Plasma processes under low and atmospheric pressure.

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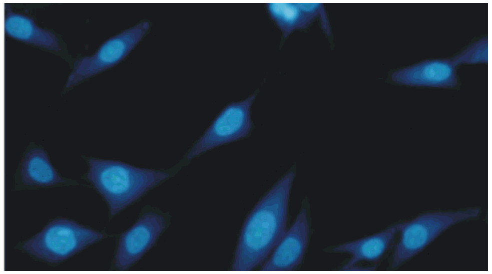
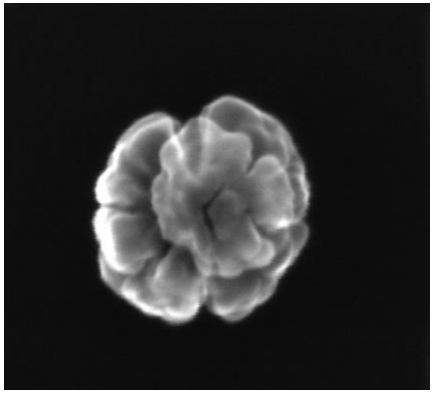
Outline

- Who we are?
- What is plasma?
- How can be plasma used for surface modification?
  - Plasma treatment of polymers
  - Sterilization



- Thin film deposition
- Nanostructured coatings
- Nanoparticles



Who we are?

Faculty of Mathematics and Physics

~ 1000 student of Physics

14 departments

Department of Macromolecular physics

Charles University in Prague has more than 7,500 employees

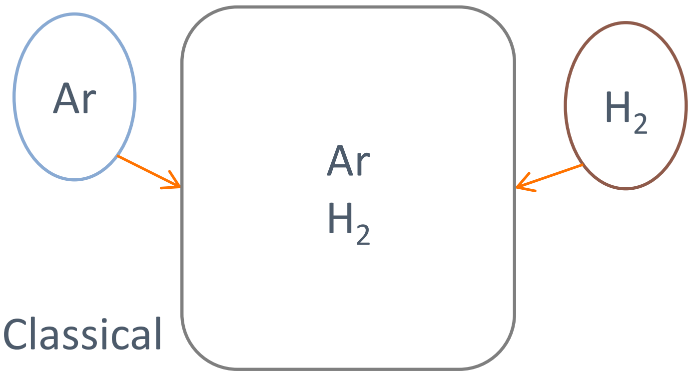
Over 51,000 students

17 faculties

5 researchers
8 students (6 PhD)

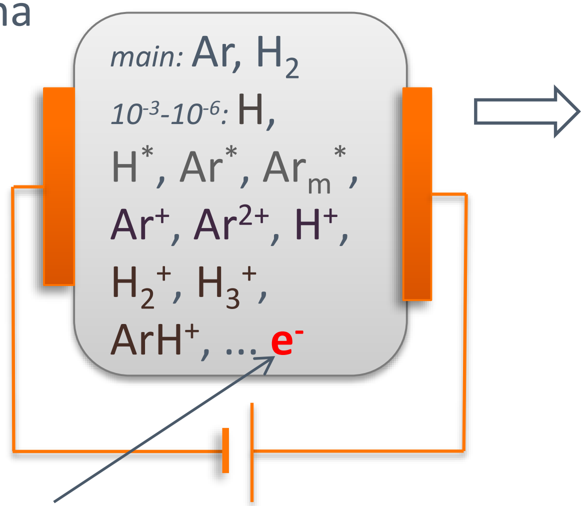
What is plasma?

- $Ar + H_2 \rightarrow ?$



Classical

Plasma



No thermal equilibrium!

$T_n \sim 0.03$eV, $T_i \sim 0.1$eV, $T_e \sim 1$eV

+fast (>10eV) ions and **electrons**

Table 2 Reactions taken into account in the Monte Carlo models

Electron Monte Carlo model—	
Elastic scattering	$e^- + Ar \rightarrow e^- + Ar$
Ionization	$e^- + Ar \rightarrow e^- + Ar^+ + e^-$
Total excitation (including up to the Ar metastable levels)	$e^- + Ar \rightarrow e^- + Ar^*$ (incl. Ar_m^*)
Ionization from the Ar metastable levels	$e^- + Ar_m^* \rightarrow e^- + Ar^+ + e^-$
Total excitation from the Ar metastable levels	$e^- + Ar_m^* \rightarrow e^- + Ar^*$
Elastic scattering	$e^- + H_2 \rightarrow e^- + H_2$
Total vibrational excitation	$e^- + H_2 \rightarrow e^- + H_2^*$ (v)
Total electron excitation to singlet states	$e^- + H_2 \rightarrow e^- + H_2^*$ (s)
Total electron excitation to triplet states, followed by dissociation	$e^- + H_2 \rightarrow e^- + H_2^*$ (t) $\rightarrow e^- + H + H$
Ionization	$e^- + H_2 \rightarrow e^- + H_2^+ + e^-$
Dissociative ionization	$e^- + H_2 \rightarrow e^- + H^+ + H + e^-$
Total excitation	$e^- + H \rightarrow e^- + H^*$
Ionization	$e^- + H \rightarrow e^- + H^+ + e^-$
Ar^+ Monte Carlo model—	
Elastic (isotropic) scattering	$Ar^+ + Ar \rightarrow Ar^+ +$ fast Ar
Elastic scattering in backward direction (or so-called "symmetric charge transfer")	$Ar^+ + Ar \rightarrow$ fast Ar + slow Ar^+
Ionization	$Ar^+ + Ar \rightarrow Ar^+ + Ar^+ + e^-$
Excitation to the metastable levels	$Ar^+ + Ar \rightarrow Ar^+ + Ar_m^*$
H-atom transfer	$Ar^+ + H_2 \rightarrow ArH^+ + H$
Asymmetric charge transfer	$Ar^+ + H_2 \rightarrow$ fast Ar + H_2^+
ArH^+ Monte Carlo model—	
Elastic scattering	$ArH^+ + Ar \rightarrow ArH^+ +$ fast Ar
Collision-induced dissociation	$ArH^+ + Ar \rightarrow$ fast Ar + H^+ + Ar
Collision-induced dissociation	$ArH^+ + Ar \rightarrow$ fast Ar^+ + H + Ar
Elastic scattering	$ArH^+ + H_2 \rightarrow ArH^+ +$ fast H_2
Proton transfer	$ArH^+ + H_2 \rightarrow$ fast Ar + H_3^+
H^+ Monte Carlo model—	
Elastic scattering	$H^+ + Ar \rightarrow H^+ +$ fast Ar
Asymmetric charge transfer	$H^+ + Ar \rightarrow$ fast H + Ar^+
Symmetric charge transfer	$H^+ + H \rightarrow$ fast H + H^+
Total vibrational excitation	$H^+ + H_2 \rightarrow H^+ + H_2^*$ (v)
Elastic scattering	$H^+ + H_2 \rightarrow H^+ +$ fast H_2
Asymmetric charge transfer	$H^+ + H_2 \rightarrow$ fast H + H_2^+
H_2^+ Monte Carlo model—	
Proton transfer	$H_2^+ + Ar \rightarrow H + ArH^+$
Asymmetric charge transfer	$H_2^+ + Ar \rightarrow$ fast H_2 + Ar^+
Proton transfer	$H_2^+ + H_2 \rightarrow H + H_3^+$
Symmetric charge transfer	$H_2^+ + H_2 \rightarrow$ fast H_2 + H_2^+
H_3^+ Monte Carlo model—	
Elastic scattering	$H_3^+ + Ar \rightarrow H_3^+ +$ fast Ar
Proton transfer	$H_3^+ + Ar \rightarrow$ fast H_2 + slow ArH^+
Charge transfer + dissociation	$H_3^+ + Ar \rightarrow$ fast H_2 + fast H + slow Ar^+
Collision-induced dissociation	$H_3^+ + Ar \rightarrow$ fast H^+ + fast H_2 + slow Ar
Collision-induced dissociation	$H_3^+ + Ar \rightarrow$ fast H_2^+ + fast H + slow Ar
Elastic scattering	$H_3^+ + H_2 \rightarrow H_3^+ +$ fast H_2
Proton transfer	$H_3^+ + H_2 \rightarrow$ fast H_2 + slow H_3^+
Proton transfer + dissociation	$H_3^+ + H_2 \rightarrow$ fast H_2 + slow H_2 + slow H^+
Proton transfer + dissociation	$H_3^+ + H_2 \rightarrow$ fast H_2 + slow H + slow H_2^+
Charge transfer + dissociation	$H_3^+ + H_2 \rightarrow$ fast H_2 + fast H + slow H_2^+
Collision-induced dissociation	$H_3^+ + H_2 \rightarrow$ fast H_2^+ + fast H + slow H_2
Collision-induced dissociation	$H_3^+ + H_2 \rightarrow$ fast H^+ + fast H_2 + slow H_2
Collision-induced dissociation	$H_3^+ + H_2 \rightarrow$ fast H^+ + 2 fast H + slow H_2
Fast Ar^0 Monte Carlo model—	
Elastic scattering	fast Ar + slow Ar $\rightarrow$ fast Ar + fast Ar
Ionization	fast Ar + slow Ar $\rightarrow$ fast Ar + Ar^+ + e^-
Excitation to the metastable levels	fast Ar + slow Ar $\rightarrow$ fast Ar + Ar_m^*

Advantage:
Rich physics and chemistry!

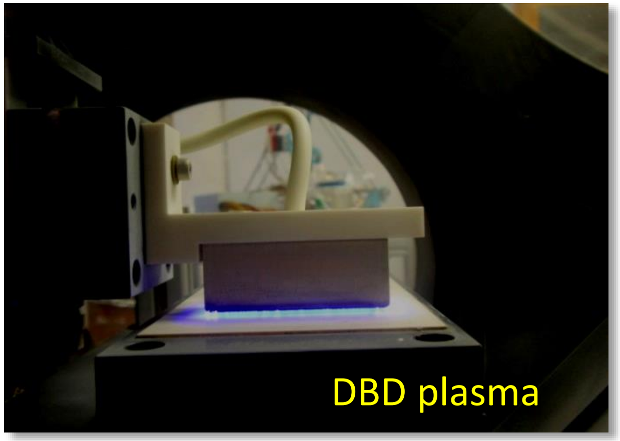
Disadvantage:
Rich physics and chemistry!

Bogaerts et.al. 2002

What is plasma?

Low pressure plasma

Atmospheric pressure plasma



Plasma is a complex mixture of electron, ions, neutrals, radicals, excited species.
Plasma emits radiation in wide spectral range.

Plasma interacts with solid surfaces and may change their properties (chemical composition, morphology, bioresponsive properties etc.)

What is plasma?

Plasma is a complex mixture of electron, ions, neutrals, radicals, excited species.
Plasma emits radiation in wide spectral range.

Surface modification
Surface cleaning
Surface sterilization

Biomedical applications

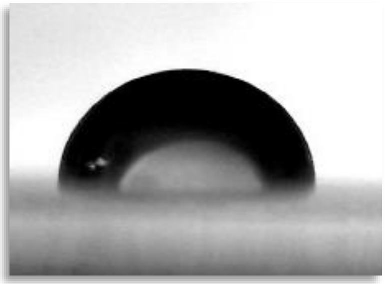
Deposition of thin films
Deposition of nanostructured coatings
Deposition of nanocompoiste materials

Biomedical applications
Photovoltaic, Fuel cells
Barrier and protective coatings

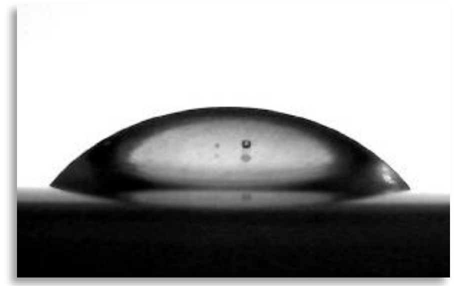
Advantages:

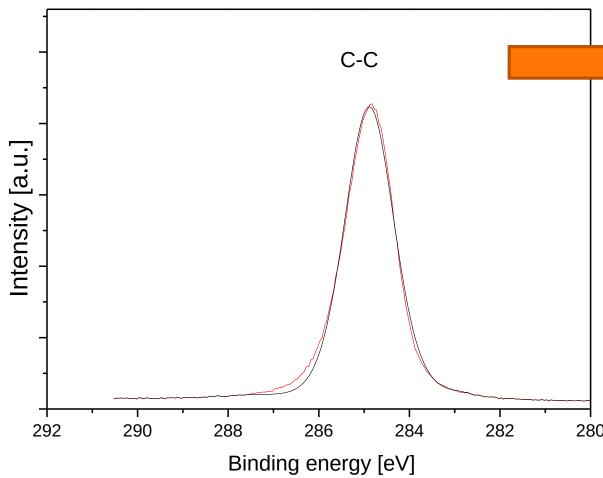
Possibility to process virtually any substrate material
Fast, cost-effective, environmentally friendly
High flexibility

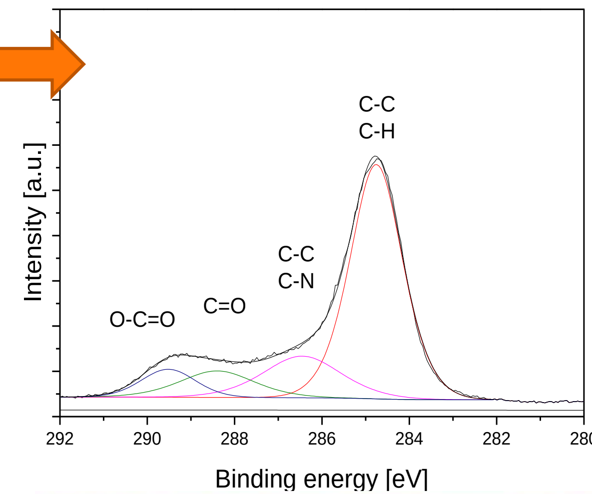
I. Plasma treatment of polymers

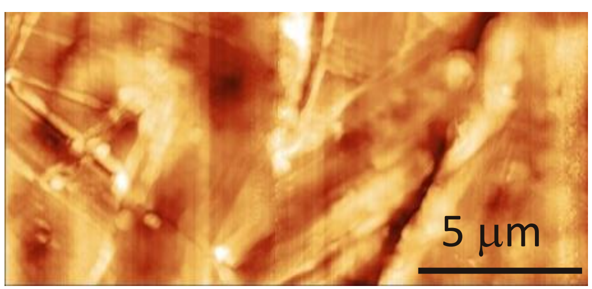


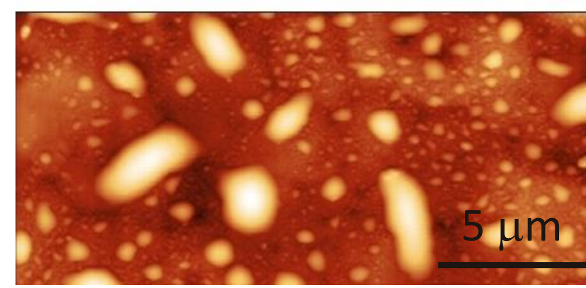
DBD plasma
30 W
1 atm
air
1” plasma treatment







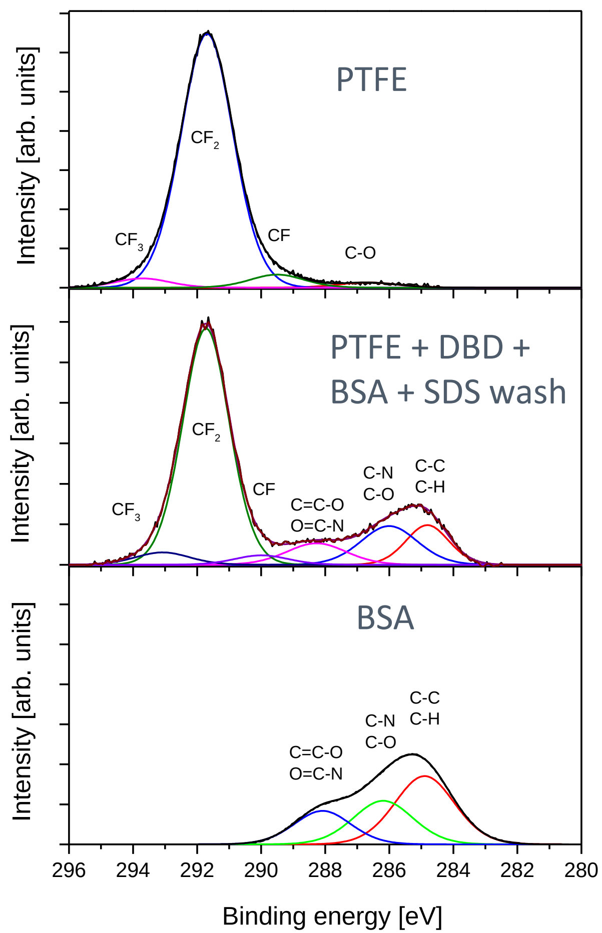




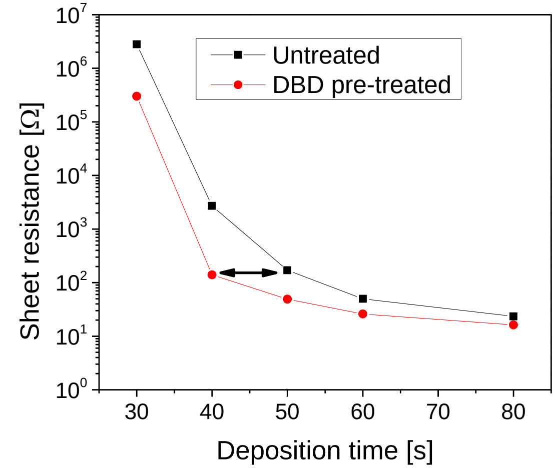
DBD plasma may change surface energy, chemical composition as well as morphology of polymers.

Applications

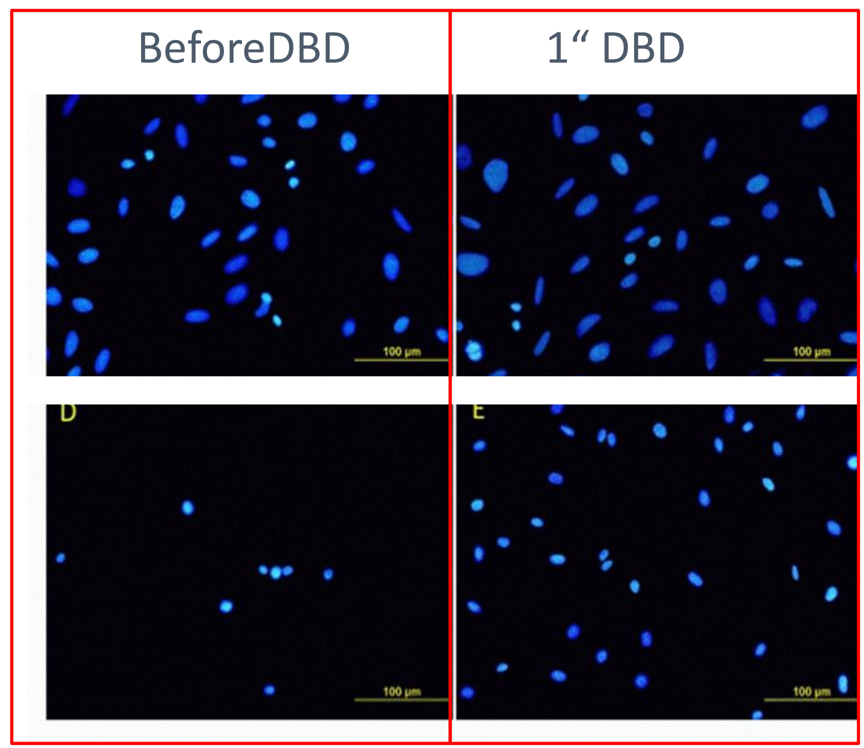
Covalent immobilization of biomolecules



Improved metallization of polymers



Improved biocompatibility



Ostoblast-like cells

SAOS

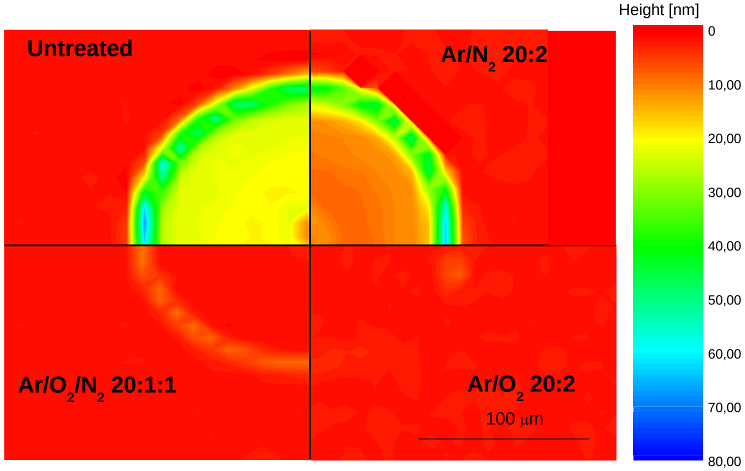
Endotel cells

HUVEC

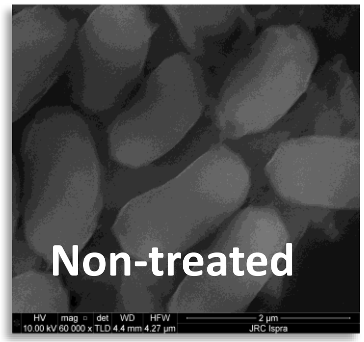
3 days after seeding

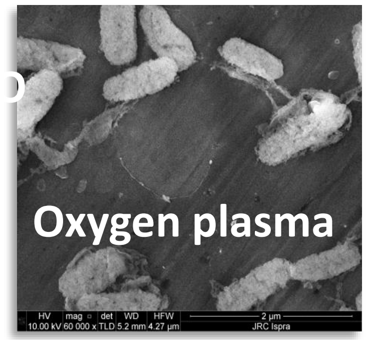
II. Plasma based sterilization

By means of plasma it is possible to sterilize/decontaminate surfaces.

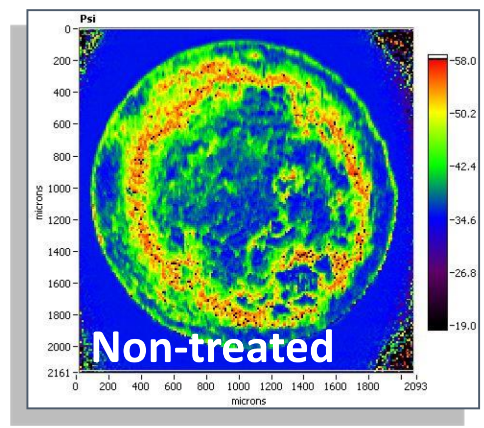


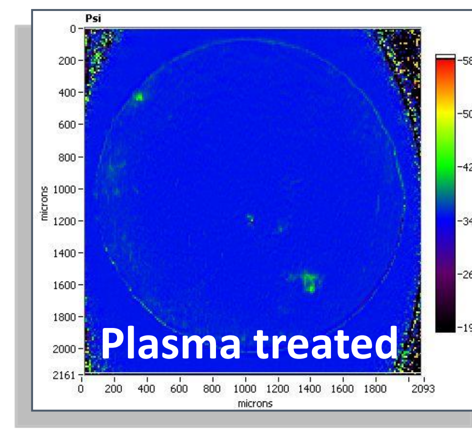
Effect on proteins





Effect on bacterial spores





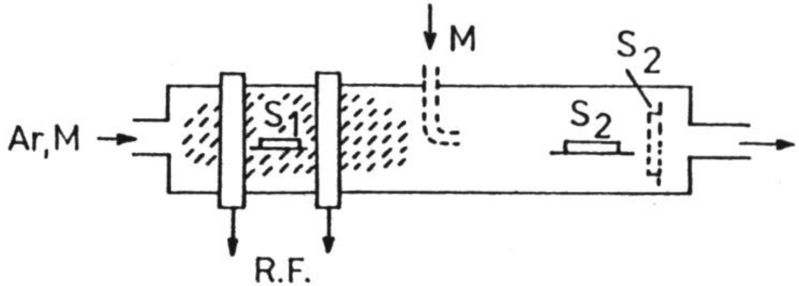
Effect on endotoxins

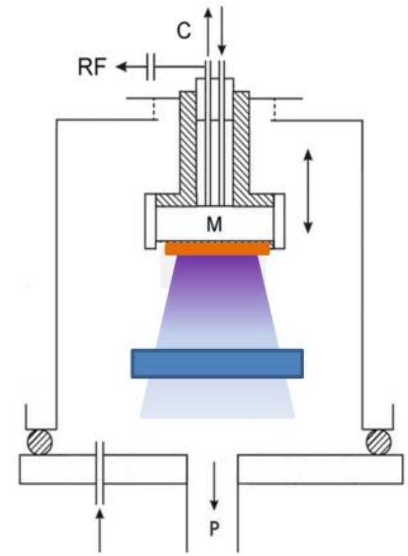
Highly competitive with other sterilization methods!!!

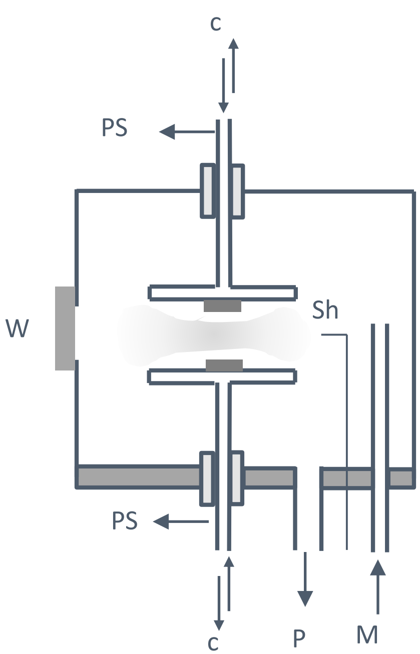
O.Kylián et. al. J.Phys.D: Appl. Phys 41, 2008, Art. No 095201
Kylian and Rossi . Phys. D: Appl. Phys. 42 (2009) 085207
Kylian et.al. Plasma Process. Polym. 2011, 8, 1137
Fumagalli et. al. J. Phys. D: Appl. Phys. 45 (2012)

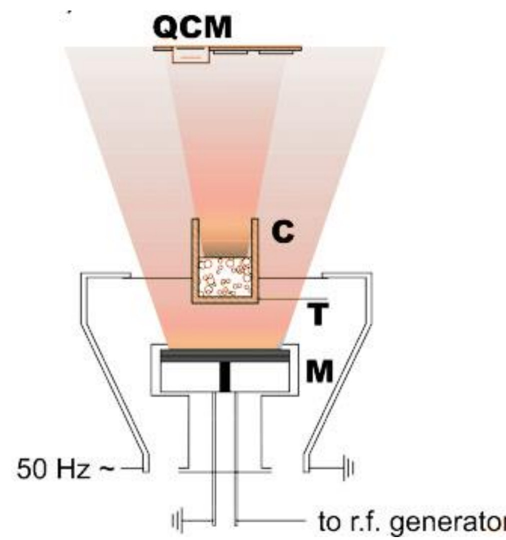
III. Thin films deposition

Plasma may be used for deposition of thin films of metals, metal-oxides as well as plasma polymers.



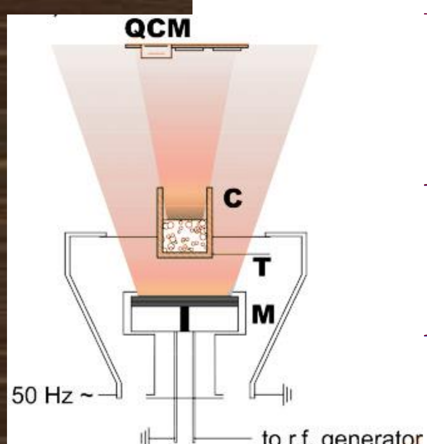


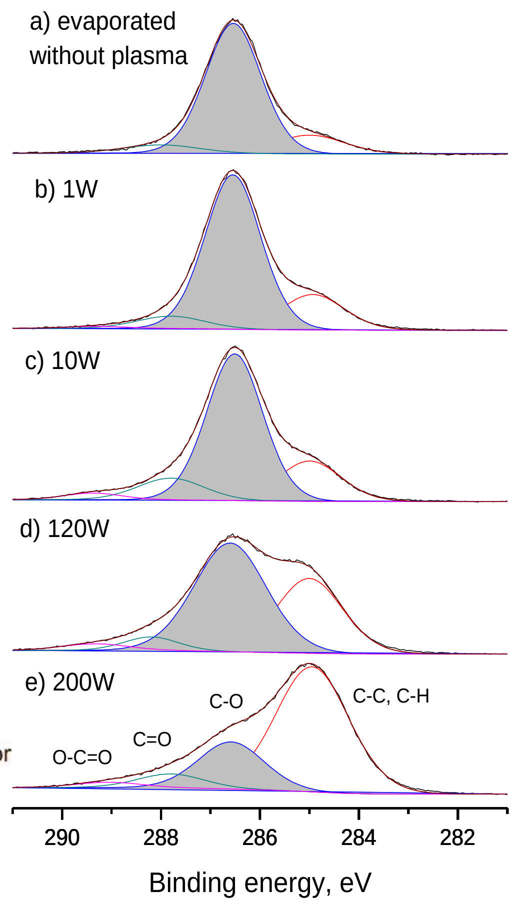


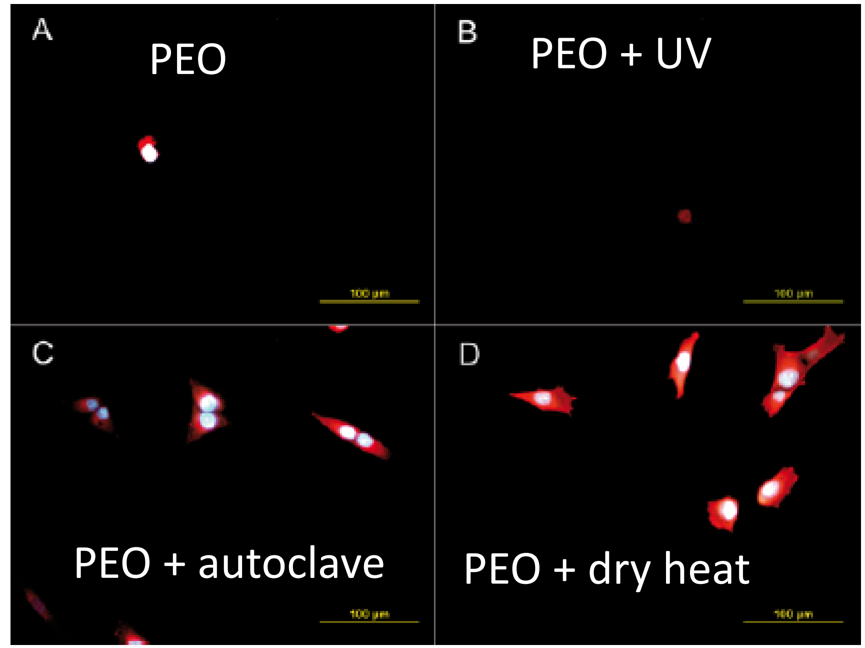


III. Thin films deposition - examples

Non-fouling PEO-like thin films





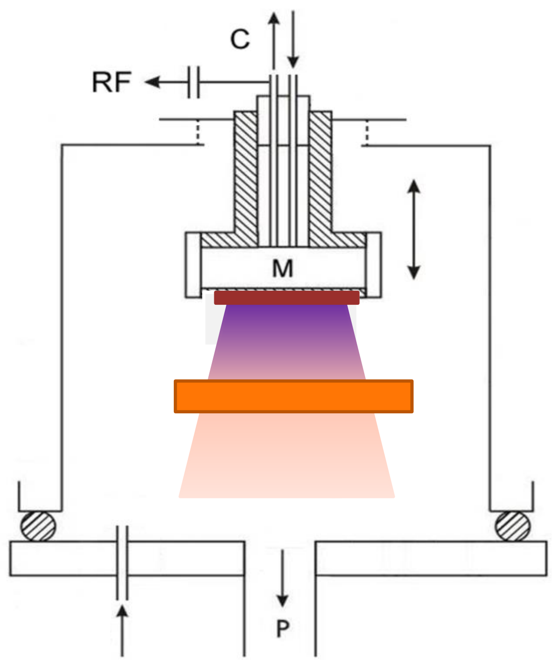


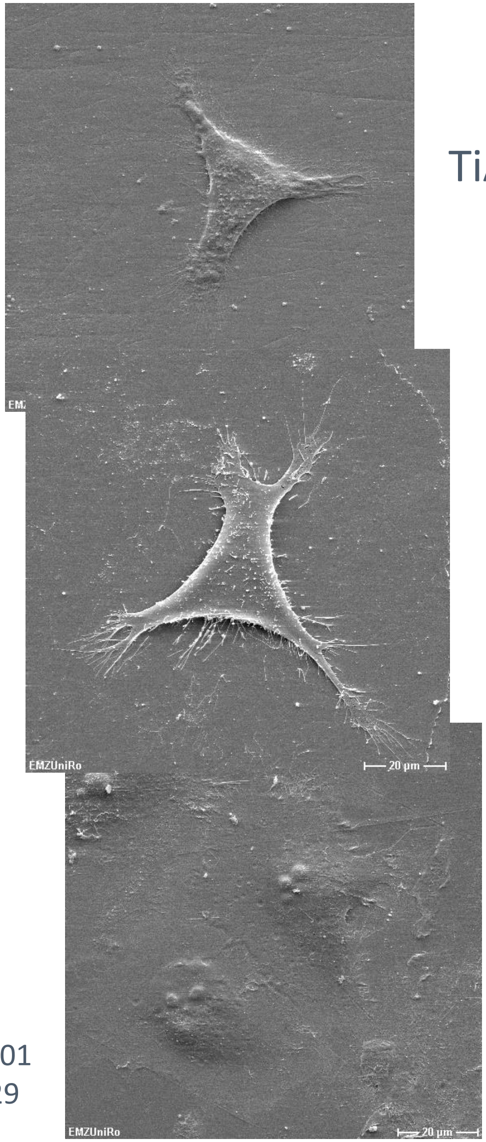
It is possible to fabricate non-fouling PEO-like coatings that withstand UV light sterilization.

A. Choukourov et al. Plasma Process. Polym. 2012, 9, 48
A. Artemenko et. al. Thin Solid Films 2012, 520, 7115

Thin films deposition - examples

Amino-rich thin films





TiAlV

TiAlV + Nylon sputtered in Ar

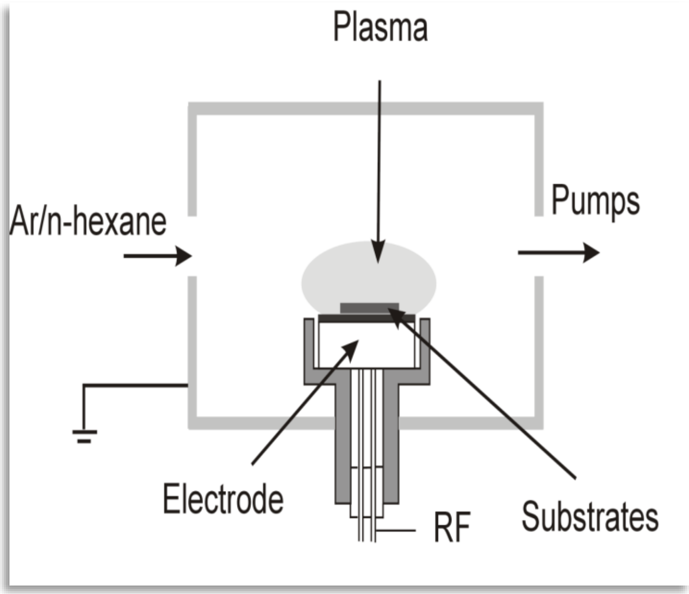
TiAlV + Nylon sputtered in mixture nitrogen-hydrogen

It is possible to fabricate coatings that promote cells growth.

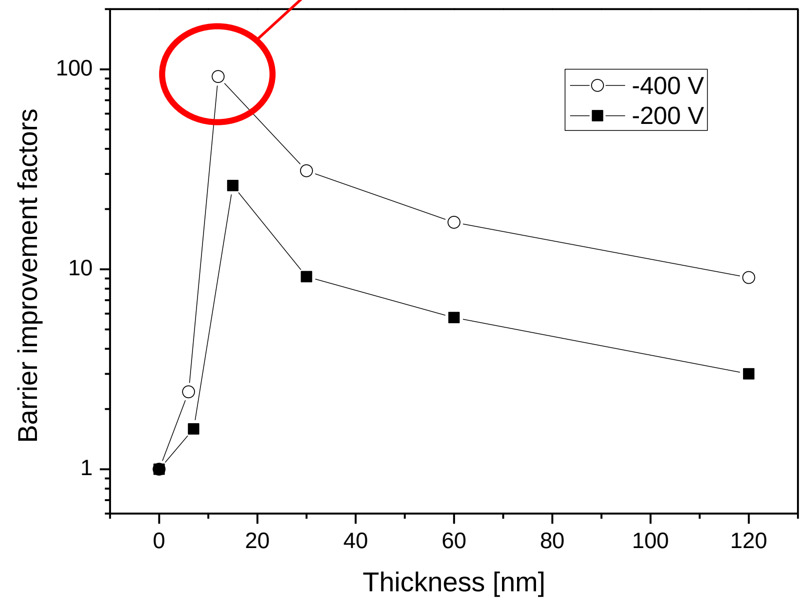
O. Kylian et al. J. Phys. D. Appl. Phys. 2009, 42, 142001
A. Artemenko et. al. Surf. Coat. Tech. 2011, 205, S529

Thin films deposition - examples

Barrier a-C:H coatings



100x better barrier properties of PET !!

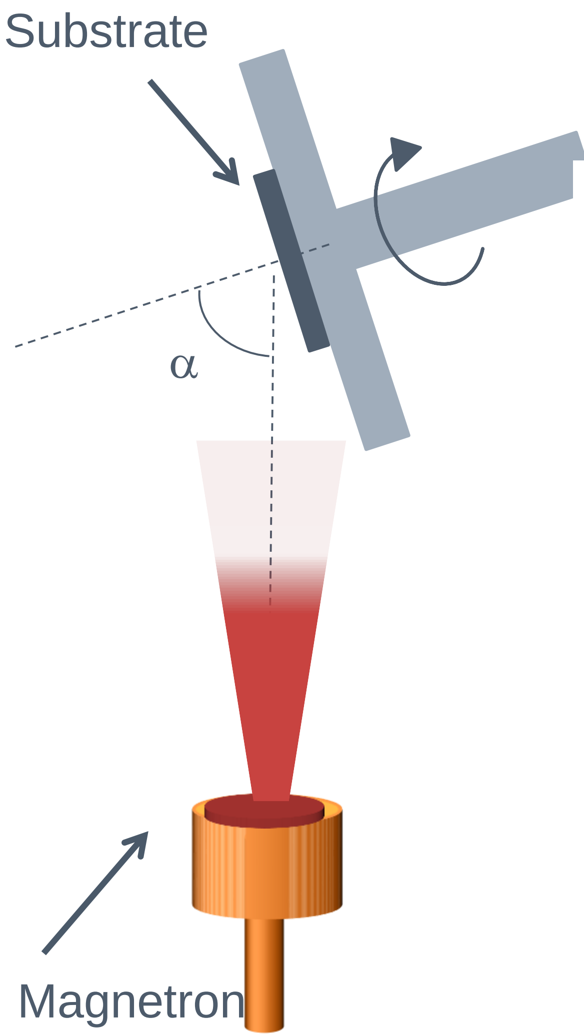


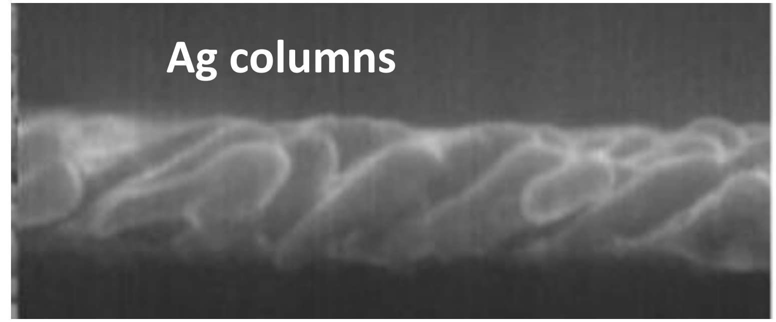
Thin a-C:H films may significantly improve barrier properties of polymeric foils.

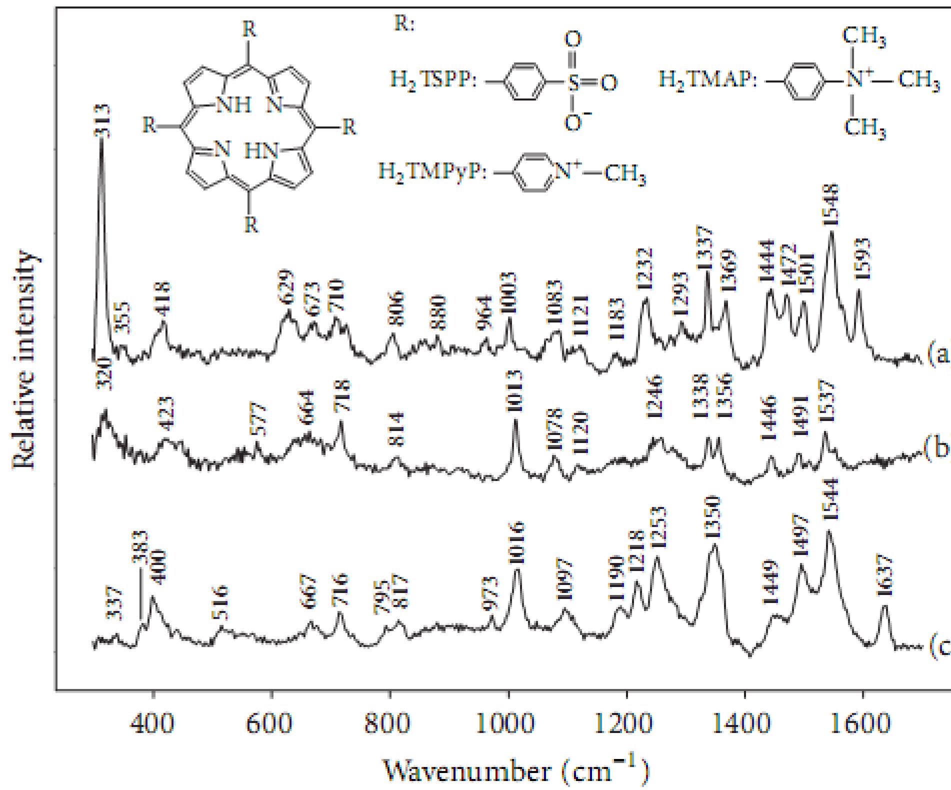
O. Polonskyi et al. Thin Solid Films 2013, 540, 65

III. Thin films deposition - examples

(Bio)sensing





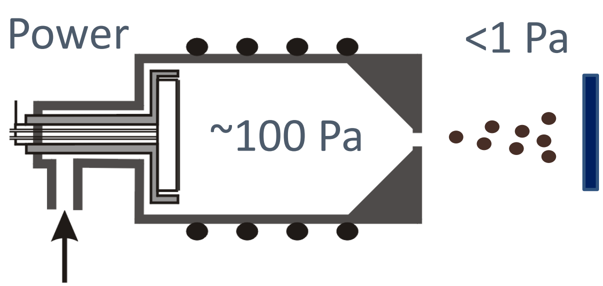


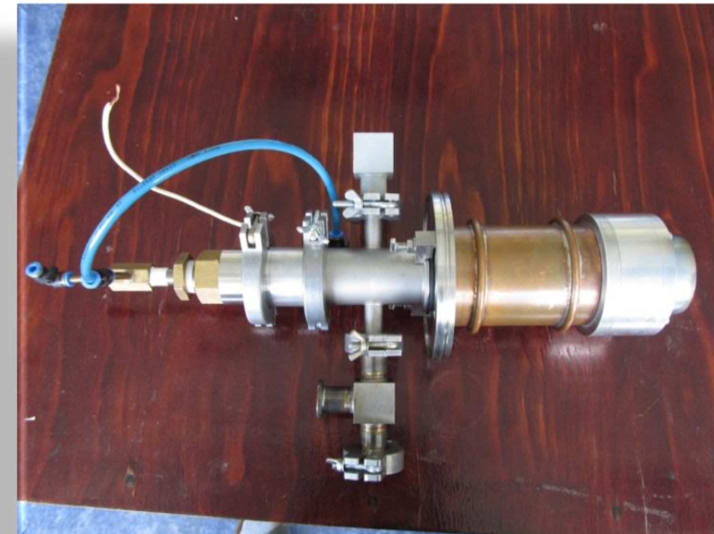
SERS spectra of three free-base porphyrins

Concentrations $<10^{-6}$

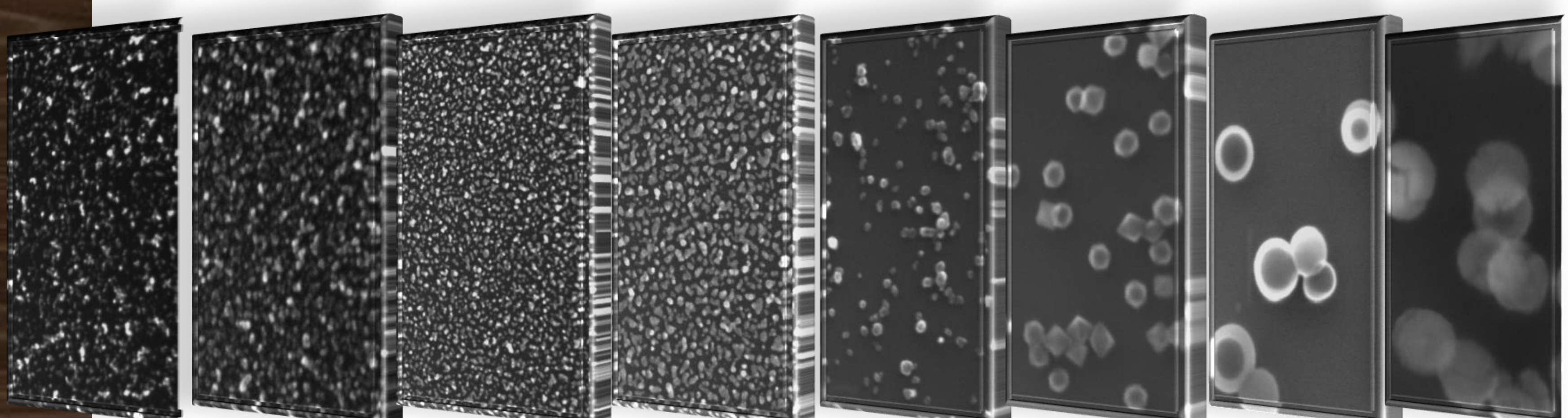
M. Subr et al. J. Nanomat. in press.

IV. Fabrication of nanoparticles





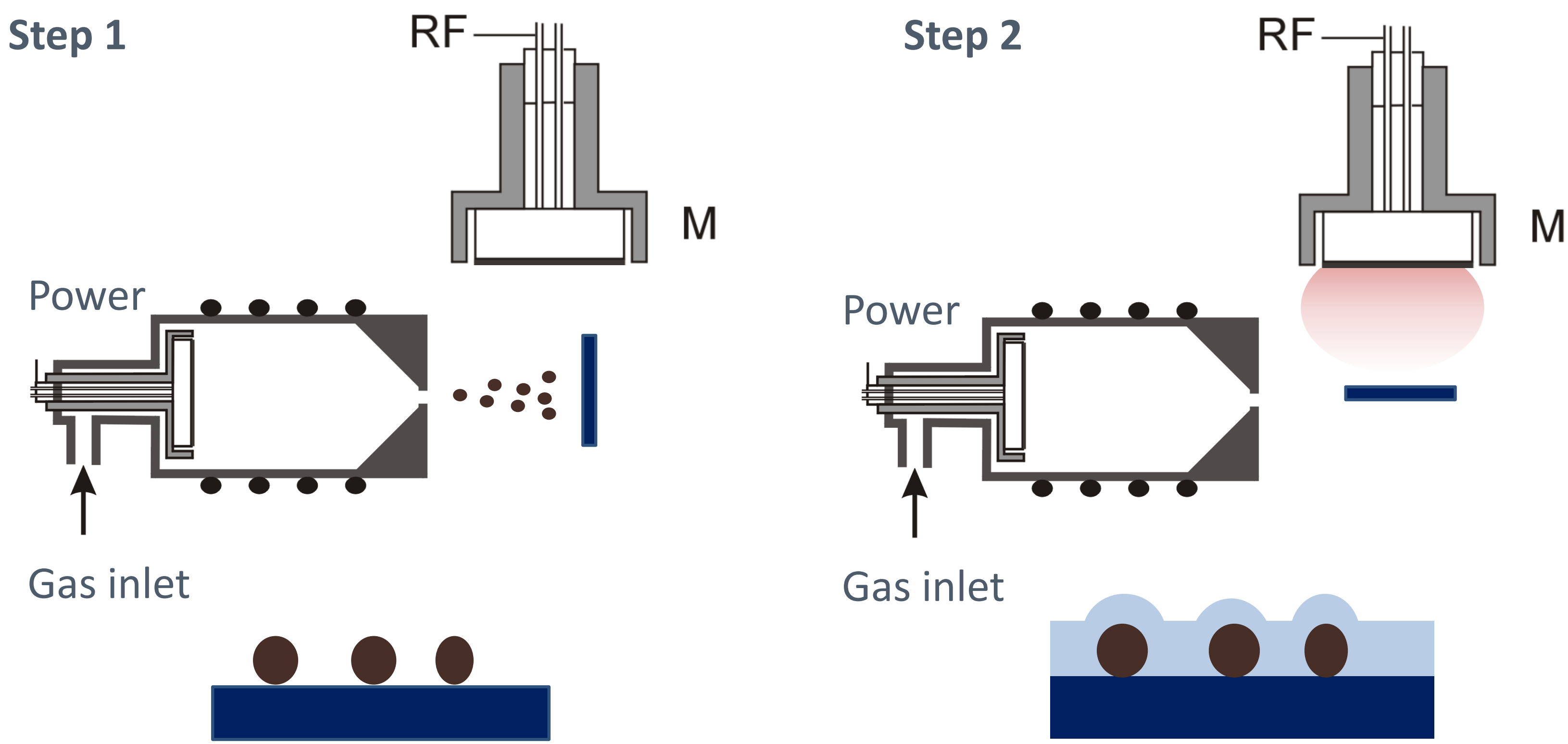
Solar et al. Surface Coat. Technol. 2011, 205, S42
Drabik et al., Plasma Proces Polym, 2011, 7, 544
Kylian et al., Material Letters 2012, 79, 229
Polonskyi et al., J. Phys D. Appl. Phys. 2012, 45, 495301
Kylian et al. Thin Solid Films 2014, 550, 46
Solar et al. Vacuum 2015, 111, 124
.....



Pt Cu Ag Au Ti Al C:H C:H:N

V. Nanostructured coatings prepared by means of gas aggregation sources

Overcoating nanoparticles by plasma polymer

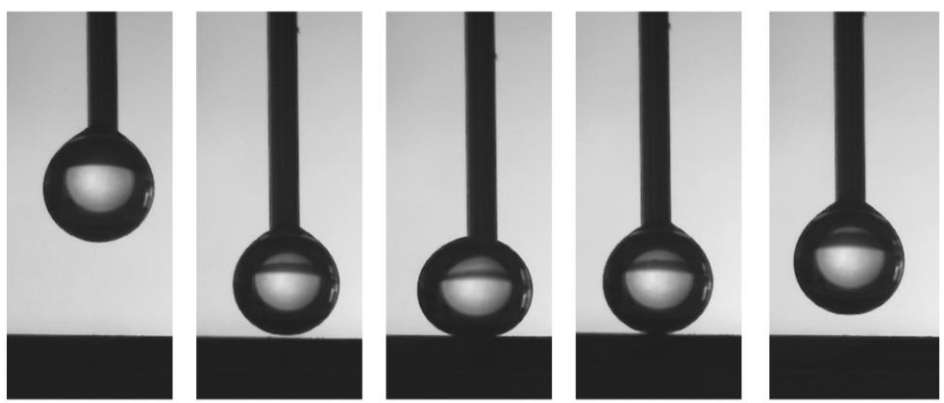


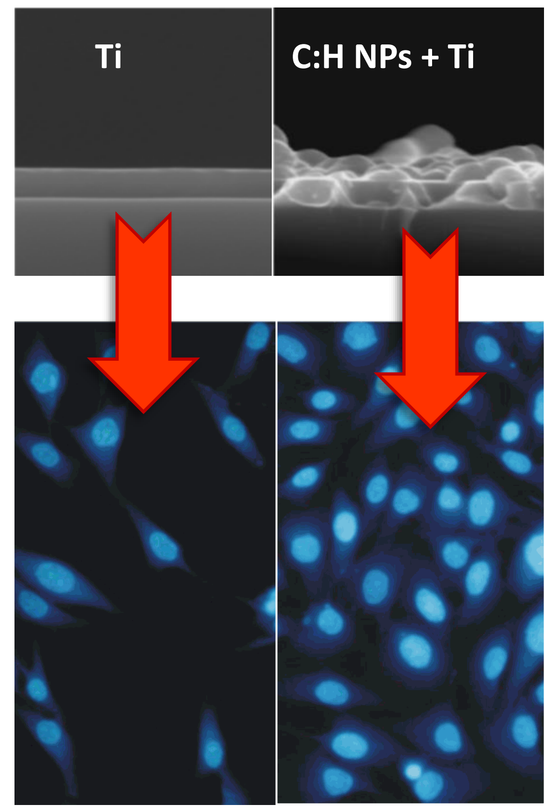
As a source of the overcoat material may be used PECVD or magnetron sputtering.

V. Nanostructured coatings prepared by means of gas aggregation sources

It is possible to control independently surface roughness and surface chemical composition.

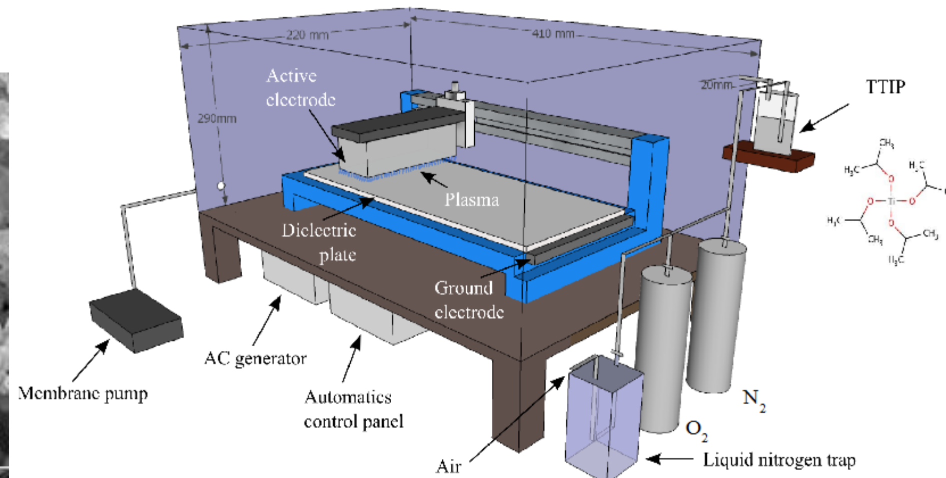
We can prepare nanorough surfaces e.g. for faster osseo-integration or water repellent character

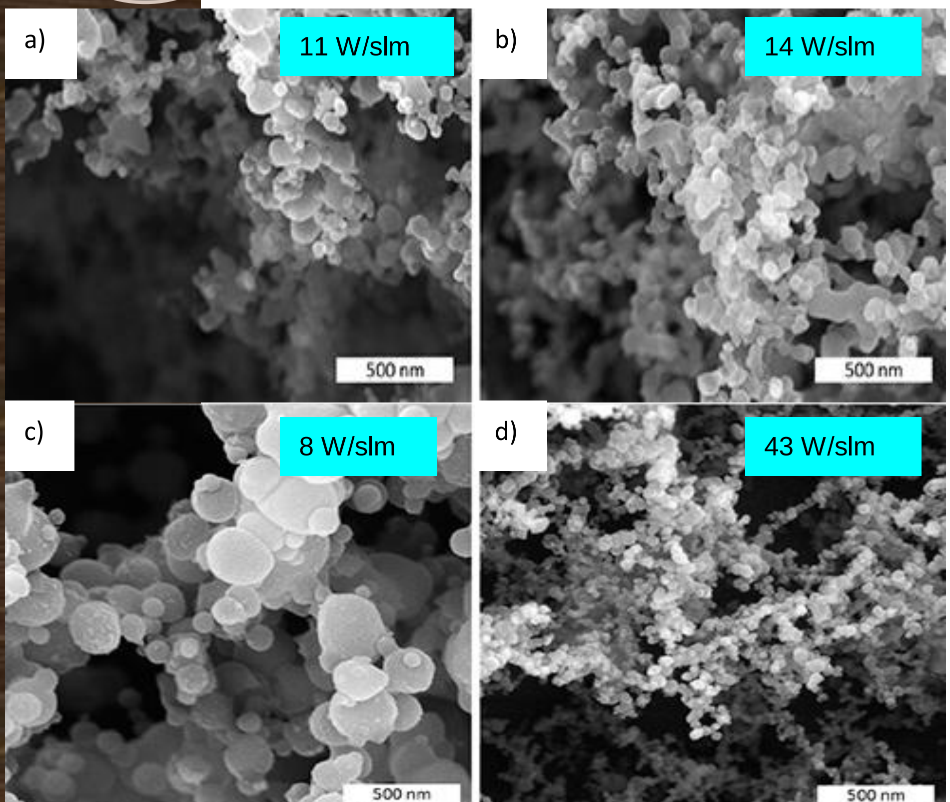




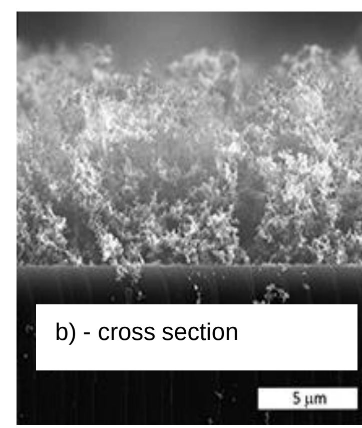
Atmospheric pressure processes: deposition

- dielectric barrier discharge (typical):
  - 20 W, 23 kHz, 15 kVPP, substrate(glass) -electrode gap 1.5 mm
  - monomer: titanium tetraisopropoxide (TTIP), 0.5 mass% in gas (N_2, air)
  - gas flow: 0.7-2.5 slm





SEM images of the films deposited in N_2 at various Yasuda parameter -
a) 11 W/slm (8W, 0.7slm)
b) 14 W/slm (20W, 1.4slm)
c) 8 W/slm (20W, 2.5slm)
d) 43 W/slm (30W, 0.7slm)



- A. Shelemin, A. Choukourov, J. Kousal, D. Slavinska, H. Biederman: Nitrogen-Doped TiO2 Nanoparticles and Their Composites with Plasma Polymer as Deposited by Atmospheric Pressure DBD, PLASMA PROCESSES AND POLYMERS 11, 9 (2014) 864-877

Conclusions

Plasma is versatile tool for surface modification and for deposition of thin functional coatings.

By means of plasma it is possible to tailor surface properties of solid objects.

Possible applications include:

- Biomedical applications
- (Bio)sensors
- Barrier coatings
- Surfaces with controllable wettability
- etc.

Thank you for your attention.