or recombination and reactions. Oxygen presence reduces electron density.

Choices

Even in DBD design

No kilohertz regime → intense streamers

High voltages and low frequencies lead to the formation of intense streamers with high energy stored, close to arc transition.

Reactive species produced → mainly metastable molecules
Defects on surfaces (hot spots)

No nanosecond pulse regime → low removal rate

Low temperature
Active reactive species
Reduced streamers effect
Used for biomedical or aerospace applications

BUT

Slow for manufacturing

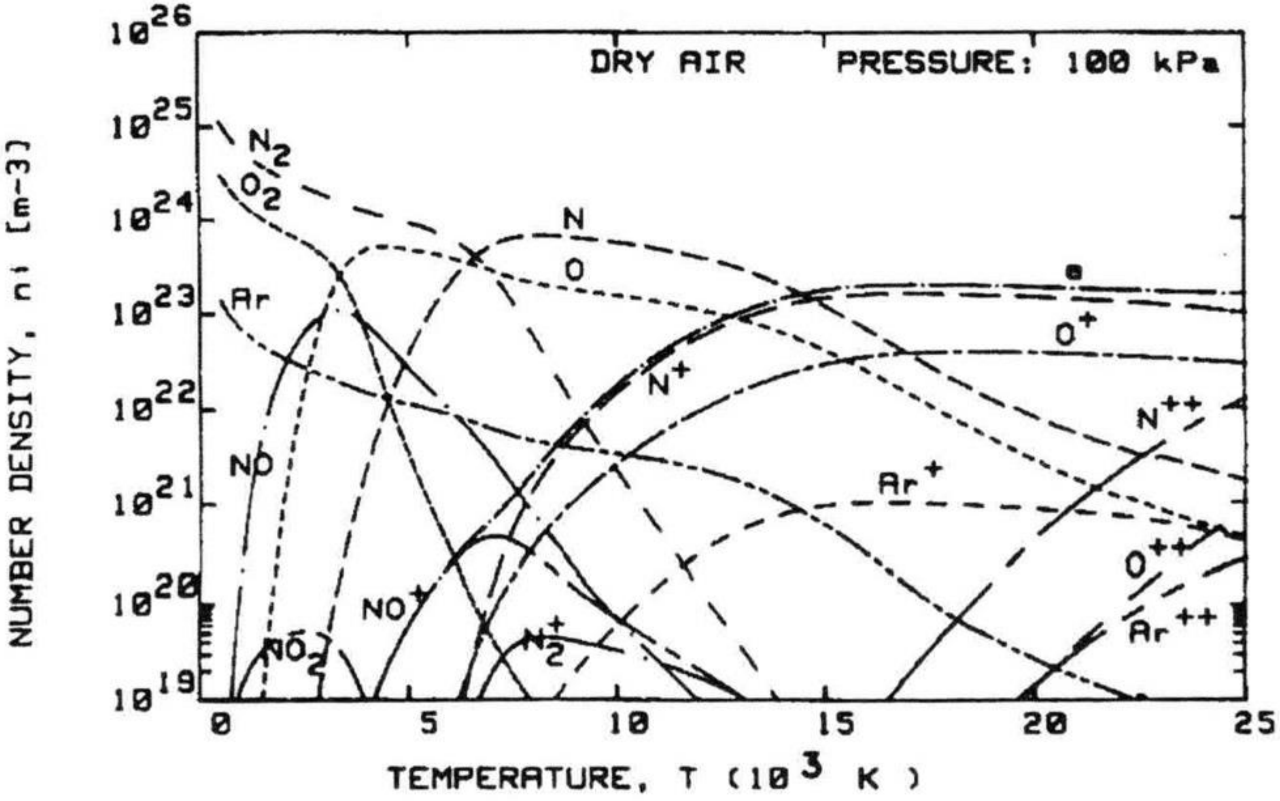
Choices

Nanopulse → Fast transient electric fields → High electron energies

→ High concentration of highly reactive species

Composition of an atmospheric pressure dry plasma versus temperature

(P. Frauchais, Summer School, ISPC-16 2003)



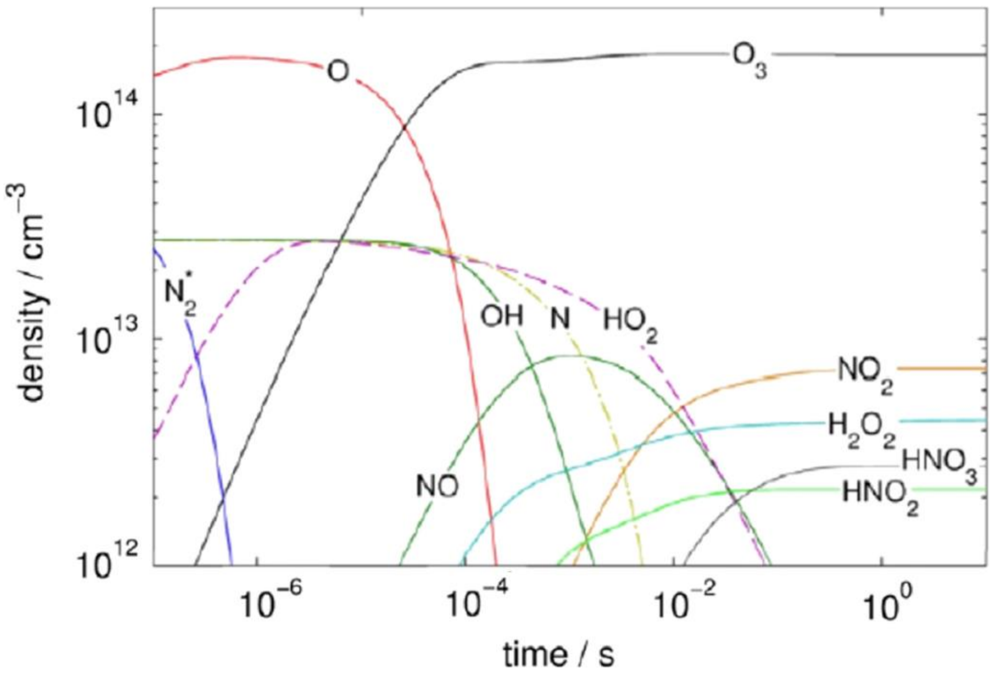
Choices

Nanopulse → Fast transient electric fields → High electron energies

→ High concentration of highly reactive species

Variation of densities of reactive species with time. The shielding gas is air with a relative humidity of 18%

(A. Schmidt-Bleker et al., J. Phys. D: Appl. Phys., 47 (2014), 145201)

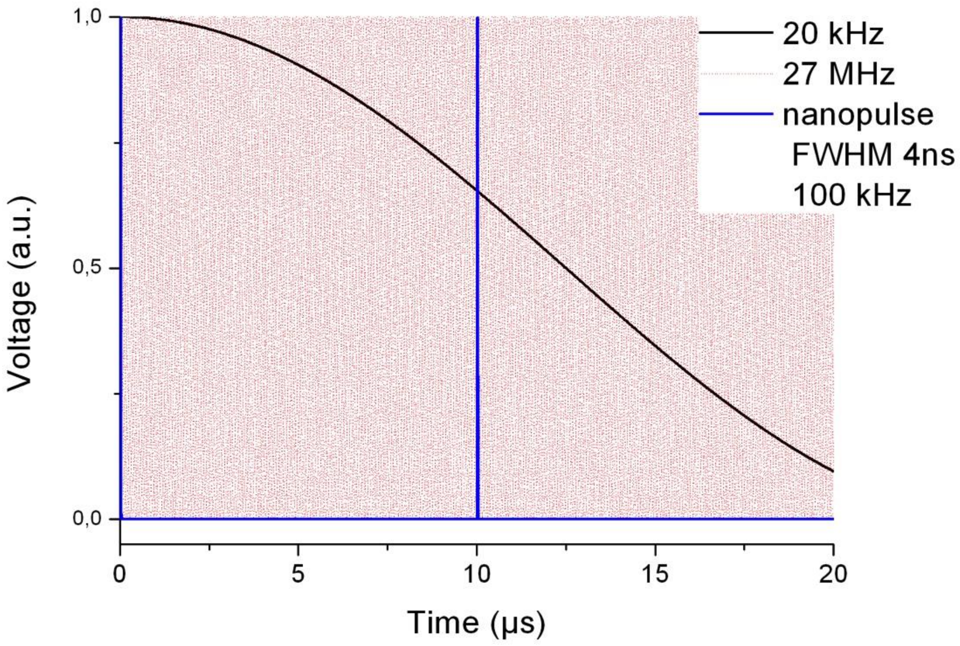


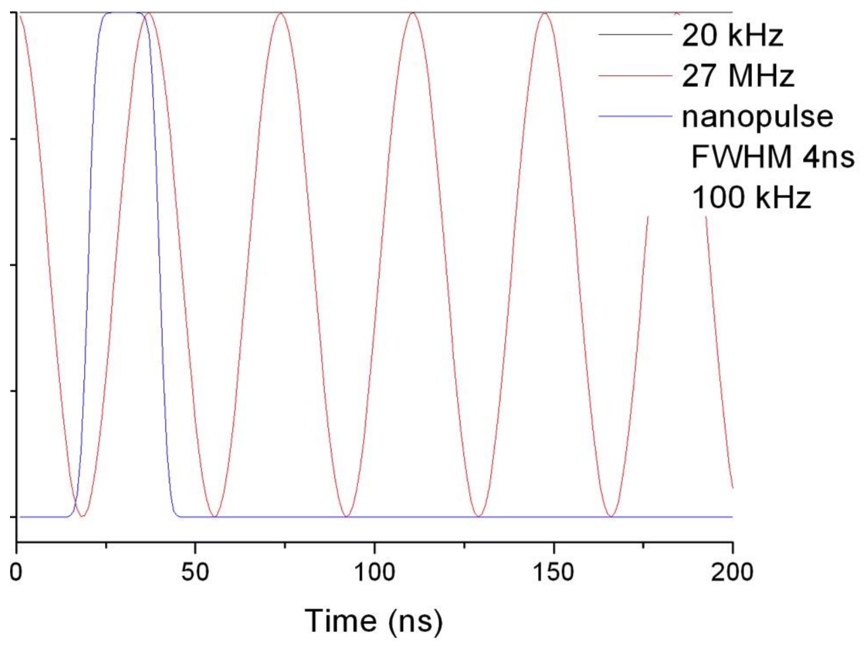
Frequency choice

27.12 MHz vs nanopulse

Disadvantages:
Smoother transient
Smaller electric fields
Sustain problems
Power matching problems

Advantages:
Higher power delivery
Transient in nano range
Lower breakdown voltage
Volume excitation





Plasma Stylus Noble - APPJ

3 ducts:

- Chemicals as vapours or aerosols
- Process gas: Ar (> 4.0) (5-10 slm)
- Shielding gas: air or N_2

Power supplies:

- HF 17 kHz up to 10 W
- RF 27 MHz up to 80 W
  (about 15-20% in the plasma)
- Pulsing HF and RF

All electrodes external to the dielectric duct

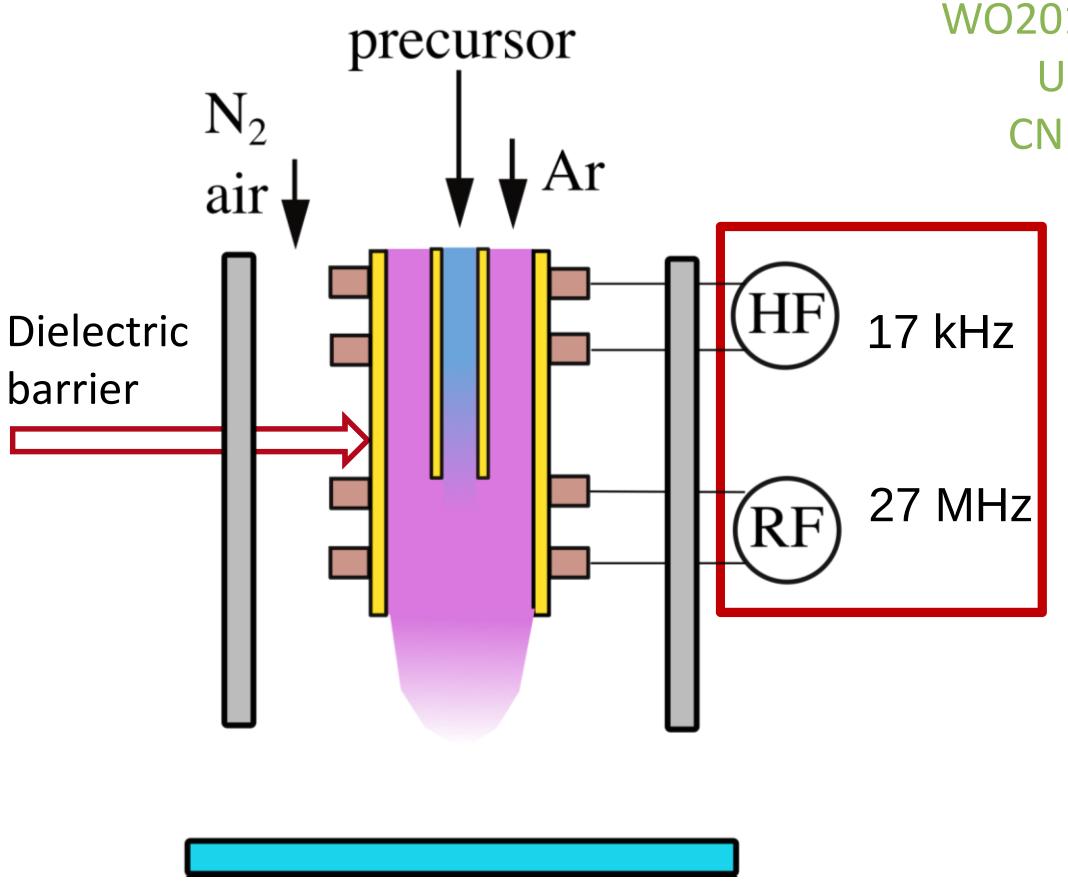
Efficiency:

- Spot area Φ 5 mm
- Deposition rate about 20 nm/s

NADIR
Plasma & Polymers

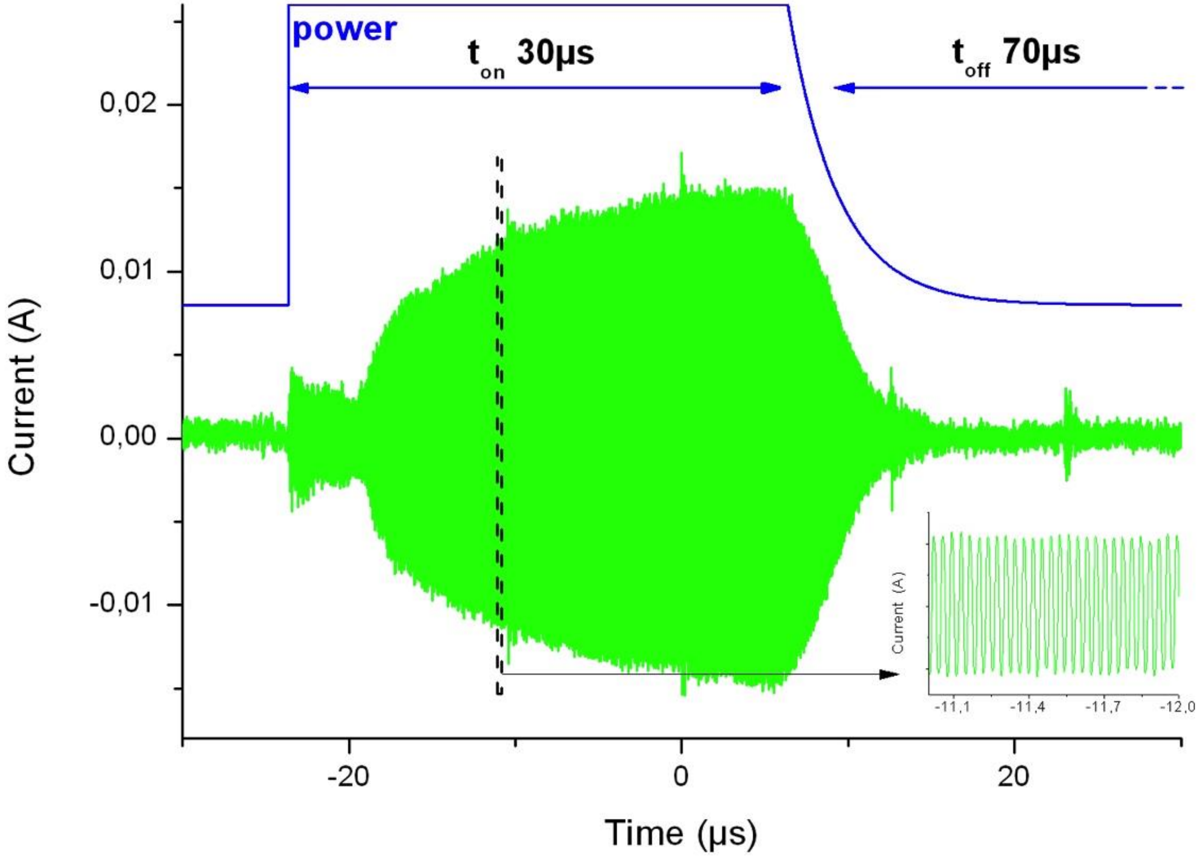
PATENTED

PD2013A000310
WO2015071746A1
US9693441B2
CN105900532B



Pulsing

Pulsing can reduce further the treatment temperature



Fully scalable

FAST
Functionally graded
Additive Manufacturing scaffolds
by hybrid manufacturing

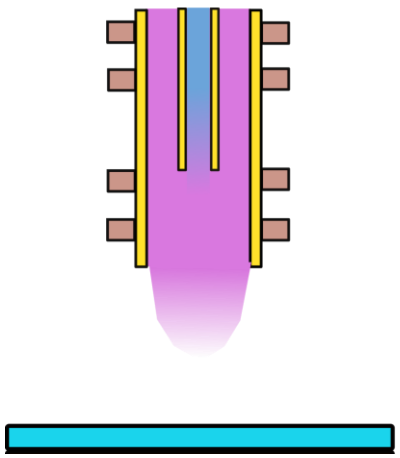
H2020-NMP-PILOTS-2015
1/12/2015 – 30/11/2019

http://project-fast.eu/en/home

While 3D printing scaffolds → functionalisation inside the scaffold.

It is possible because really
LOW TEMPERATURE
even if Ar as process gas

How it looks like



on a glass slide

HF
17 kHz

RF
27 MHz

HF + RF

Interreg Italia-Österreich
European Regional Development Fund
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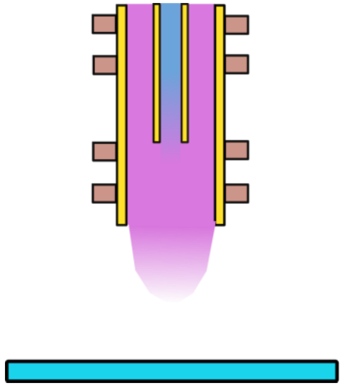
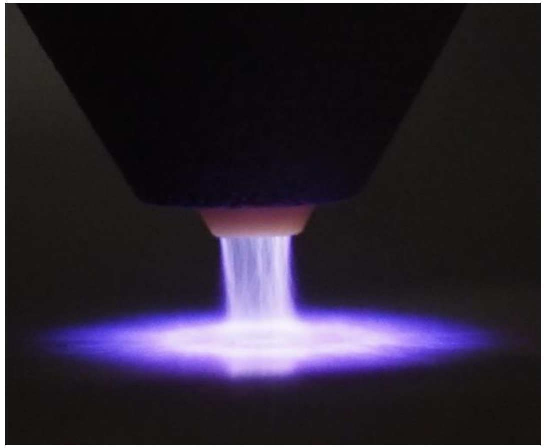
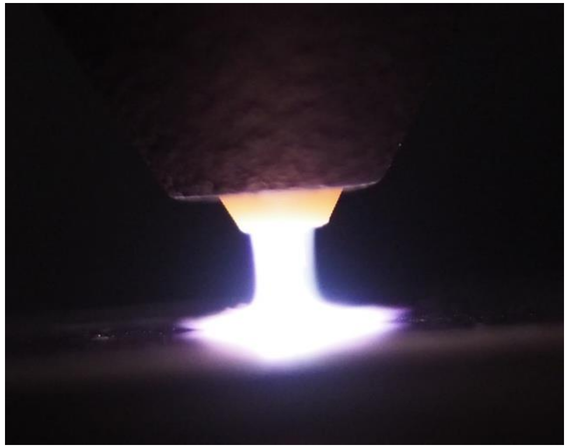
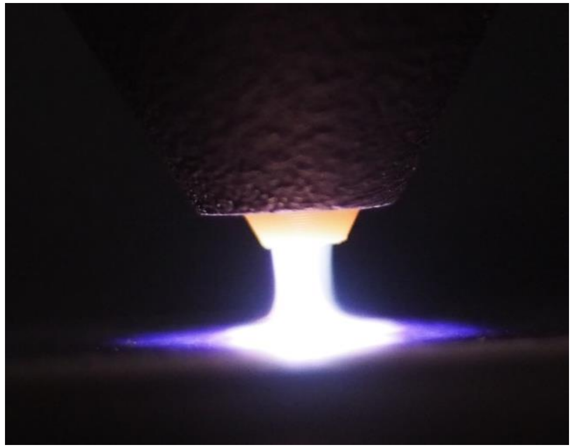
Enhanced surface charging





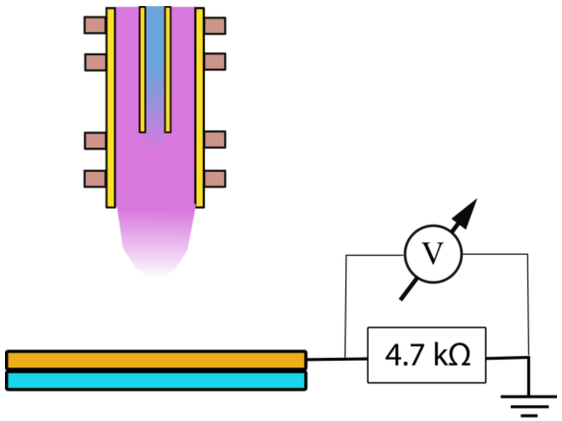


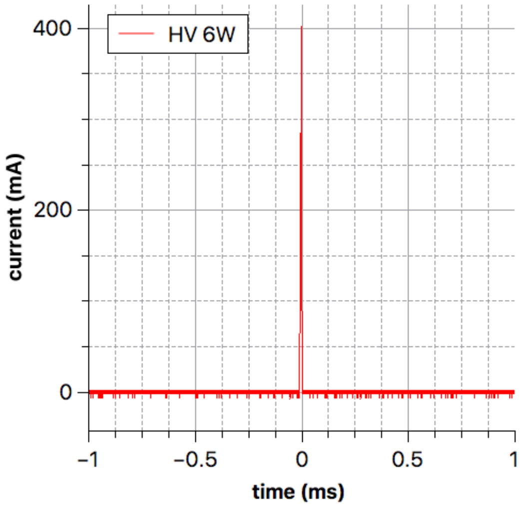


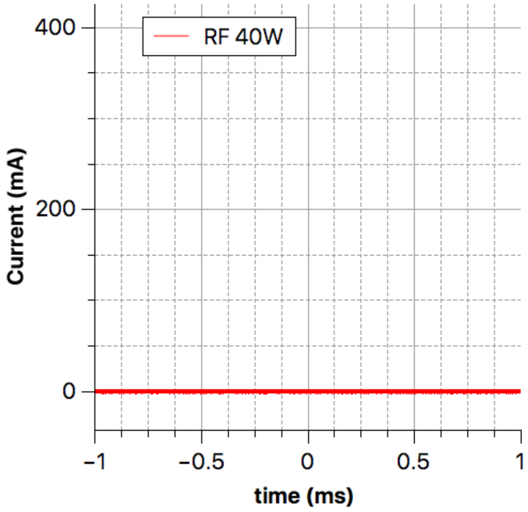
HF
17 kHz

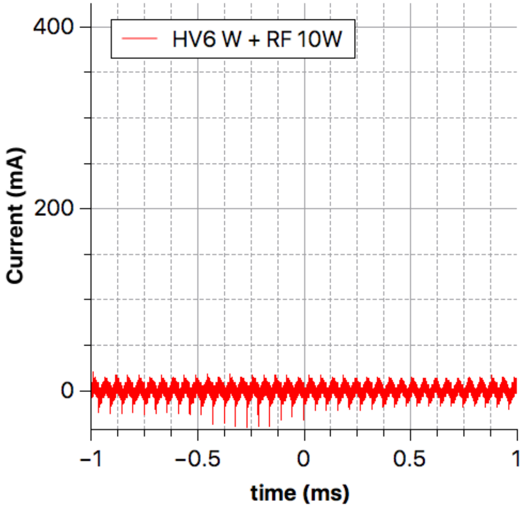
RF
27 MHz

HF + RF









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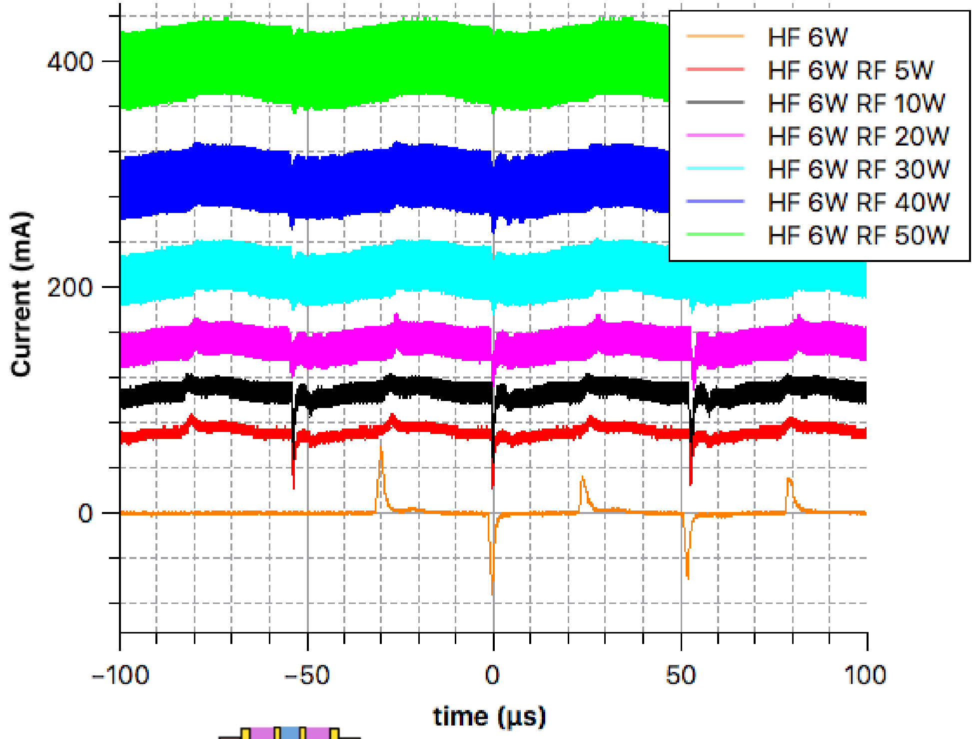
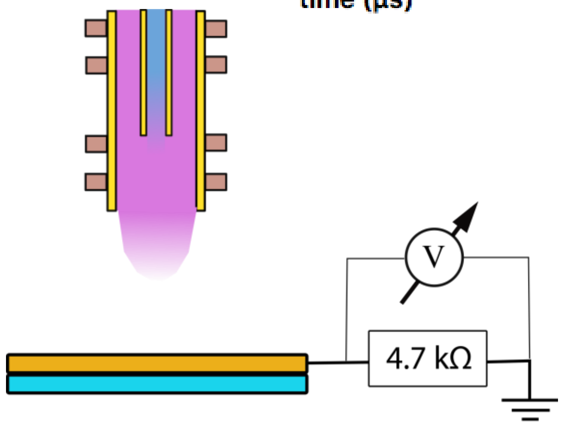
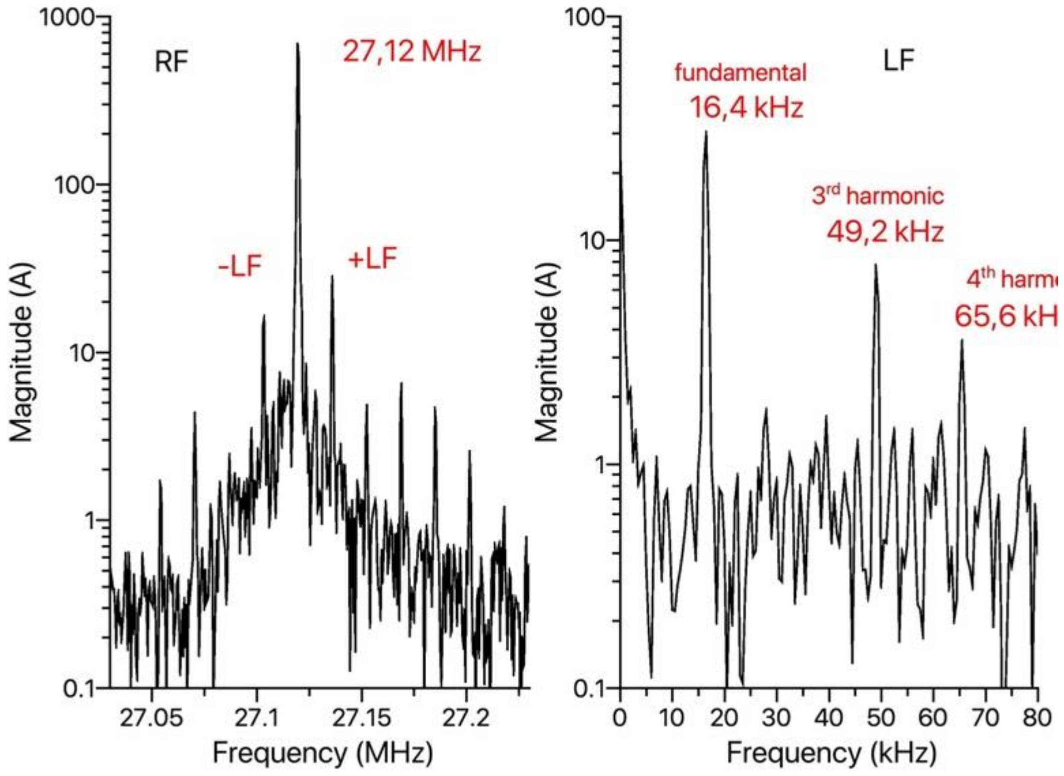
Streamers currents reduction

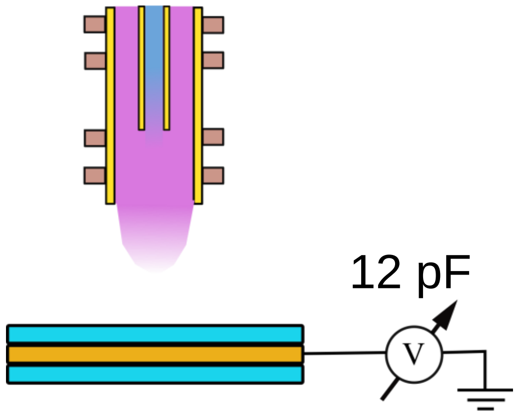




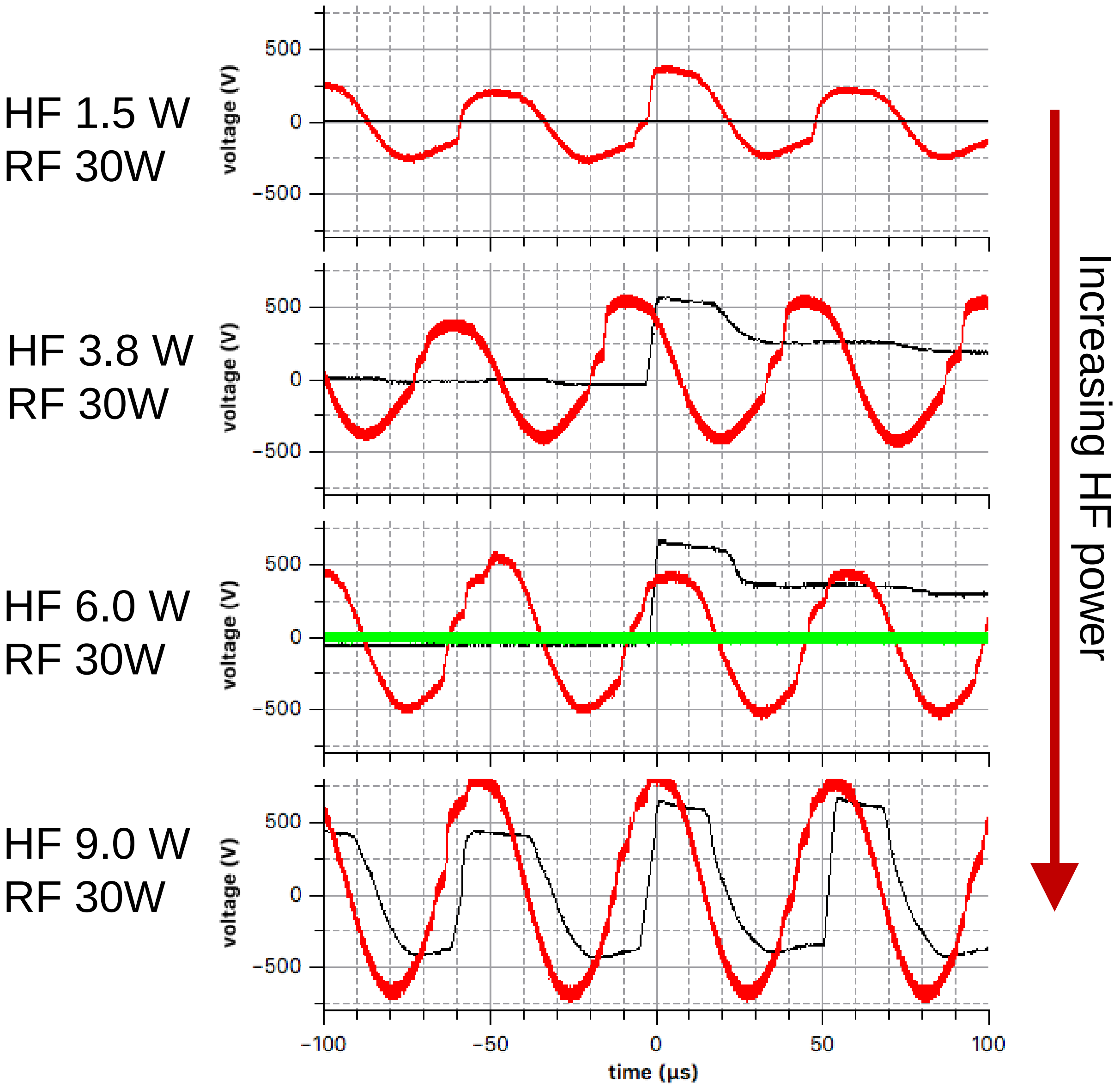


- Real plasma coupling
- HF streamers current reduced
- Glowing behaviour – Displacement currents for both HF and RF on the substrate

What happens to substrate surface voltage?



- With only RF no voltage on the substrate
- Voltage depends on HF power; not RF
- HF voltage on the substrate can be obtained also when streamers wouldn't reach it
- Increasing the HF power, the only HF gets close to HF+RF but still high current streamers
- Low current streamers present also in HF+RF



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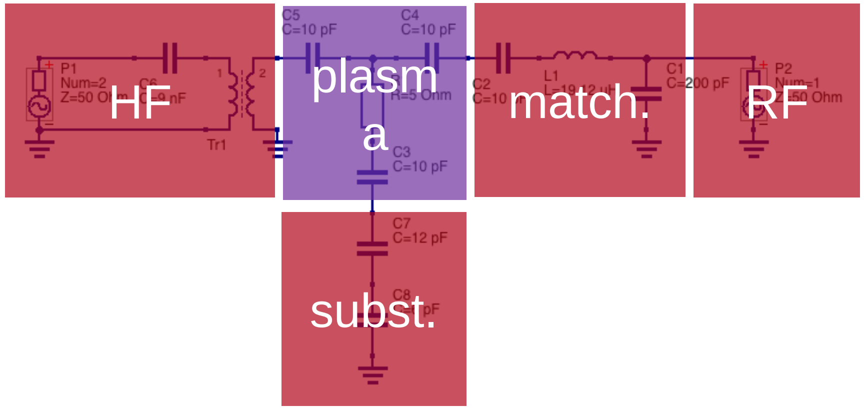
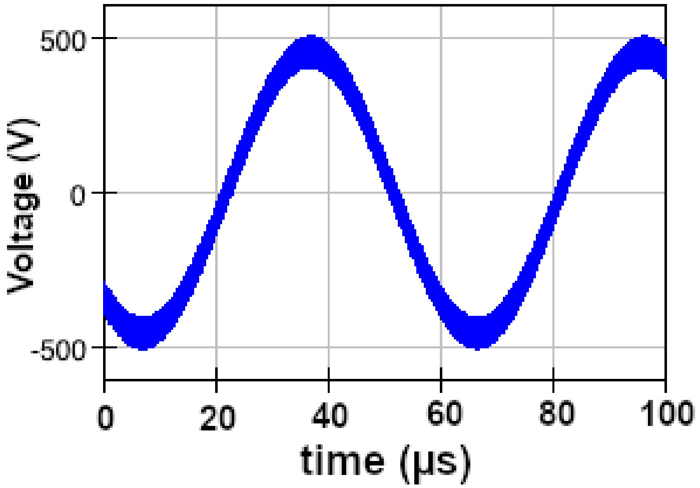
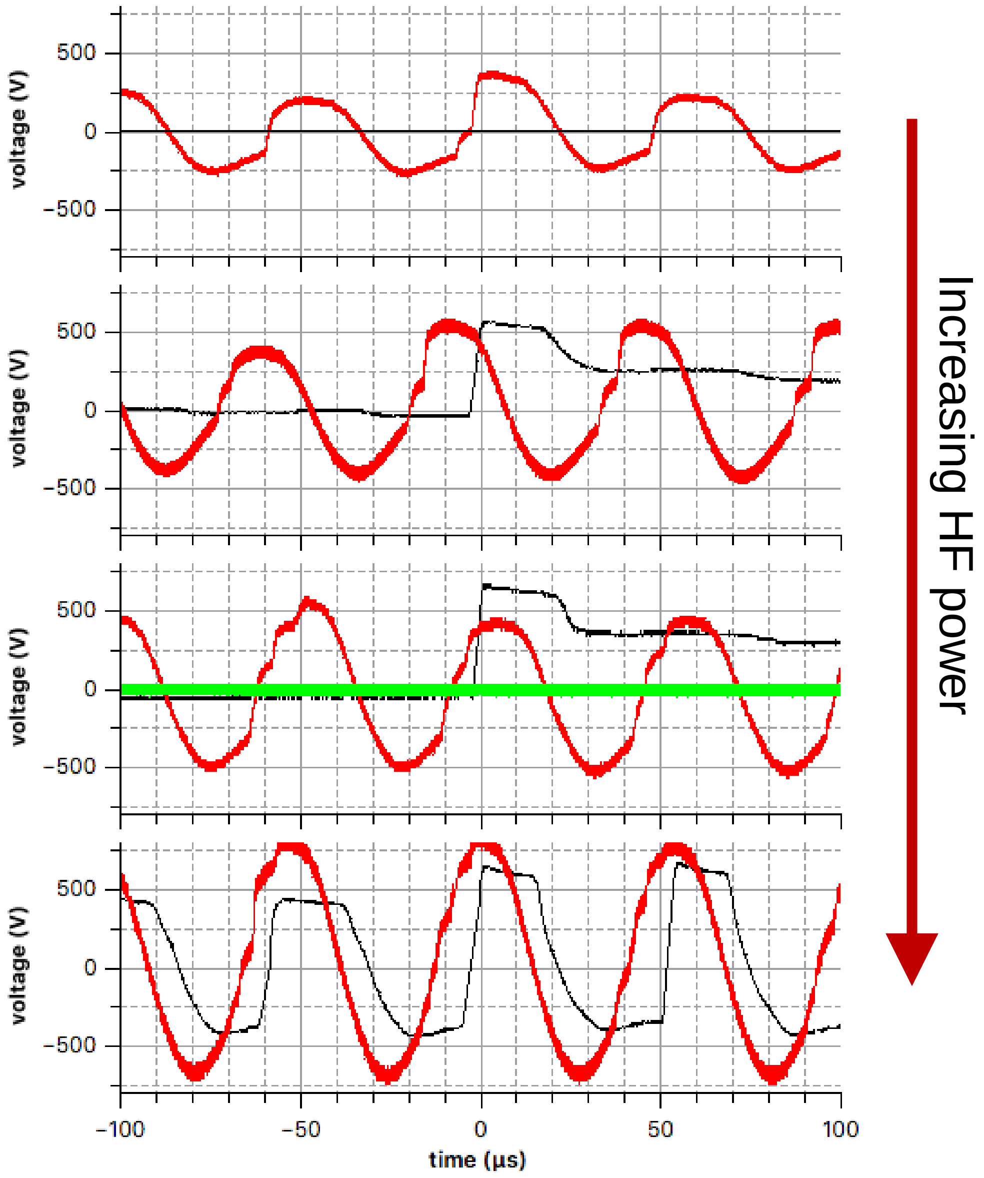
What happens to surface voltage?



Nearly a glow behaviour





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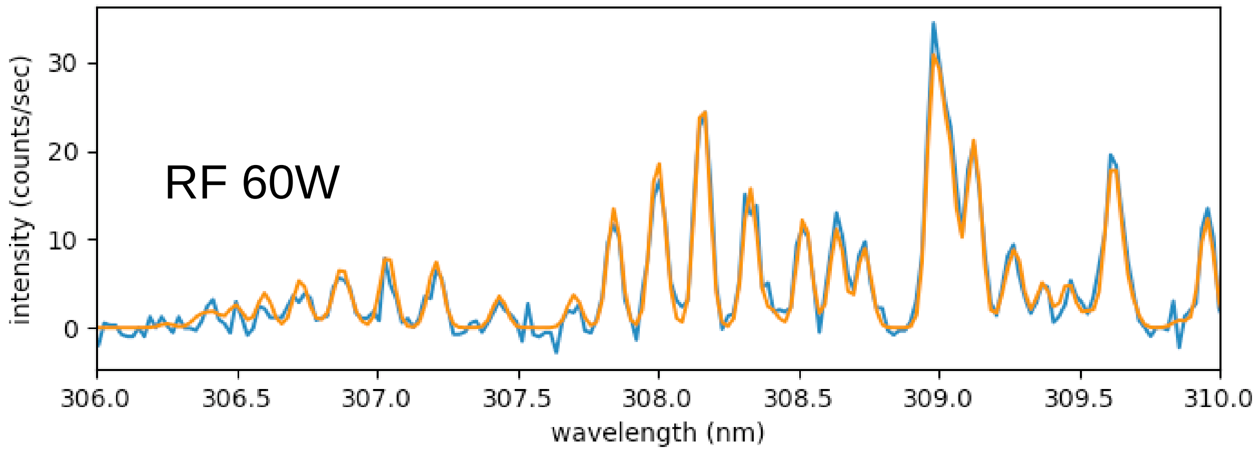
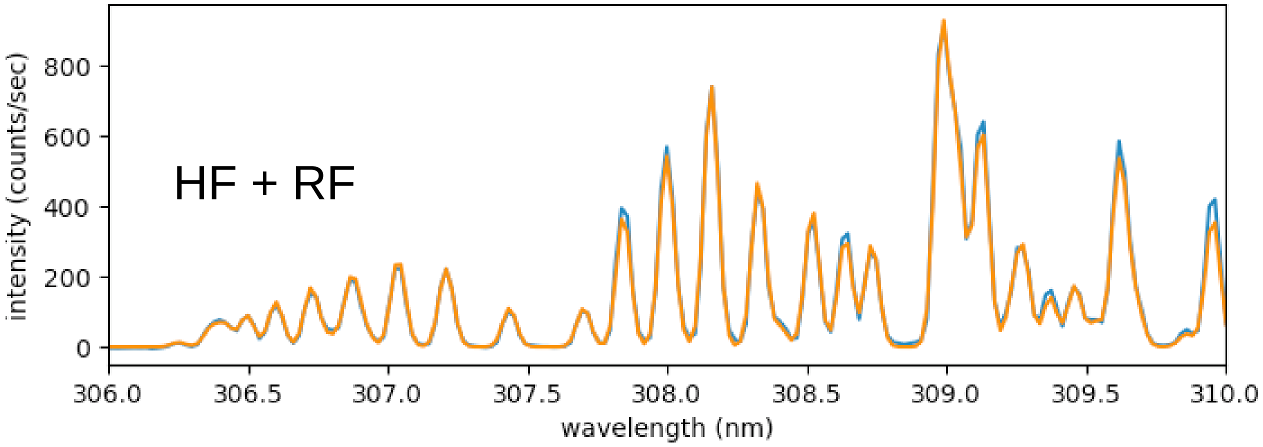
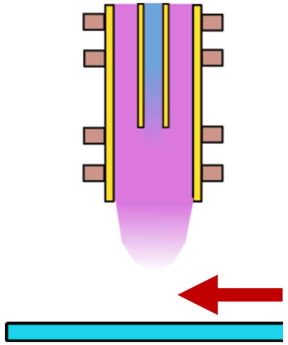
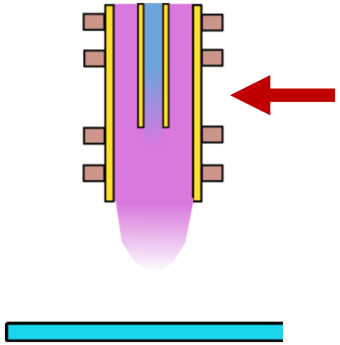
OH rotational temperature

OES close to sample surface









OH – T_{rot}

HF 8W 360 +\- 30 K

RF 60W 580 +\- 20 K

HF + RF 640 +\- 20 K

SPS N_2 – T_{rot}

Rotational temperature

RF 60W 840 +\- 40 K

HF + RF 780 +\- 20 K

SPS N_2 – T_{vib}

RF 60W 1910 +\- 120 K

HF + RF 1530 +\- 20 K

Temperature by OH lines

Zaniol

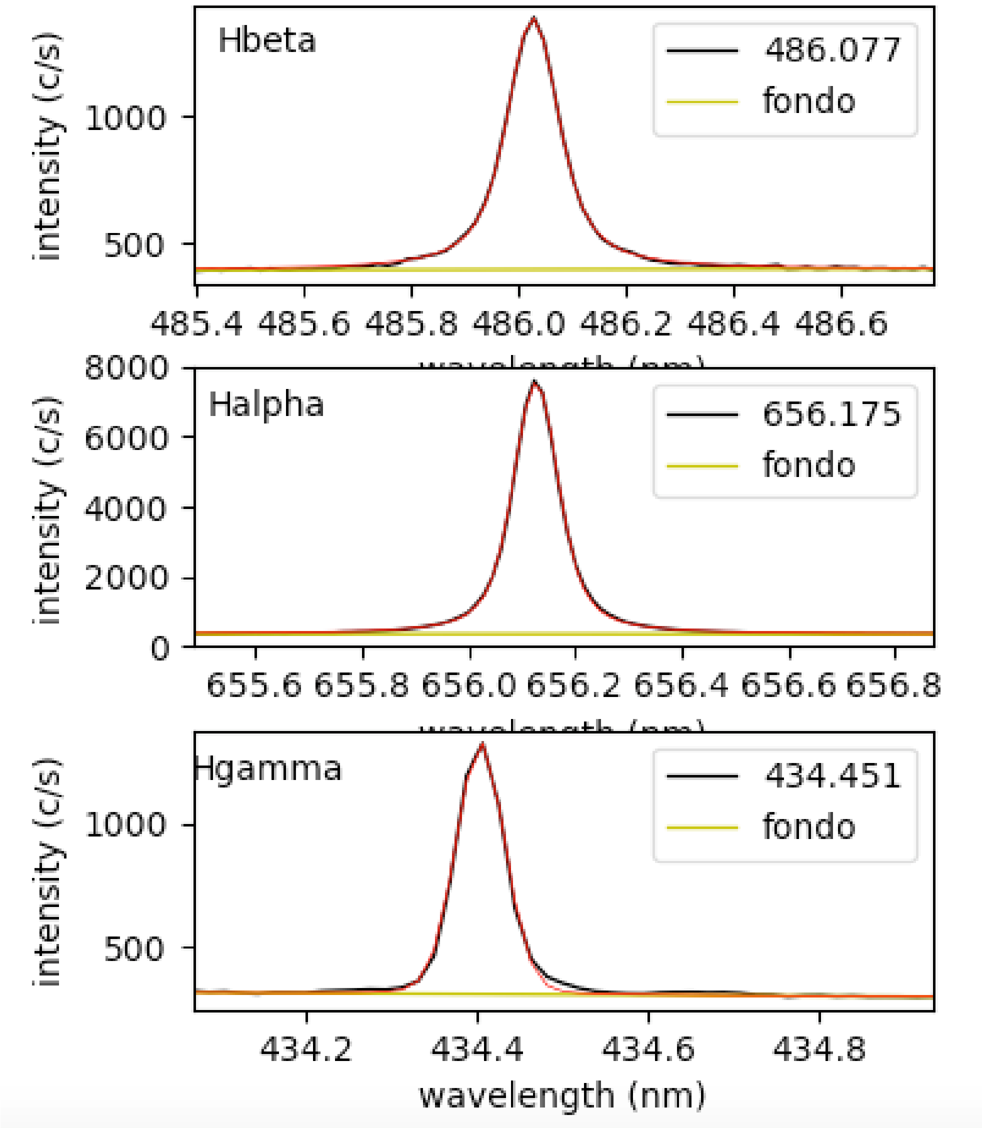
RF 60W 700 +\- 30 K

HF + RF 770 +\- 30 K

Paradisi

Marotta

Electron density



H beta

RF 60W

ne = 4. 5 ± 0.4 E14 cm^{-3}

HF + RF

ne = 5.8 ± 1.0 E14 cm^{-3}

Ar I(419.82nm)/I(420.05nm)

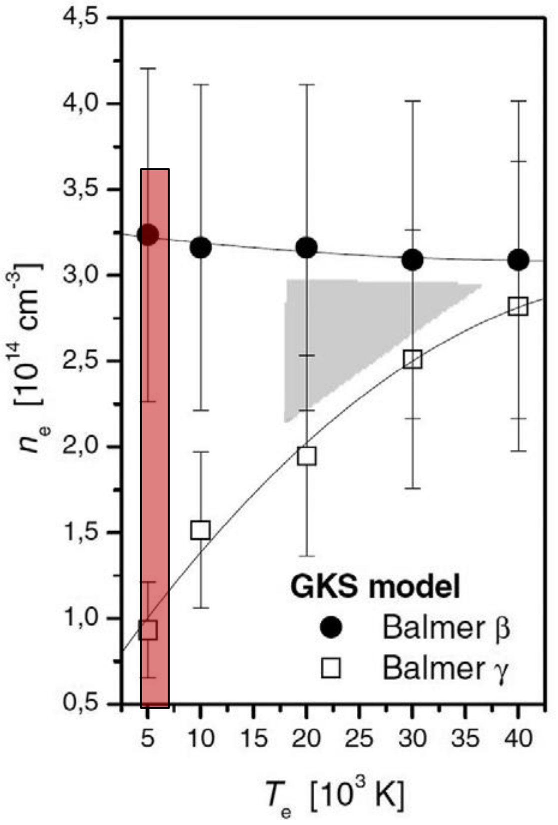
RF 60W

Te = 0.4 ± 0.1 eV

HF + RF

Te = 0.6 ± 0.1 eV

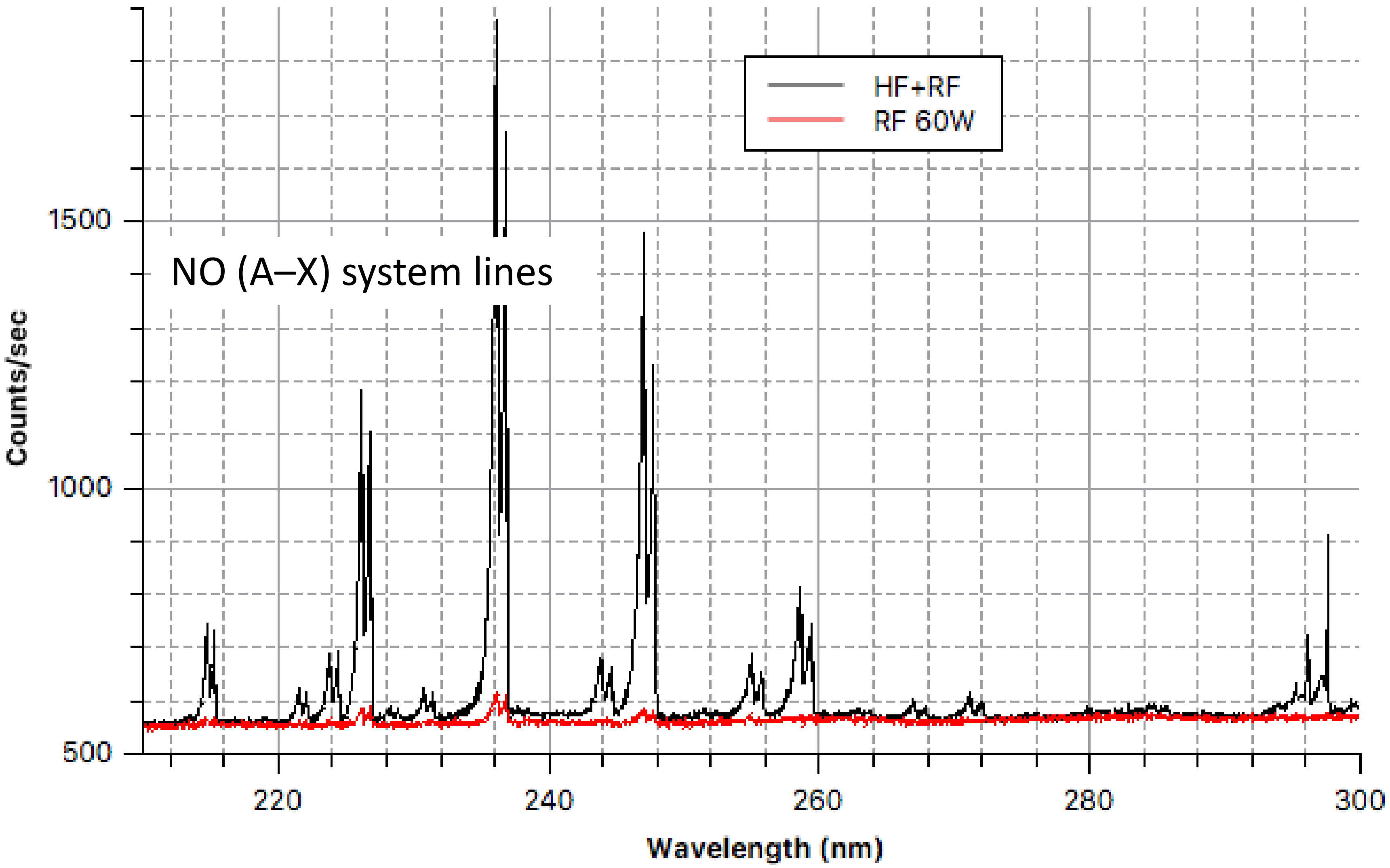
John B Boffard et al 2012 J. Phys. D: Appl. Phys. 45 045201



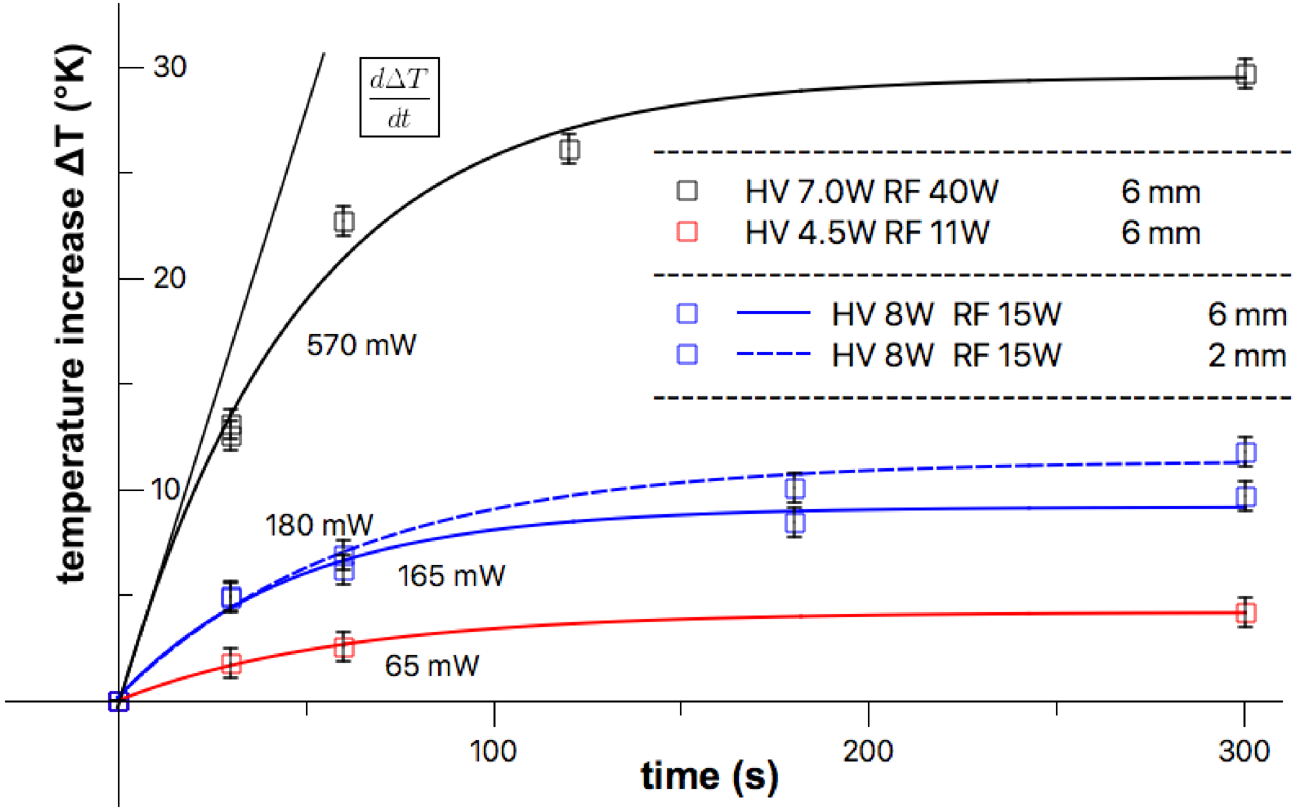
Scheafer J et al., 2010 Eur. Phys. J. D 60 531–8

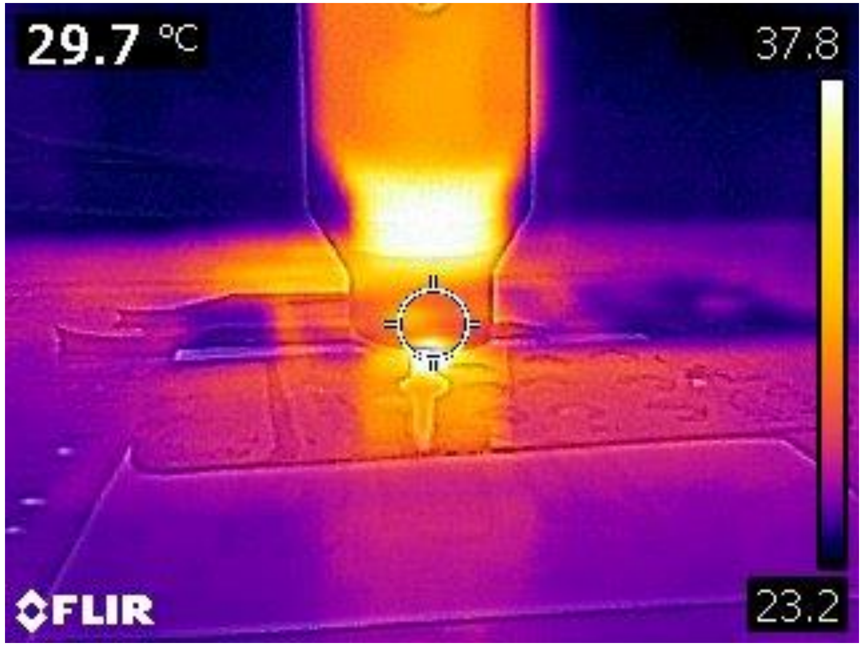
NO emission

Surface propagation



Thermal load

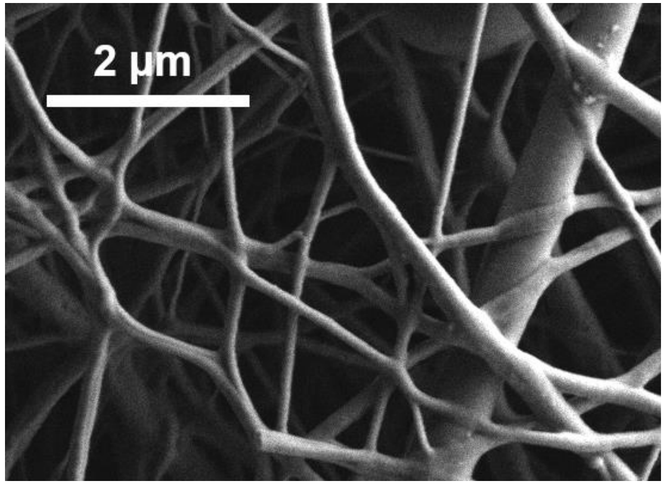




Patelli A, et al.,(2018), IOP CONF. SERIES: Mater. Sci. Eng., 364, 012079

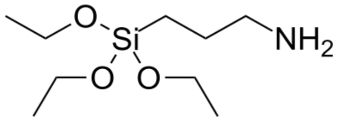
Thermal load can be comparable to the temperature in medical devices
Depends mainly on the RF power

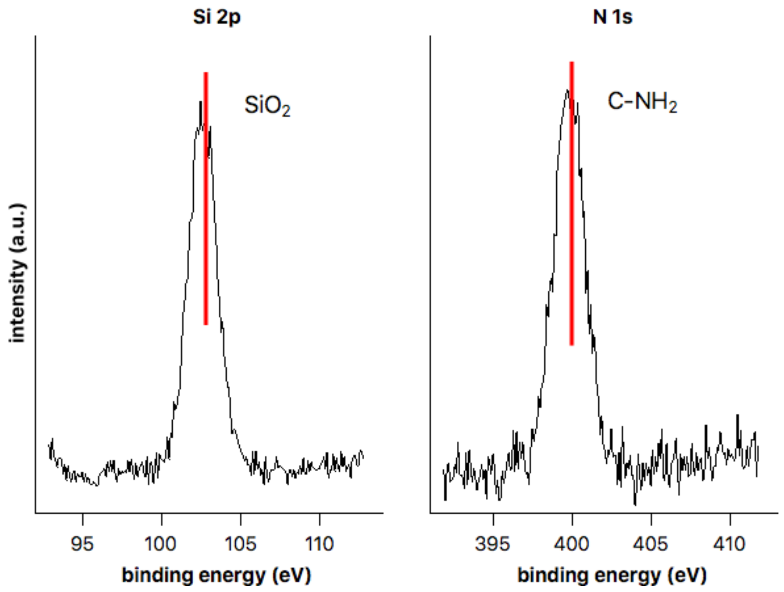
COLD - PCL electrospun fibers



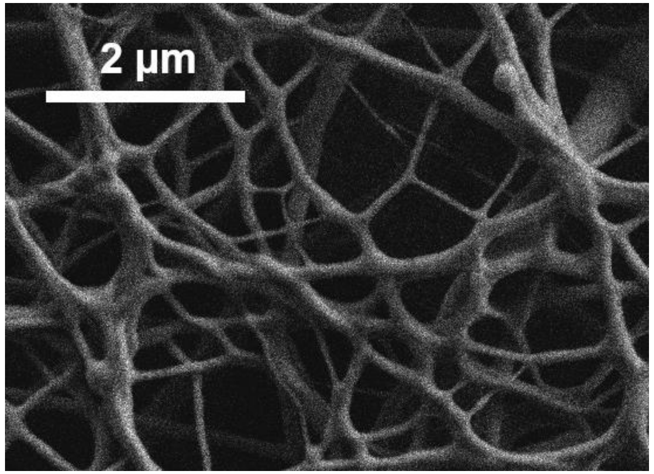
precursor

APTES

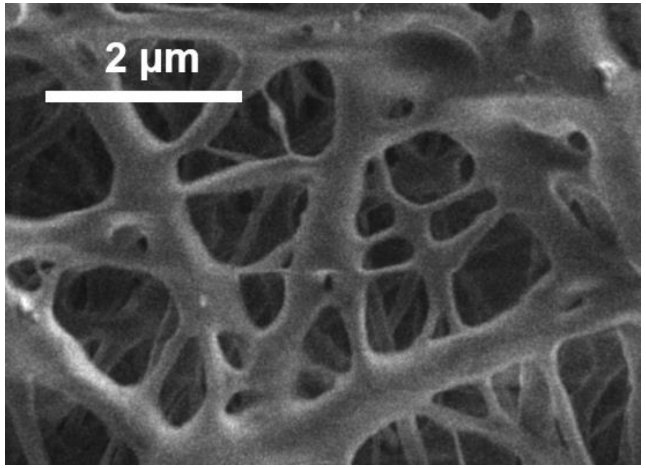




- No melting
- Top coating



30 nm coating



300 nm coating

A. Maffei *submitted*

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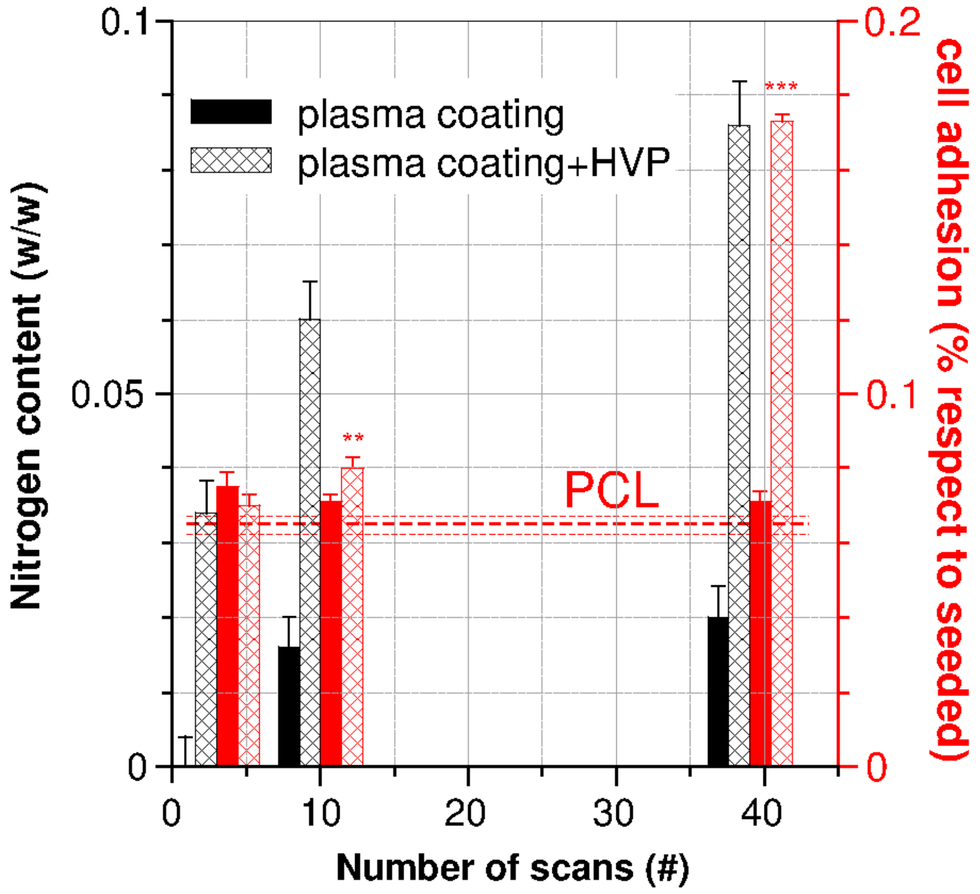
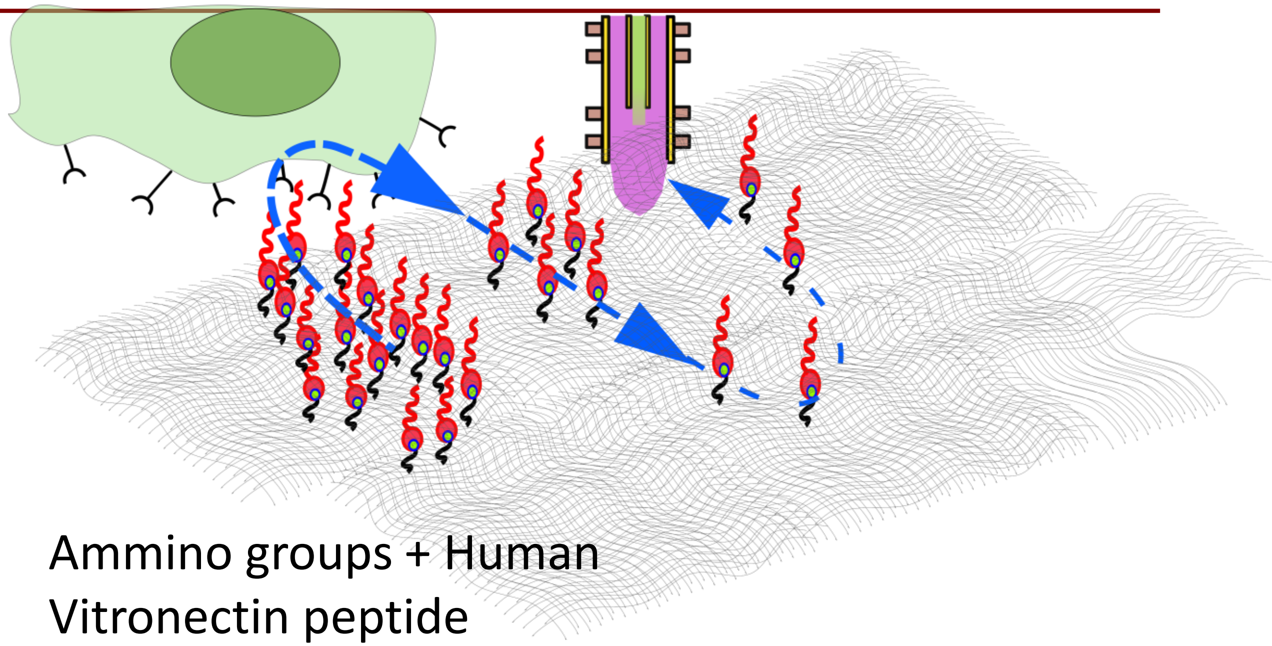
EUROPEAN UNION

COLD - PCL electrospun fibers





Ammino groups + Human Vitronectin peptide

Human osteoblasts improved adhesion

Chemotactive gradients just with 1-parameter control

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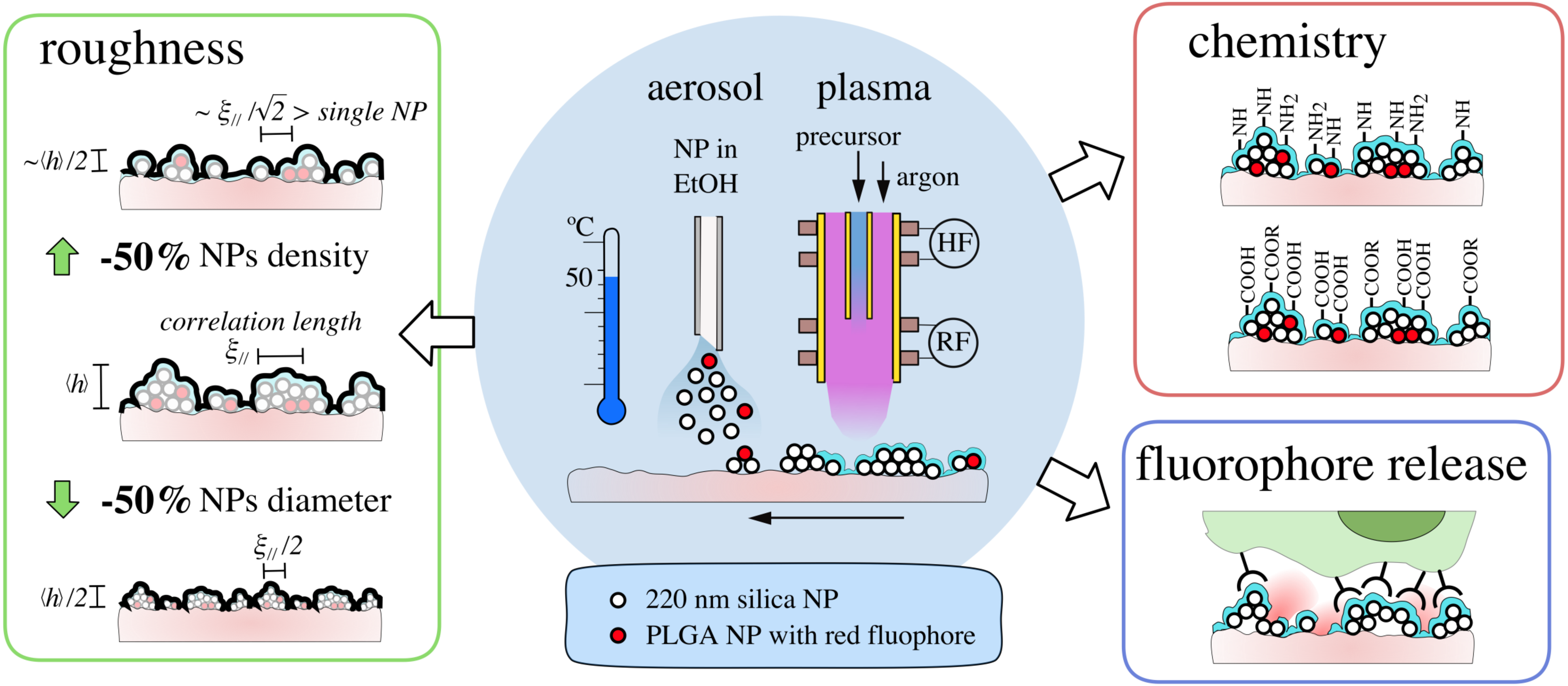
No coatings defects - Conformal



Patelli A, et al. (2018), ACS Appl. Mater. Inter.. 10(46), 39512

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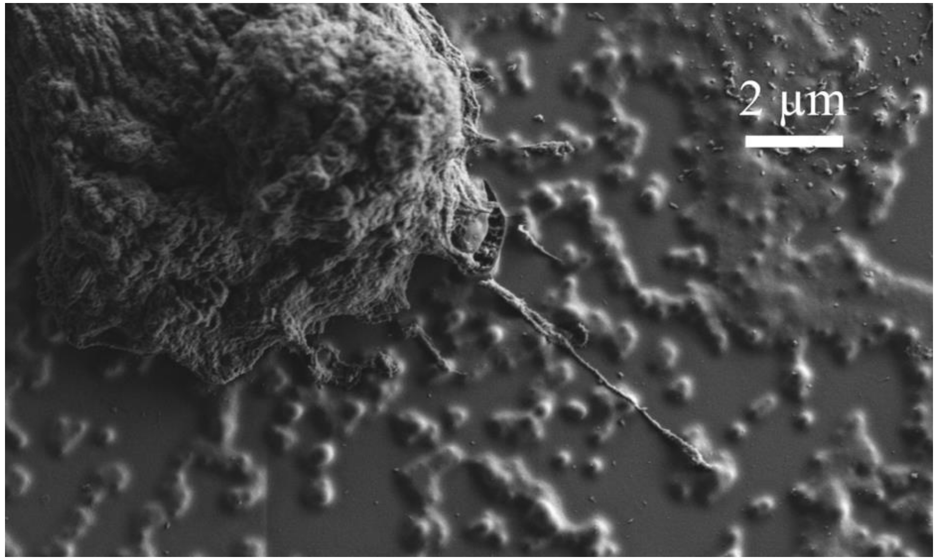
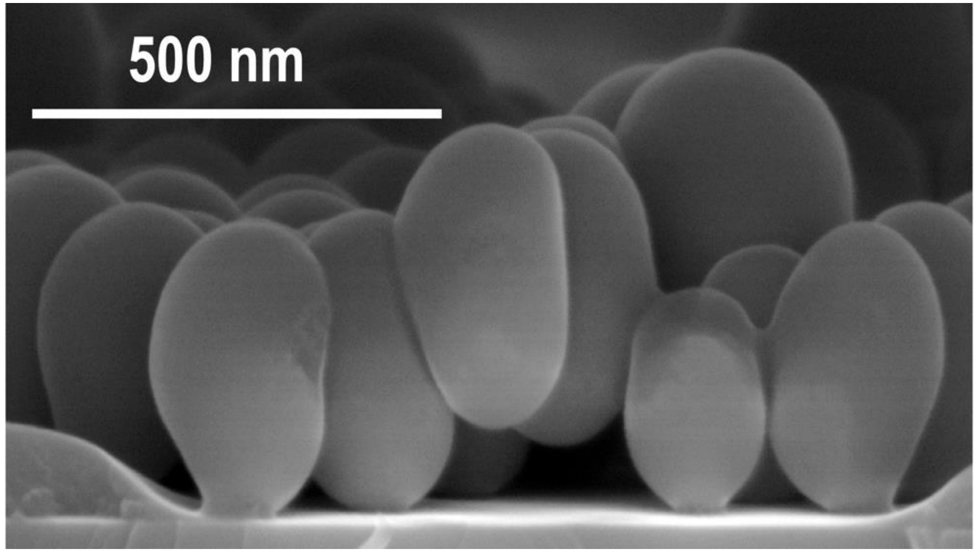
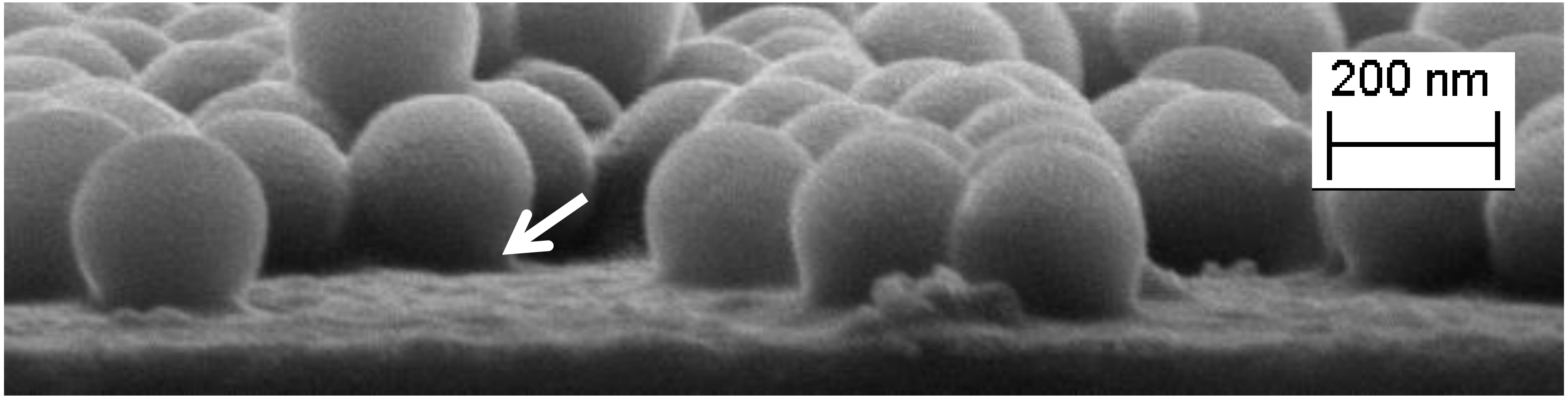
No coatings defects - Conformal







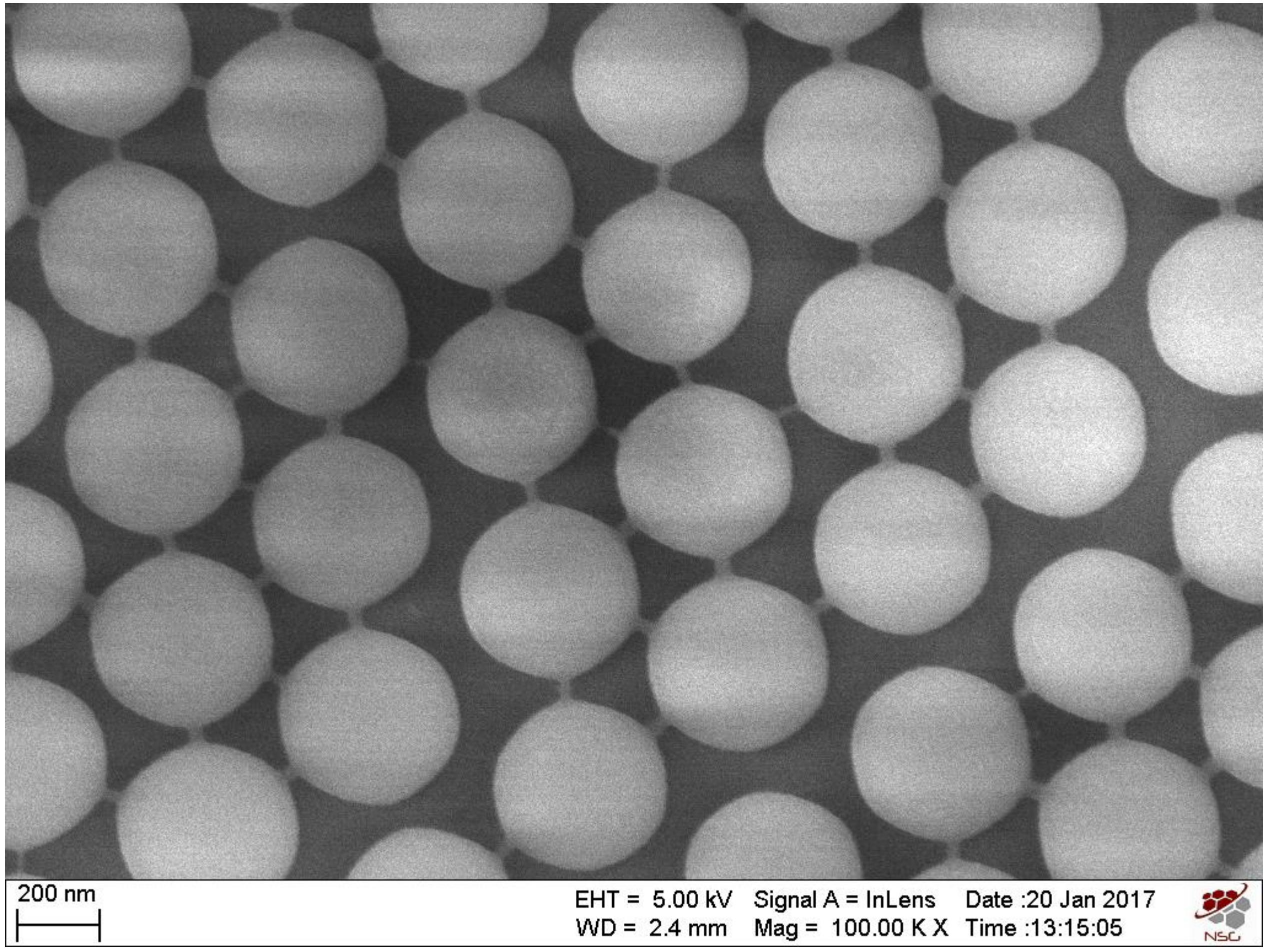
Surface charging - - No damage on nanostructures

Nanosphere lithography

Not really the same:

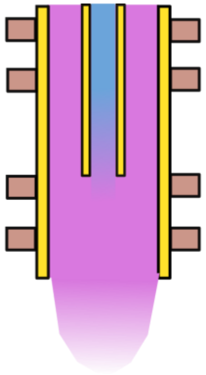
Not a random effect

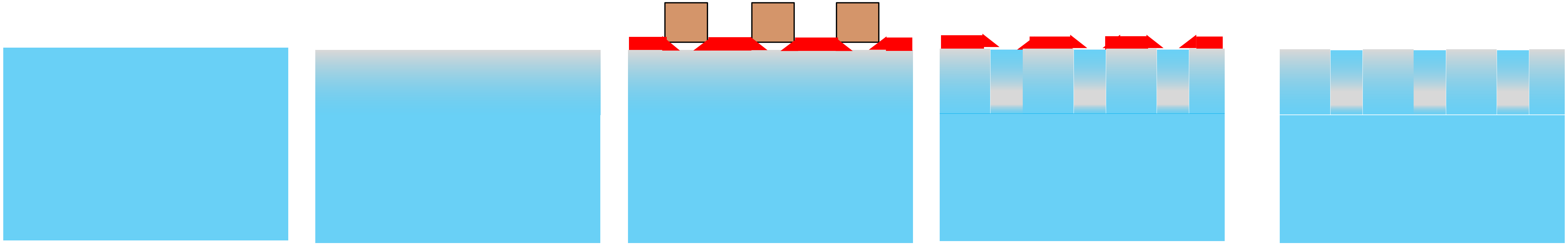
Etching is just a real surface effect



Surface charging - Buried waveguides

TEM grid





Sodalime glass

Ag+ ←→ Na+ exchange

Mask and sputter TiO_2

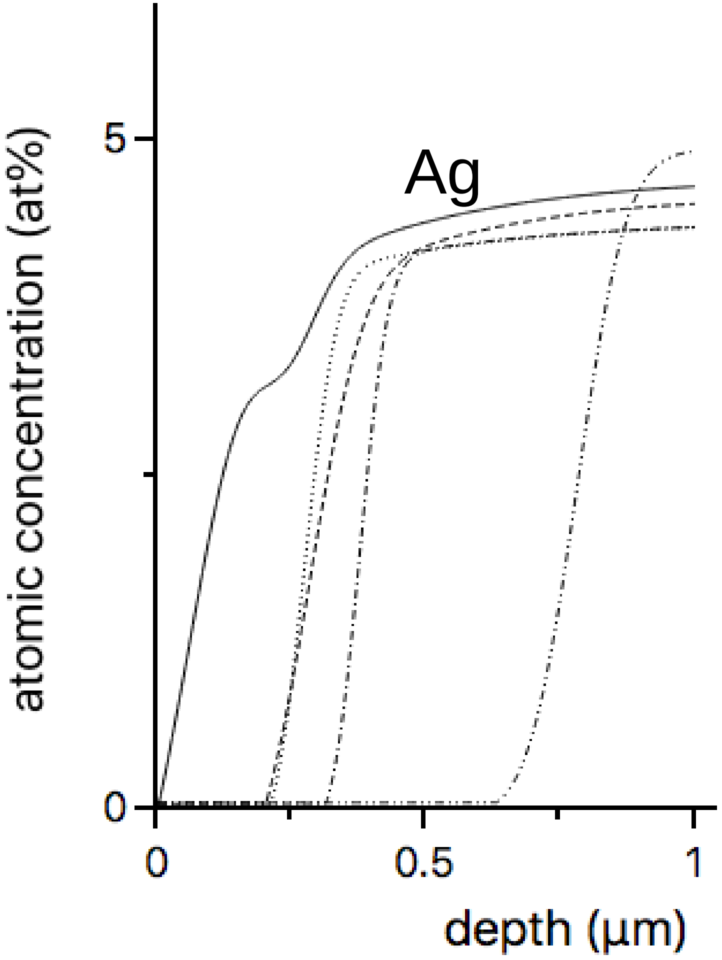
APPJ treatment

Mask removal

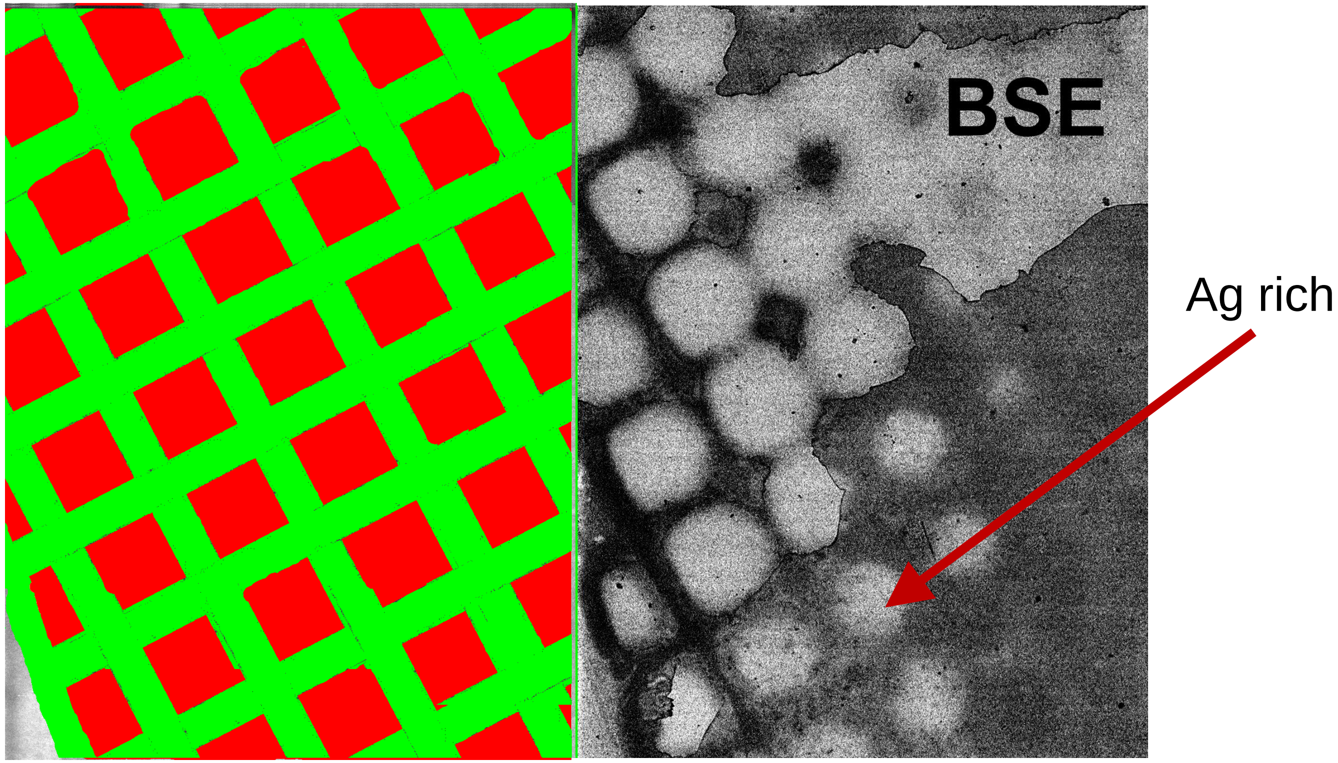
Surface charging - Buried waveguides

Cattaruzza

Sodalime glass – Ag exchanged



Dielectric masking about 1 µm thick allows to transfer patterns at the micro/nano range in the glass



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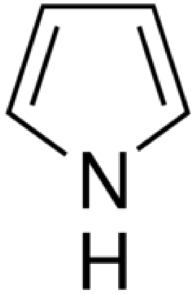
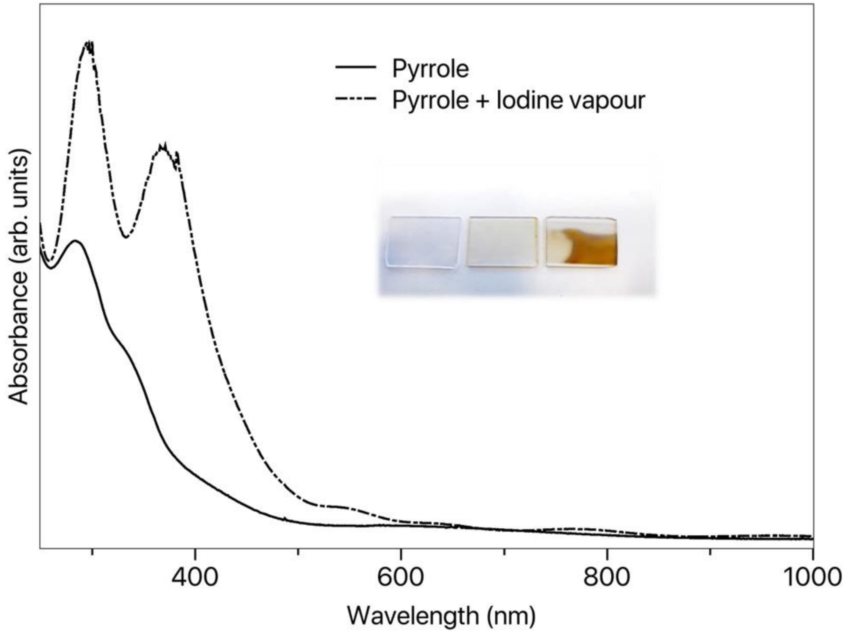
Functionalities - Polypirrole

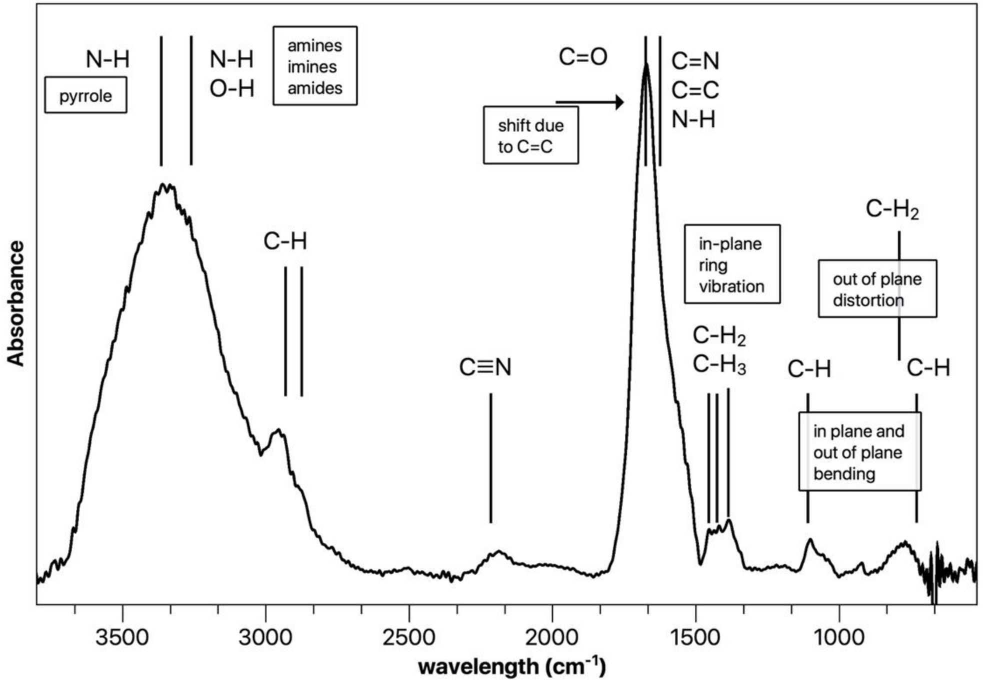
Pyrrole



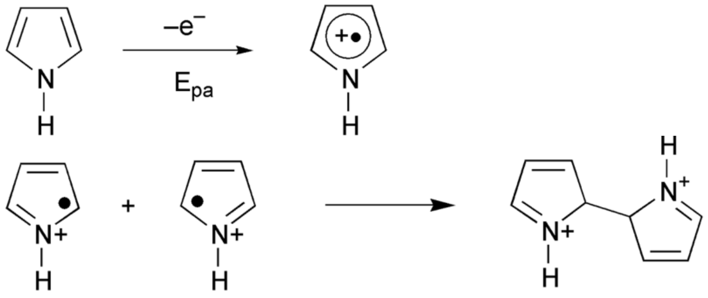
The ring is partially conserved

Stable in water and in ethanol

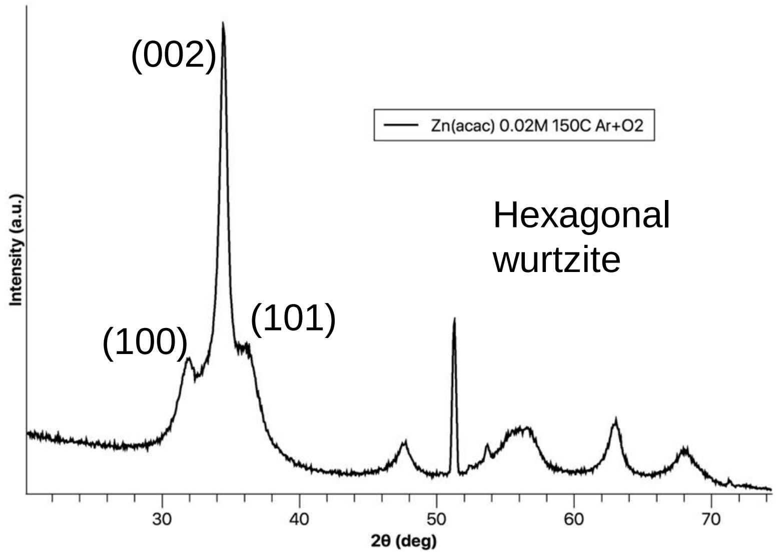


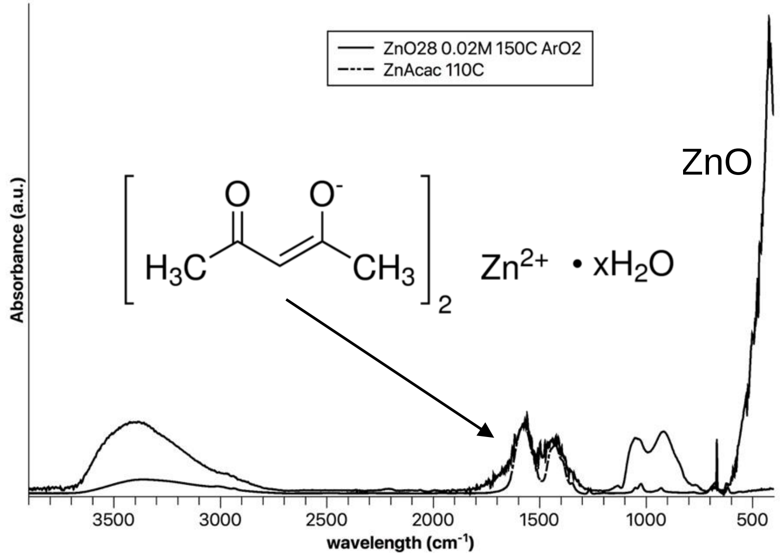


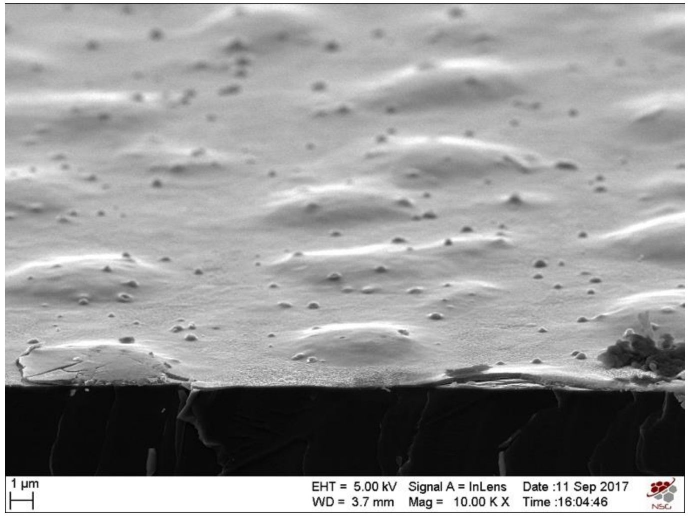
Electrochemical oxidation of pyrrole

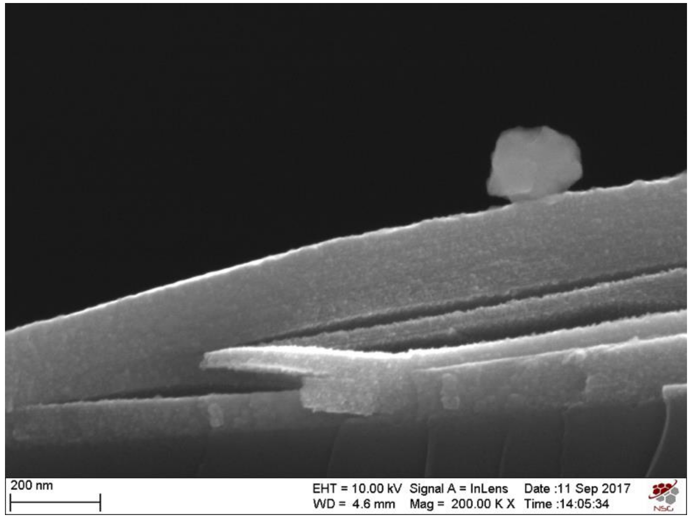


Functionalities - Deposition by aerosol precursors

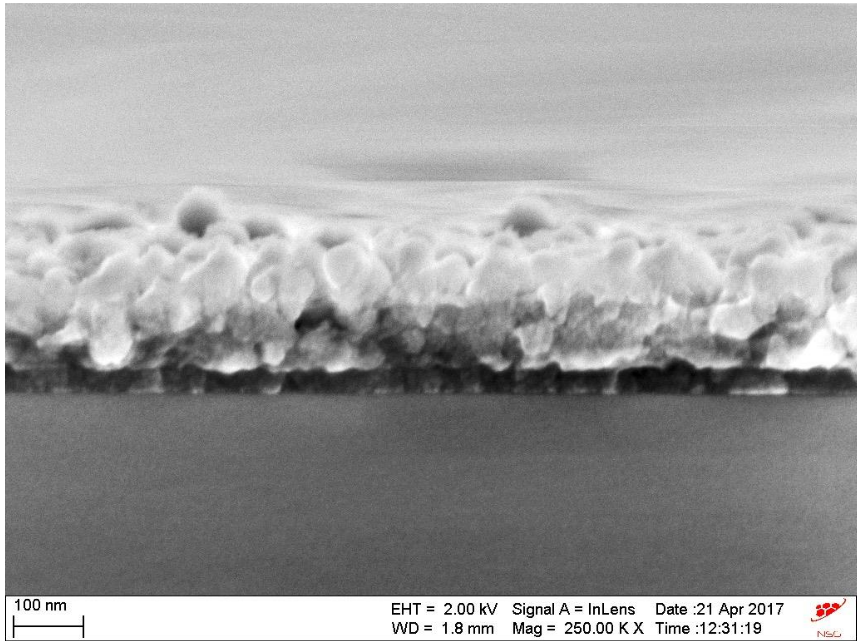


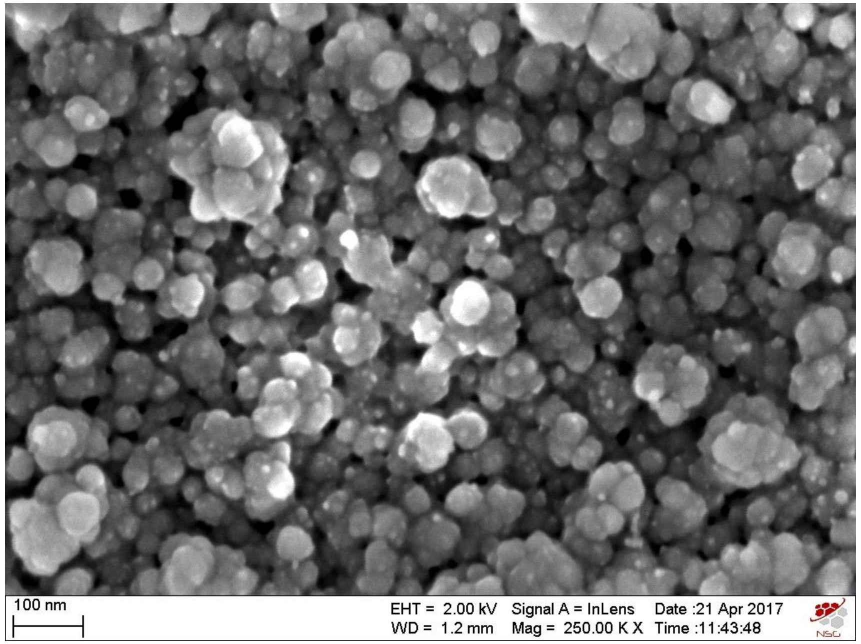






Functionalities - Nanocomposites in aerosol





Aerosil + HMDSO

Single step → Porous structure
Particles embedded in the coating

Conclusions

- efficient
- low temperature
- delicate – homogeneous
- ions close to the substrate
- enhanced surface charging

Acknowledgments

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Prof. Fridman → look at the ions to the substrate !

FAST
Functionally graded Additive Manufacturing scaffolds by hybrid manufacturing

H2020-NMP-PILOTS-2015
1/12/2015 – 30/11/2019

Università degli Studi di Padova

Thanks for the attention

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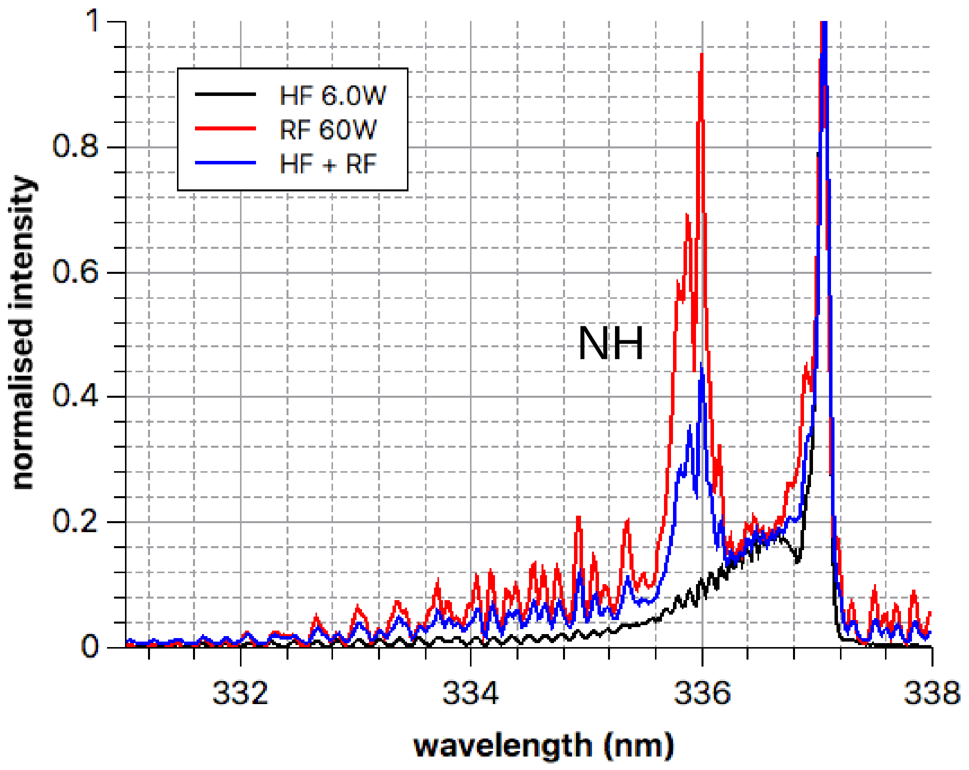
N2 roto-vibrational temperature

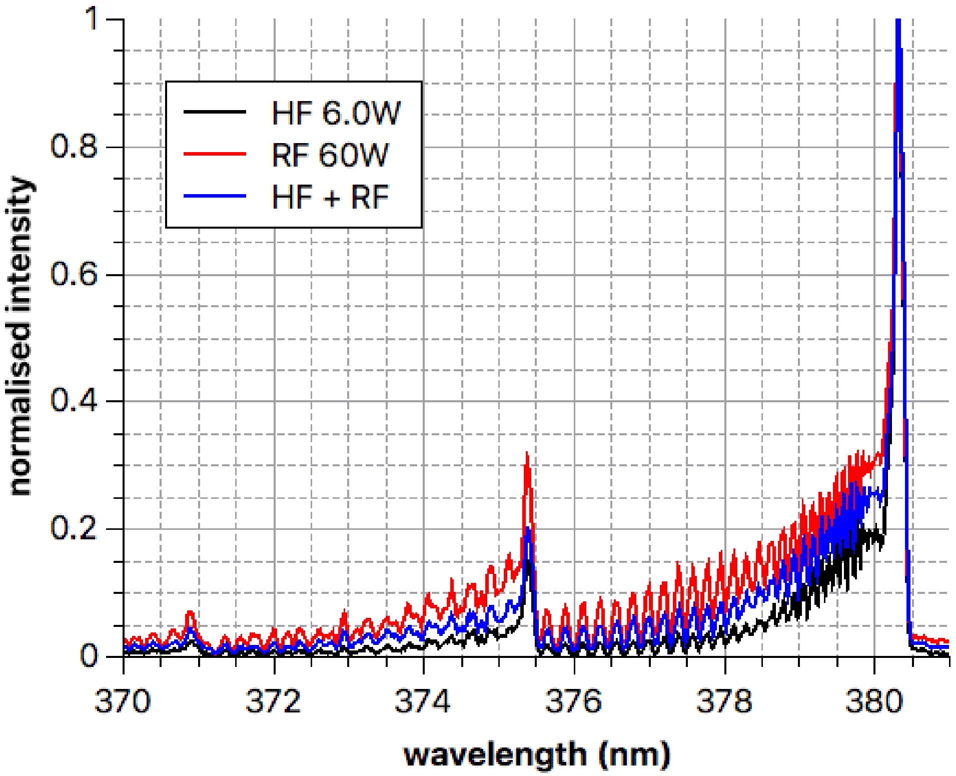
OES close to sample surface

Rotational temperature
RF 60W 840 +\- 40 K
HF + RF 780 +\- 20 K

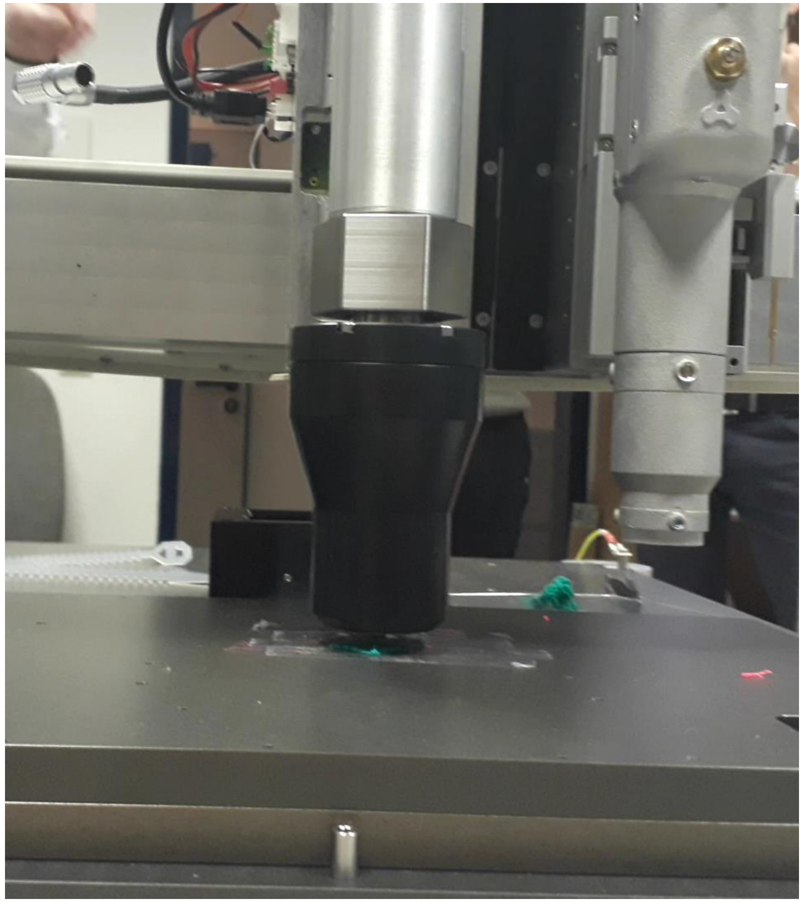
Vibrational temperature
RF 60W 1910 +\- 120 K
HF + RF 1530 +\- 20 K

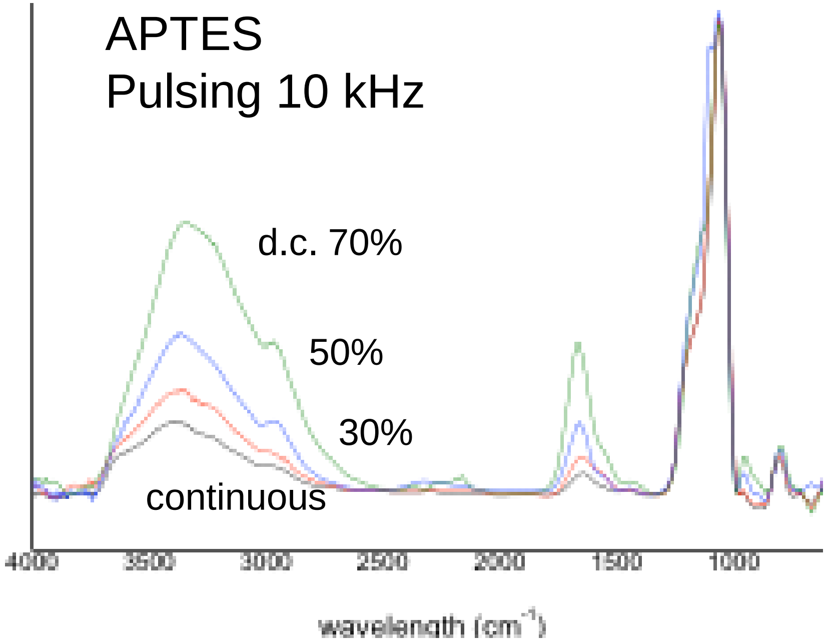
The coupling seems to reduce the temperature at the outlet





Process control





Low power
Pulsing Generators
Precursor inlet
Vapour or aerosol
Environmental atmosphere