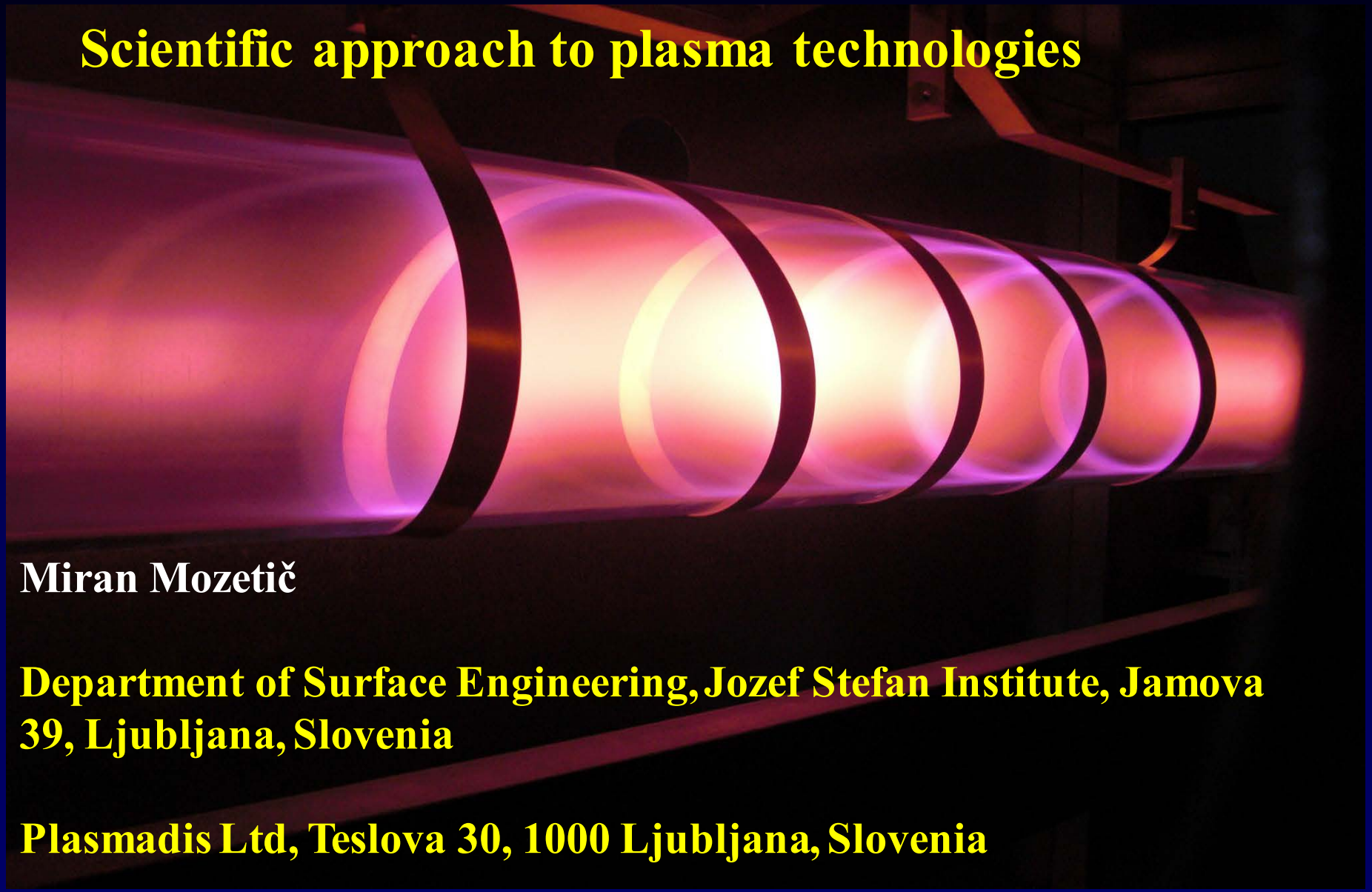
Scientific approach to plasma technologies



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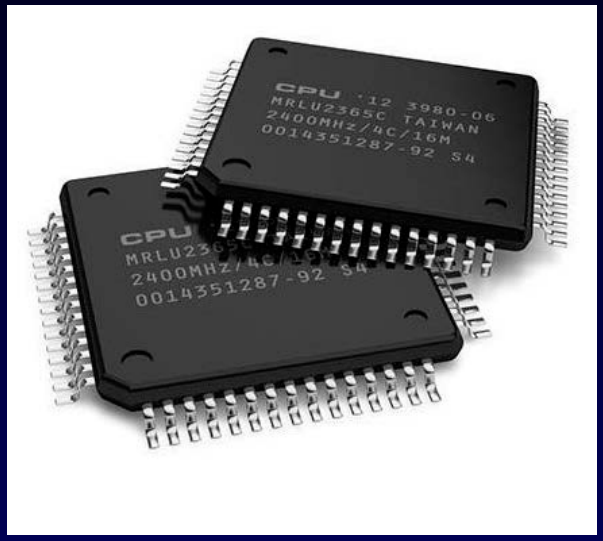
Plasma technologies are widely used for processing materials



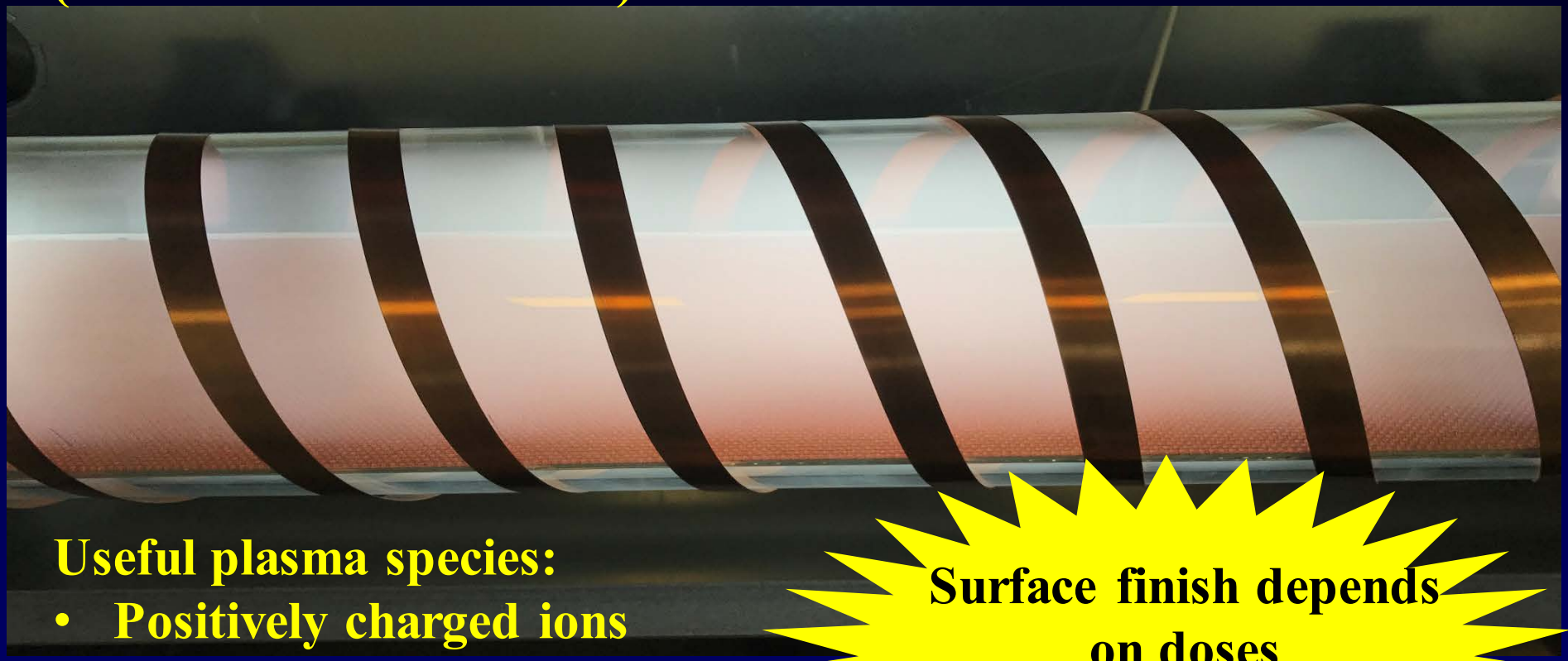
Basic principle:

1. Select appropriate gas

2. Create species of high potential or/and kinetic energy

3. Allow said species interact with substrates

Surface finish depends on the doses of reactive plasma species (sometimes also on fluxes)



Useful plasma species:

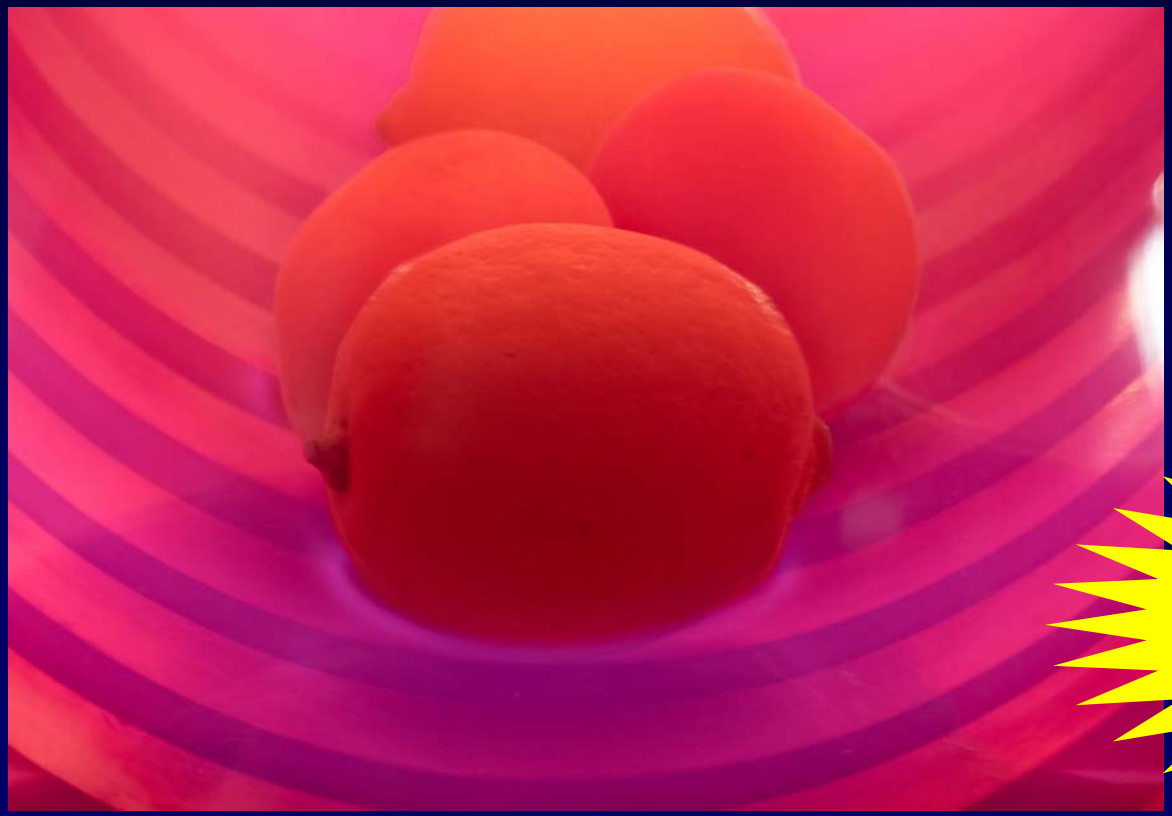
- Positively charged ions
- Radicals, incl. atoms
- VUV (UV) radiation

Surface finish depends on doses

Not on discharge parameters

Discharge parameters:

- Type of reactor
- Discharge coupling and power
- Gases, pressures, flows
- Treatment time

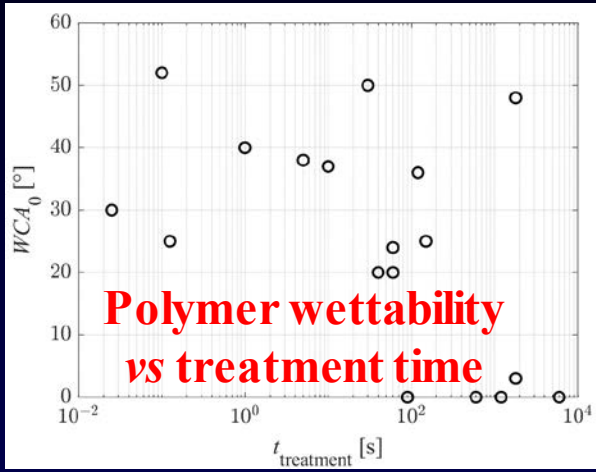


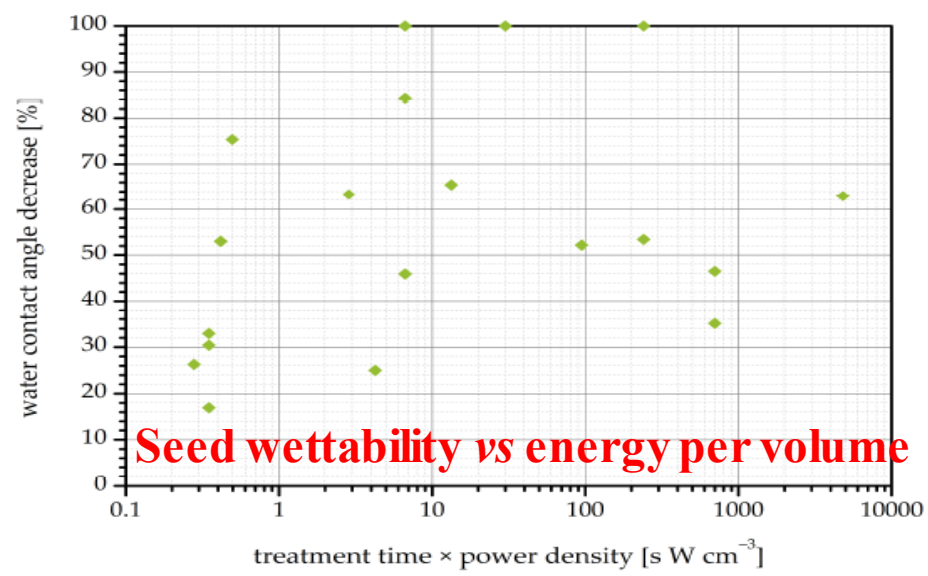
Plasma parameters:

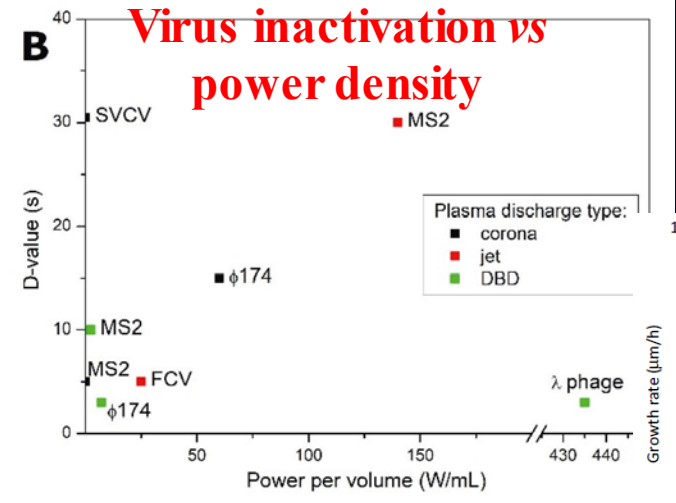
- Electron density and temperature
- Types of ions
- Voltage across sheath
- Types of radicals
- Density of radicals
- Fluxes of plasma species including VUV photons

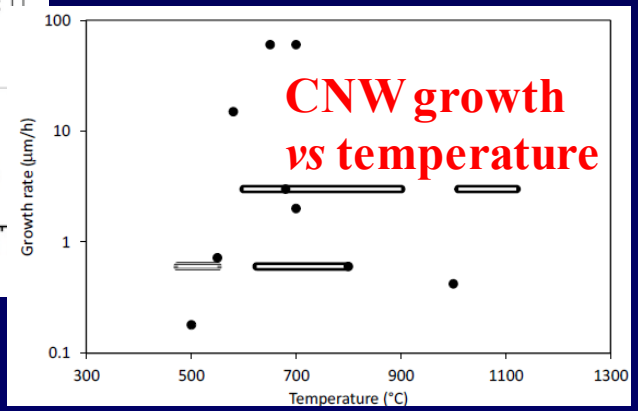
Very few articles report the plasma parameters

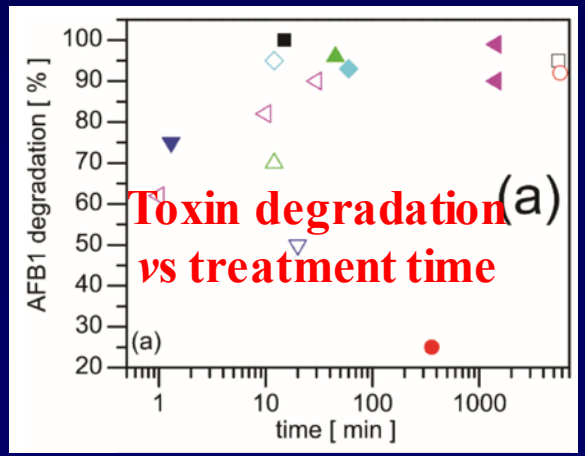
Reviewing available literature, one finds no correlation between discharge parameters and surface finish



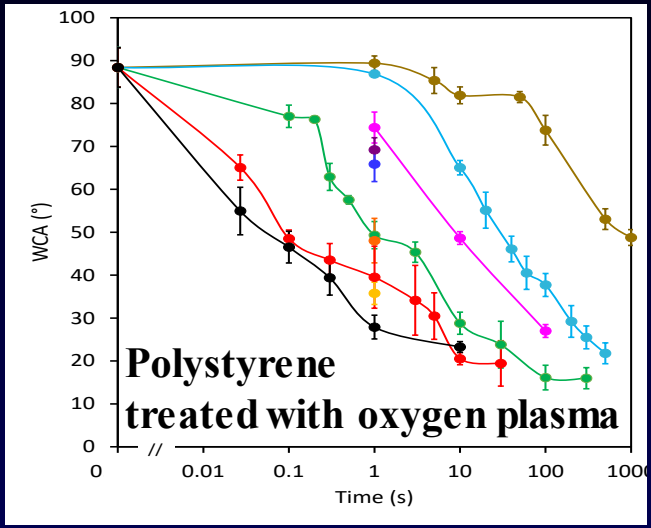






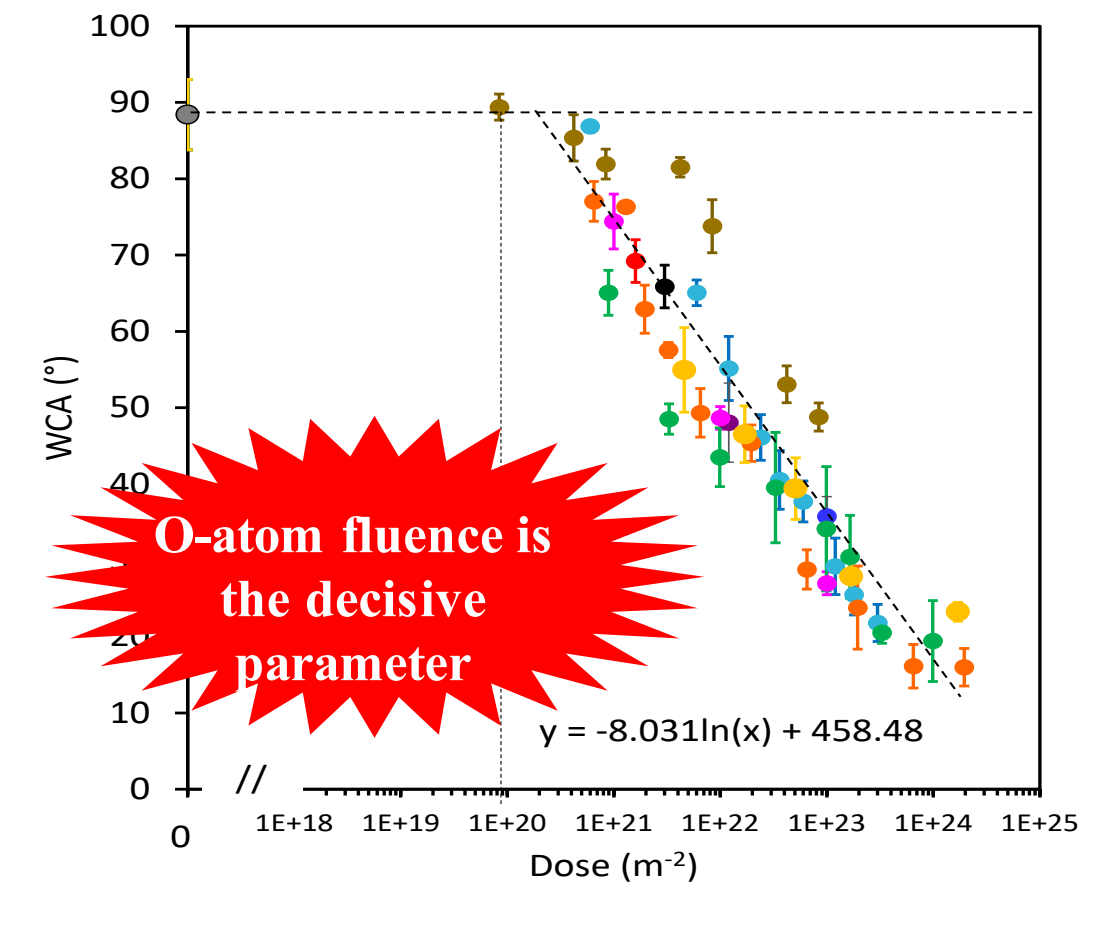


Water contact angle versus treatment time (at different experimental conditions)



Treatment time (log scale)

Versus the dose of O-atoms



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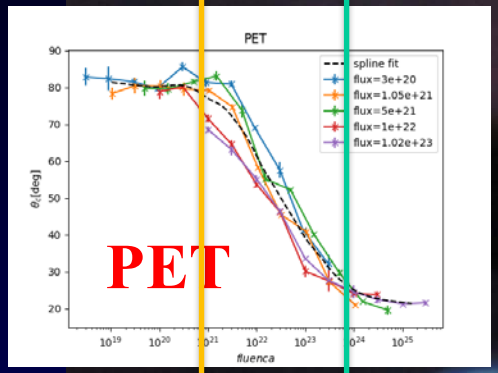
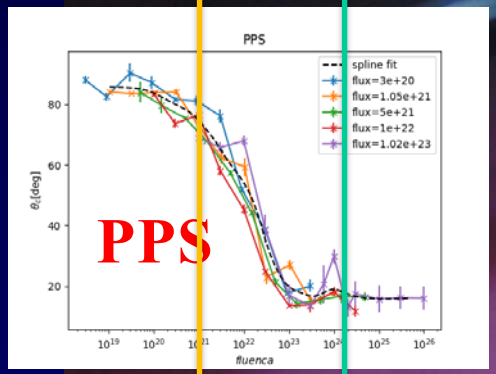
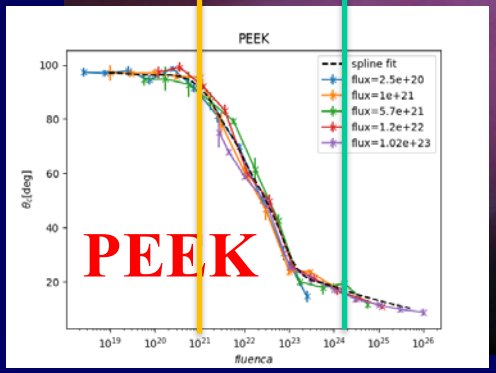
10^{21} m^{-2} 10^{24} m^{-2}





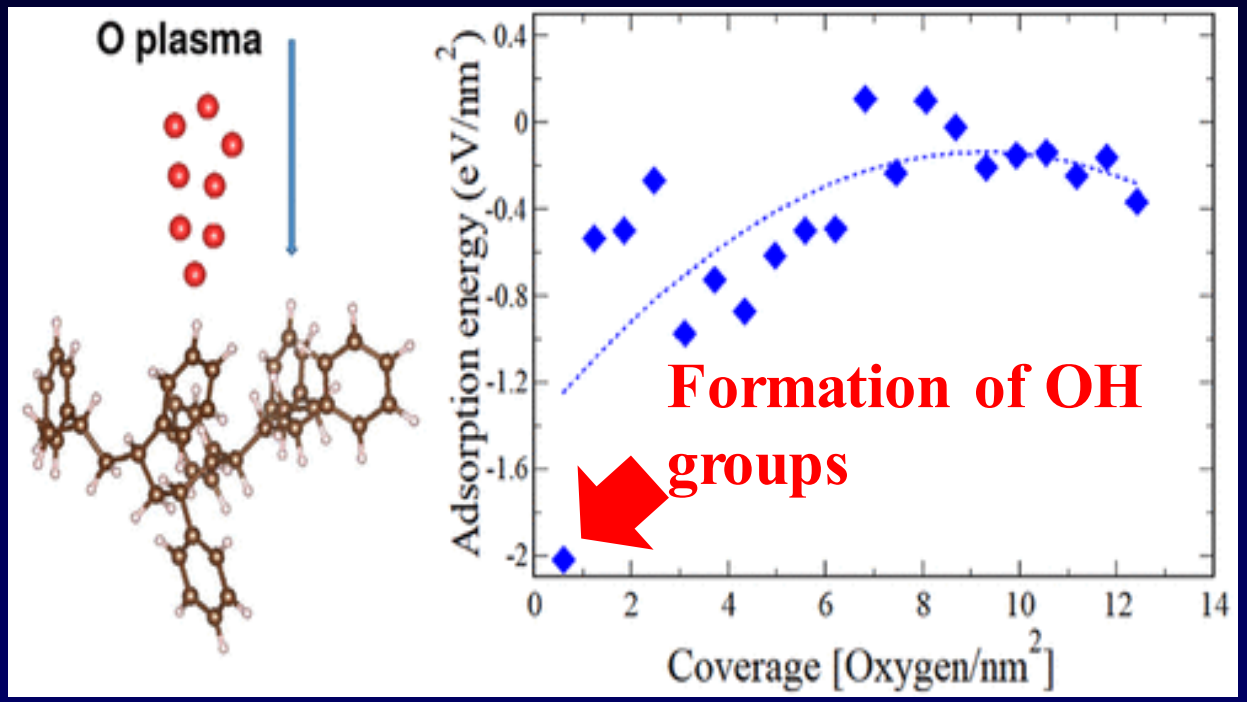


Catalytic tip (FOCP sensor)

Appropriate wettability (WCA about 20 degrees) of these polymers at O-atom doses 10^{23} m^{-2}

What exactly happens upon treatment of polymers with O atoms?

Theory: numerous binding sites for O-atoms on the polymer surface



1. Hydroxyl groups on ring C atoms
2. Degradation of aromatic ring
3. Formation of other O-rich groups

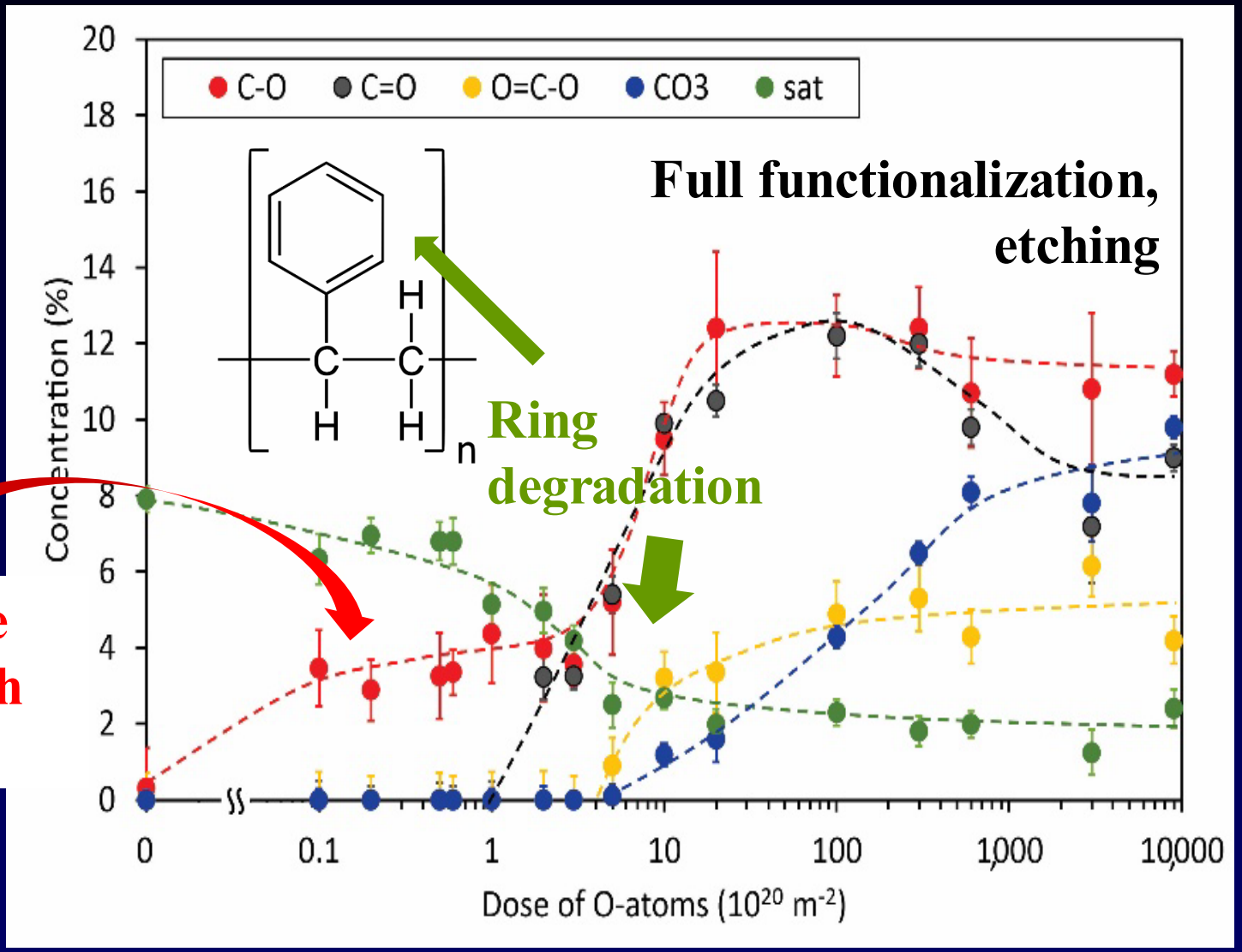
R.C. Longo, at al, Density functional theory study of oxygen adsorption on polymer surfaces, ACS Appl. Nano Mater. 3 (2020) 5189–5202.

Experiment

Polystyrene XPS C1s

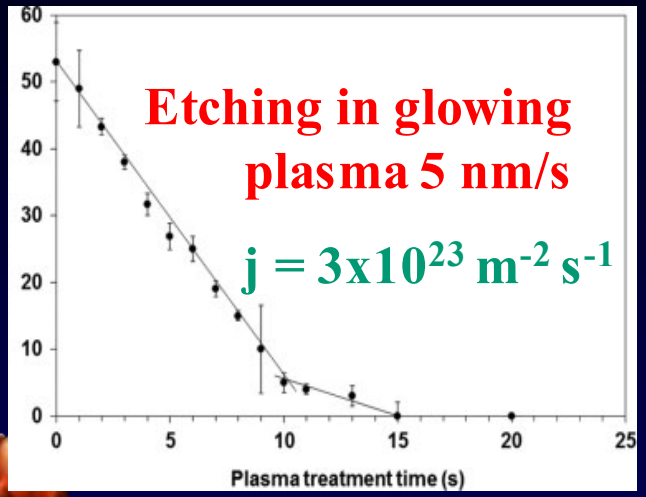
A. Vesel, Initial kinetics of functional groups formation, Appl. Surf. Sci. (2021)

C-H groups are substituted with C-OH groups

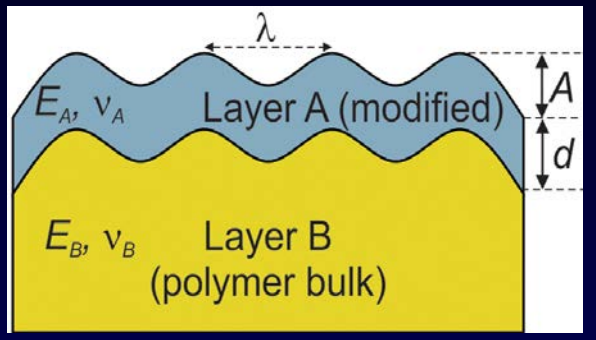


Evolution of functional groups versus the fluence of O atoms

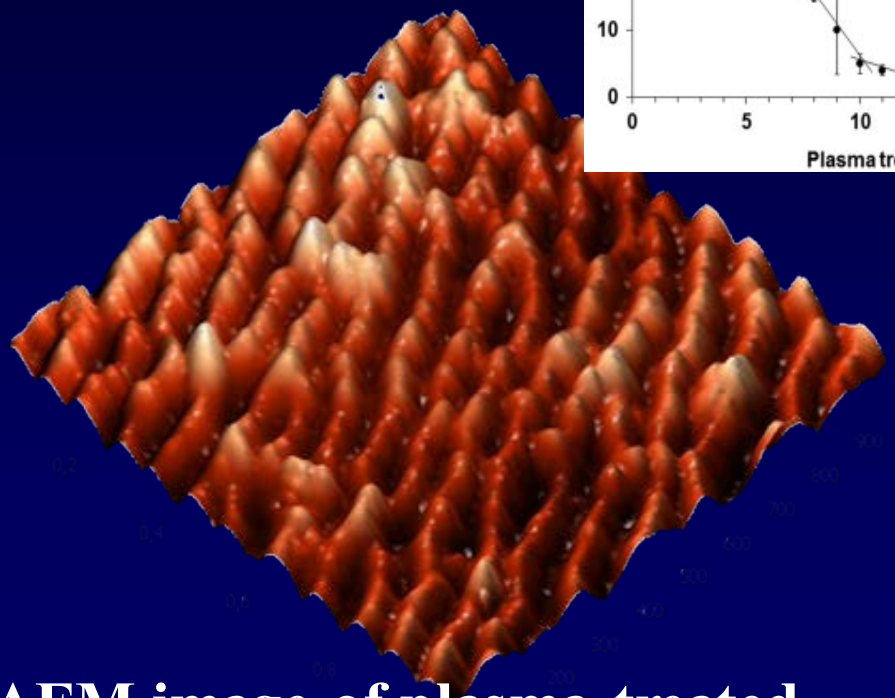
Etching should be always taken into account



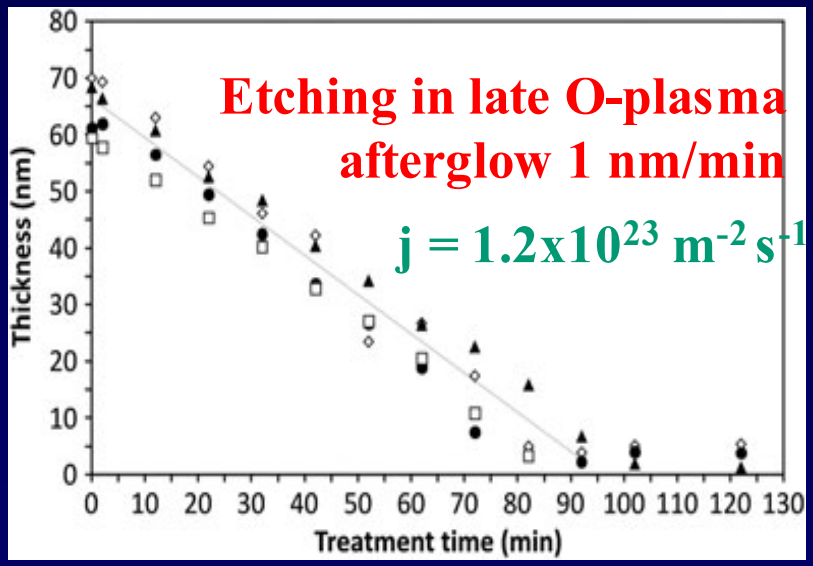
Possible explanation: compressive stress



R. L. Bruce et al, J. Appl. Phys., 2010, 107, p. 084310

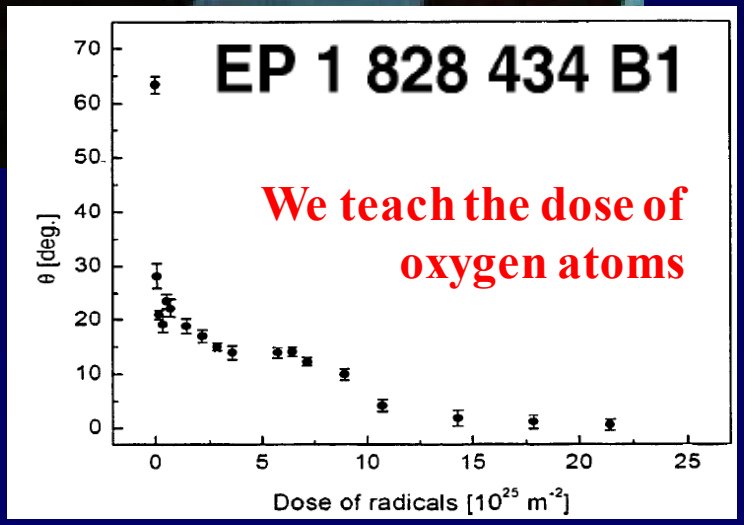


AFM image of plasma treated originally smooth polymer



Once the range of radical fluence is known, we are ready for upscaling

35M pieces are produced annually



- Plasma treatment

- Galvanic nickel

No waste,
much cheaper

Classical technology for metallization:

- Etching with NaOH
- Rinsing, drying
- Palladium seeding
- Electrodeless nickel
- Galvanic nickel

Dirty, expensive

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low-pressure plasma for treatment of seeds, granules etc

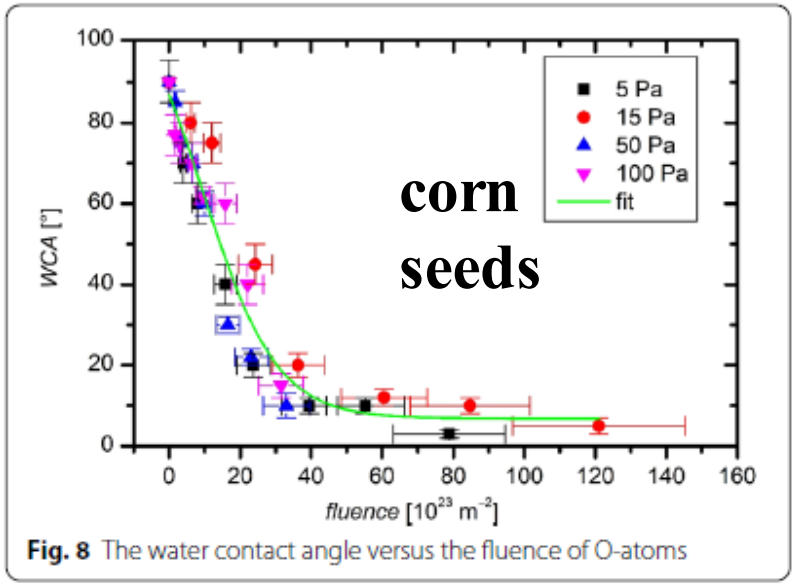
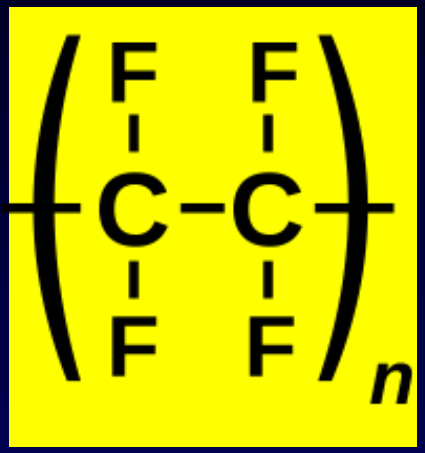


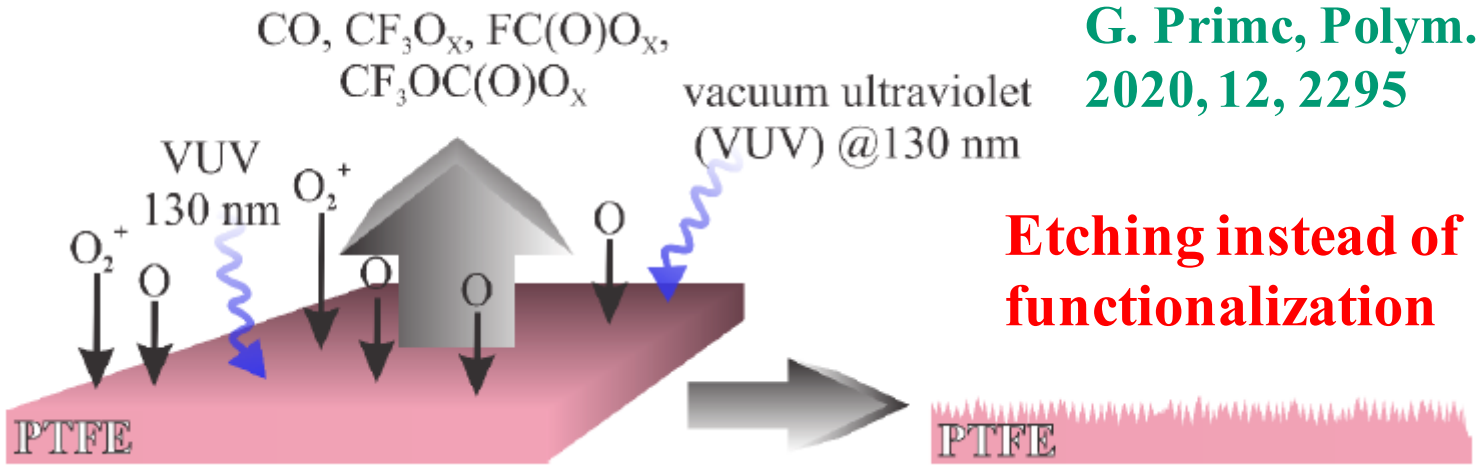
Fig. 8 The water contact angle versus the fluence of O-atoms

What about fluorinated polymers (Teflon and alike)?



Substitution of F with O is unlikely

Oxygen plasma will break C-C rather than C-F bonds



G. Primc, Polym. 2020, 12, 2295

Etching instead of functionalization

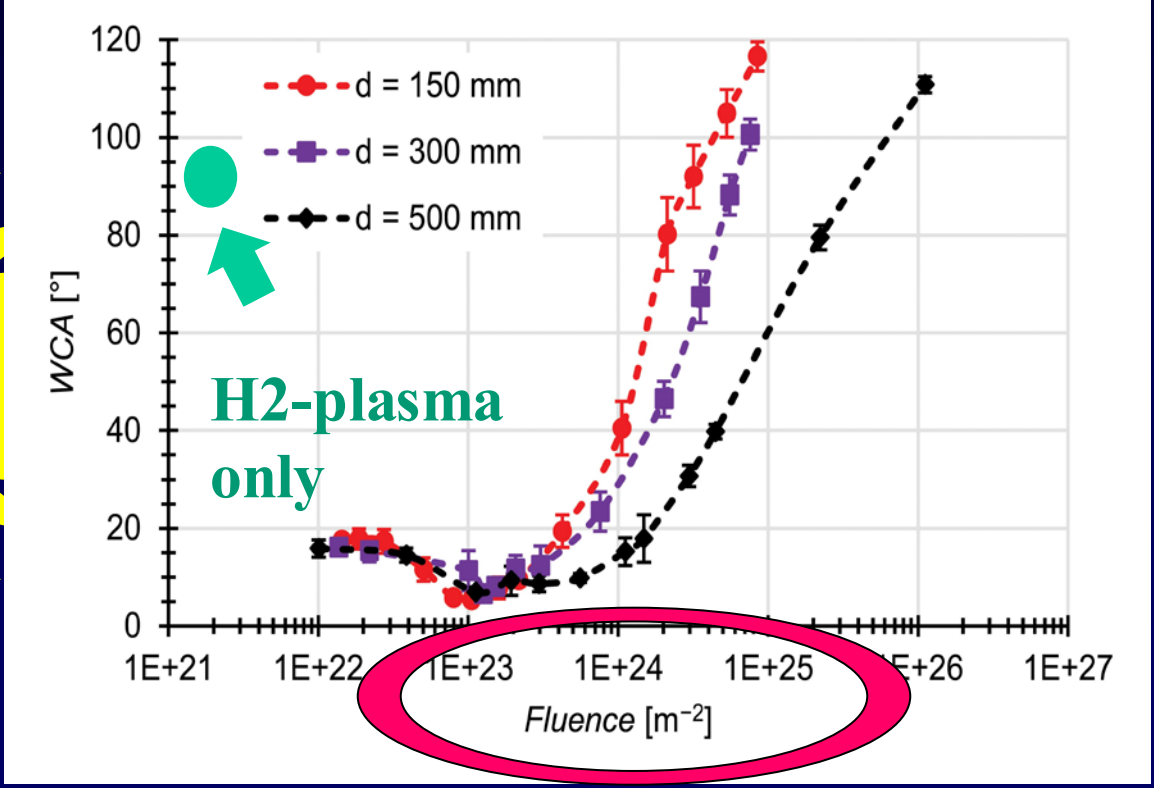
We use a two-stage plasma treatment:

1. Hydrogen (for defluorination)
2. Oxygen (for polar groups)

Polyolefin-like surface few nm

Bulk teflon

Polyolefin is functionalized with polar groups by oxygen atoms



WCA on pretreated Teflon vs oxygen-atoms fluence (dose)

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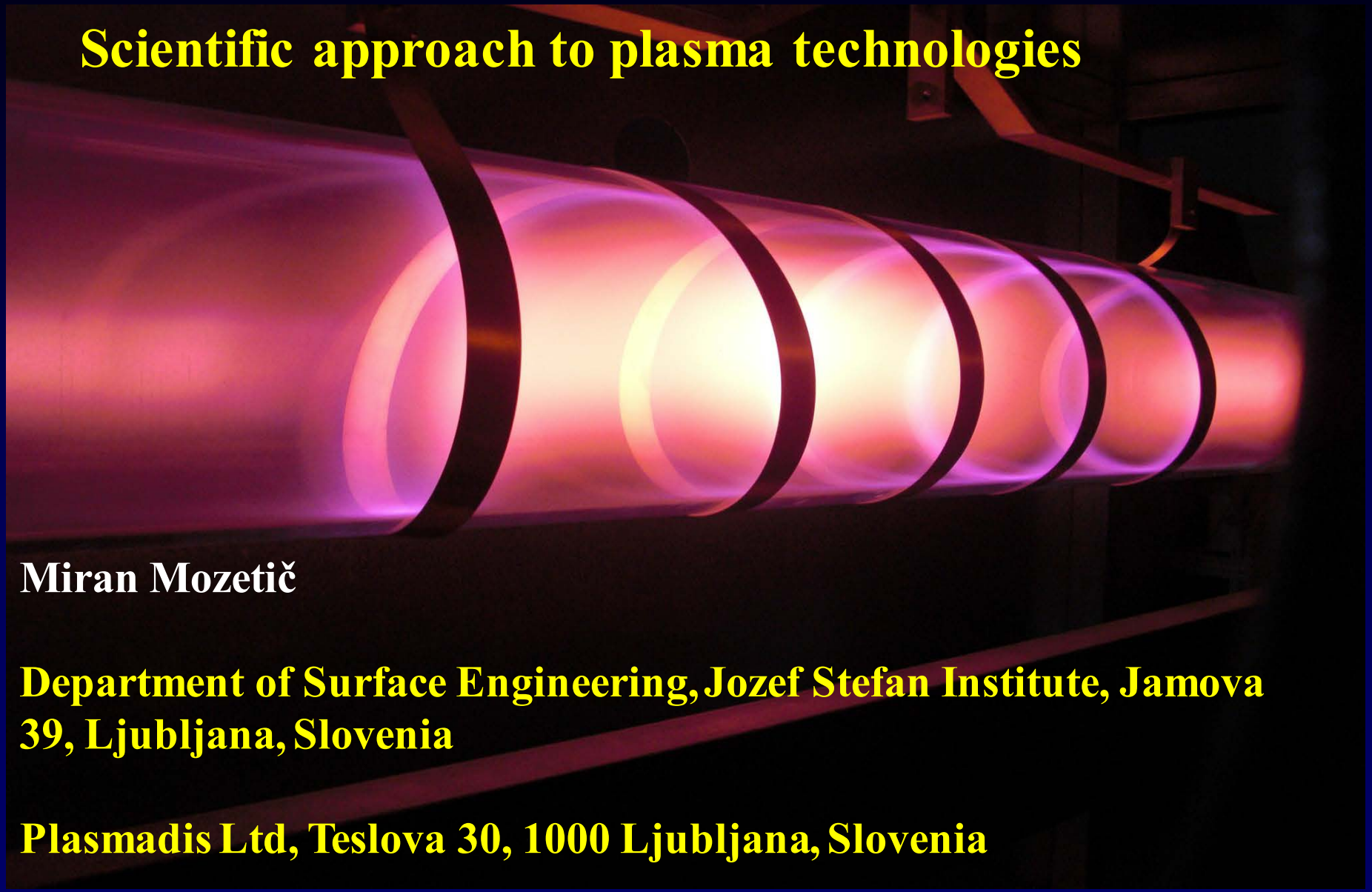
Once fluences are known, the upscaling of scientific results to industrial needs is solely a technological problem

**ICP H-mode,
absorbed RF power
5 – 50 kW**

Scientific approach to plasma technologies



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