Plasma and Dry Micro/Nanotechnologies
10. Plasma Enhanced Chemical Vapor Deposition

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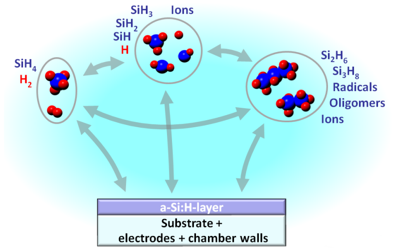
Outline

10.1 Introduction to PECVD

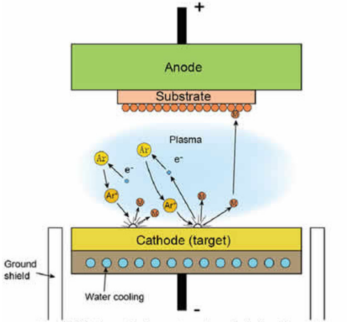
plasma enhanced chemical vapor deposition (PECVD)

- from gases and vapors
- very easy for organic materials and Si compounds (SiH_4, variety of volatile organosilicon compounds)
- for metals - necessary to find sufficiently volatile compounds (organometallic)



physical vapor deposition (PVD), namely magnetron sputtering

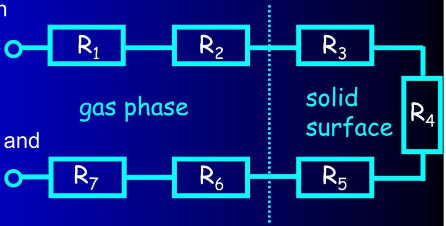
- gasification of solid targets by ion sputtering ⇒ deposition
- simple method for metals
- a bit more complex for oxides, nitrides, carbides (reactive sputtering)



CVD Diagram

thermally driven chemical deposition from gas phase:

1. transport of reactants to the deposition space
2. diffusion of reactants to the substrate surface
3. adsorption of reactants
4. phys.-chem. processes ☞ film growth and by-products
5. desorption of by-products
6. diffusion of by-products in gas flow
7. transport of by-products from deposition space



Low Pressure CVD (LPCVD) is often used in microelectronics or in applications requiring excellent control over impurities

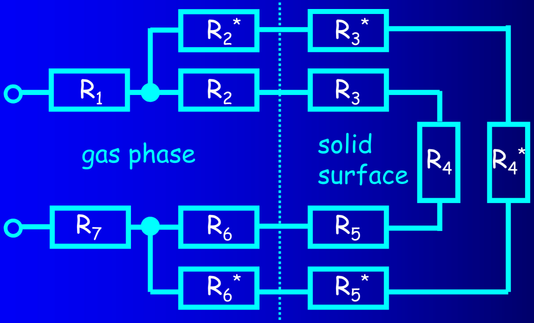
PECVD Diagram

CVD method in which discharge is ignited in the gas mixture:

☞ collisions of energetic electrons with heavy gas particles

☞ production of highy reactive species

☞ more competing processes take place, deposition can be generally divided into thermal and plasma branches



CVD versus PECVD - example

PECVD x CVD

reaction branch:

thermal $A \rightarrow B$

$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$$

700-900°C

plasma $A + e^- \rightarrow A^* + e^-$

$A^* \rightarrow B'$

$$SiH_4 + NH_3 \rightarrow SiNH + 3H_2,$$

250-350°C

plasma reaction branch at PECVD is much more important because:

☞ sticking coefficient is much higher for reactive radicals and activated surface

☞ activation energies of chemical reactions are lower for excited reactants

PECVD – lower deposition temperature, novel reaction schemes leading to new materials, replacement of toxic and dangerous reactants

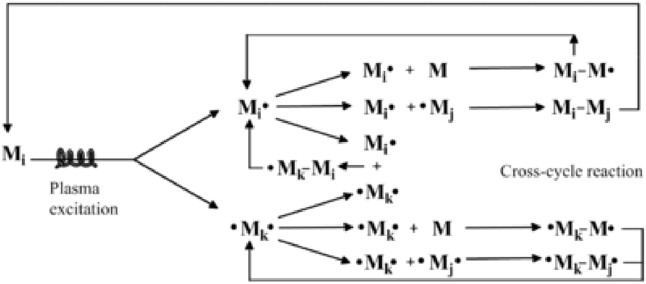
but

high complexity of chemical reactions and processes, worse selectivity and reaction control, possibility of damages by energetic ions, UV radiation or electrostaticaly (charge accumulation)

Plasma Polymerization - subset of PECVD

Plasma polymerization is a subset of plasma enhanced CVD
It produces organic thin films with specific functional groups originating from the monomer structure.
Plasma polymers **do not have the typical structure of polymers** (impossible to find a repeated unit, structure is highly branched and cross-linked).

Yasuda scheme:

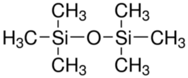


1st pathway (M•) - similar to a standard free radical polymerization mechanism,
2nd pathway (•M•) - difunctional mechanism, "polymer" can grow in multiple directions by multiple pathways off one species ⇒ a very rapid step-growth polymerization:

Different Types of Plasma Polymers

Organosilicon plasma polymers

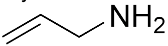
hexamethyldisiloxane



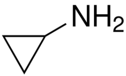
- barrier and protective coatings
- hydrophilic/hydrophobic surface
- cross-linking improvement (stabilization of organic functionalities by co-polymerization)

Amine films

allylamine



cyclopropylamine



diaminocyclohexane
ethylenediamine

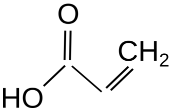
- interfacial adhesion,
- grafting of molecules with specific functionalities (reverse adhesion),
- improvement of cell colonization (tissue engineering),
- immobilization of biomolecules (biosensors, drug delivery systems).

deposition from gas mixtures:

- NH_3/CH_4
- NH_3/C_2H_4

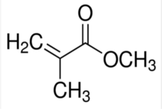
Carboxyl/ester/anhydride films

acrylic acid

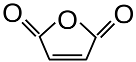


- H_2O / CO_2
- C_2H_4 / CO_2

methyl methacrylate



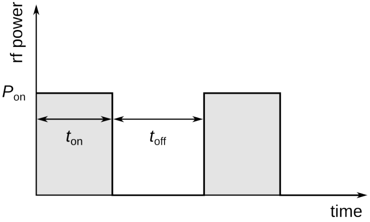
maleic anhydride



Plasma Polymerization in Pulsed RF Discharges

Quest for retaining monomer structure in plasma polymers - too much energy in plasmas!

- decreasing power (some limits apply)
- excluding ion energy flux (higher pressures, atmospheric pressure namely)
- **pulsed CCP discharges**



pulse repetition frequency

$$f_{puls} = 1/(t_{on} + t_{off})$$

duty cycle (DC) $$DC = \frac{t_{on}}{t_{on}+t_{off}} \times 100\%$$

Simplification (1 parameter instead of 2):
mean RF power $$P_{aver} = P_{on} \times DC$$

$\Rightarrow$ Macroscopic approach uses P_{aver}

$$W/F = \frac{P_{aver}}{Q} \quad [\mathrm{J/cm^3}]$$

10.2 PECVD of materials with Si

- dielectric films for microelectronics

silicon nitride: SiH_4+NH_3 or SiH_4+N_2
(final protective passivation for integrated circuit)
T=250-400 °C

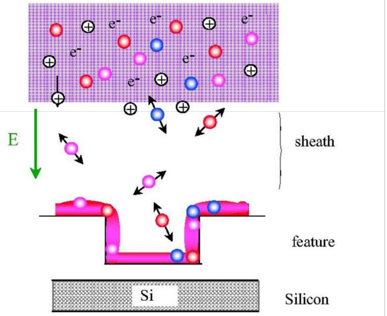
silicon oxide:
(insulating film – el. separation)

SiH_4+N_2O/NO/CO_2/O_2

T=200-400 °C

$Si(OC_2H_5)_4$ + O_2
↘
tetraetoxysilane (TEOS)

$$Si(OC_2H_5)_4 + e^- \rightarrow Si(OC_2H_5)_3(OH) + C_2H_4 + e^-$$
$$O_2 + e^- \rightarrow 2O + e^-$$
$$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$$



PECVD of materials with Si

- more dielectric films for microelectronics

  low-k dielektrics: organosilicons + O_2/… + …
  (el. separation for ULSI)

  → organosilicon glass (OSG)

- semiconducting films for microelectronics

  epitaxial silicon: SiH_4+H_2 T=800 °C

  polycrystalline silicon: SiH_4/SiH_2Cl_2+H_2/Ar T=450-700 °C
  (gate electrode, connections in MOS i.c., solar energy pannels)

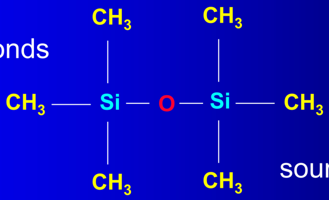
- SiO_x and $SiO_xC_yH_z$ for many other applications

  scratch resistant films for plastics, anticorrosion films for metals,
  barrier films for packaging and pharmacy,
  biocompatible films

  mixtures with organosilicons (TEOS, HMDSO, HMDSZ)

PECVD of films from HMDSO (hexamethyldisiloxane)

source of Si-O-Si bonds



SiO_2-like films

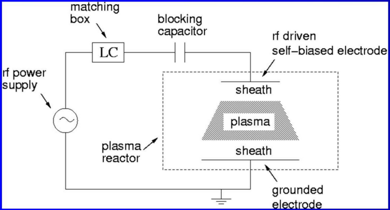
source of CH_3 groups

$SiO_xC_yH_z$ plasma polymers

- concentration of HMDSO in the gas feed, especially oxygen
- power
- bias voltage / ion energy
- pressure
- pulsing

PECVD of films from HMDSO/O_2 in CCP or ICP (13.56 MHz)

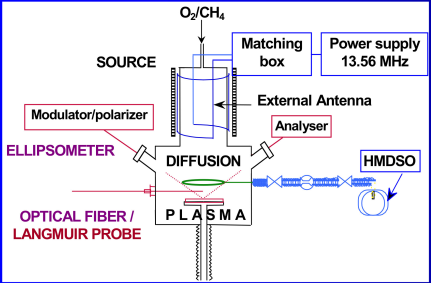
PECVD from HMDSO/O_2 in CCP and ICP (13.56 MHz)



5-100 % HMDSO in O_2

CCP:

- Q_{hmdso} = 4 sccm, Q_{o2} = 0 – 80 sccm
- pressure 1 - 40 Pa
- rf power 100 - 450 W
- dc self-bias from –20 and –335 V



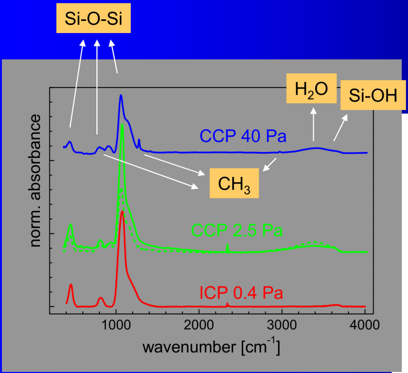
helical antenna in ICP mode:

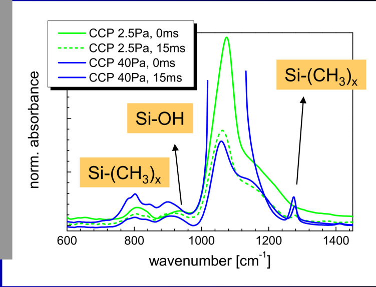
- pressure 0.4 Pa
- rf power 300 W
- substrate at ground

PECVD of films from HMDSO/O_2 in CCP or ICP (13.56 MHz)

Variation of film composition

5 % HMDSO in O_2



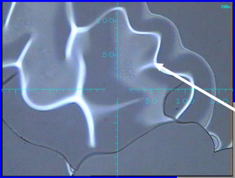


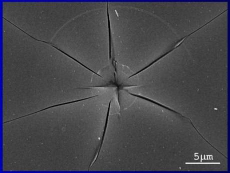
- ⇨ *0.4 Pa: SiO_2 structure, almost no impurities*
- ⇨ *2.5 Pa: SiO_2 structure, OH groups and H_2O*
- ⇨ *40 Pa: organosilicon films*

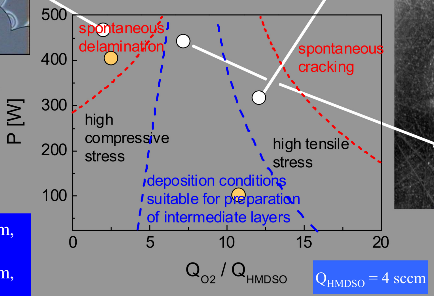
PECVD of films from HMDSO/O_2 in CCP or ICP (13.56 MHz)

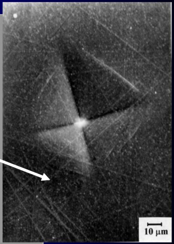
Domains of stresses

without treatment





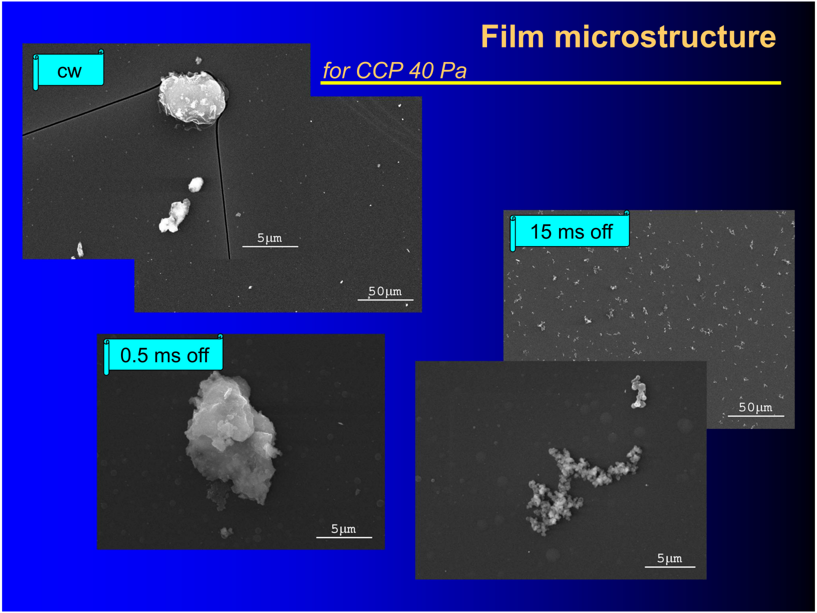




two different coatings choosen for treatment testing:

- P = 100 W, Q_{O2} = 45 sccm, d = 0.5 µm
- P = 400 W, Q_{O2} = 10 sccm, d = 1.2 µm

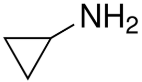
PECVD of films from HMDSO/O_2 in CCP or ICP (13.56 MHz)



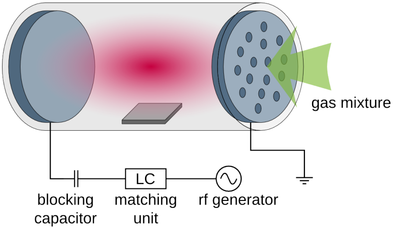
10.3 PECVD of Hard Carbon Films

10.4 Amine Plasma Polymers

- in RF (13.56 MHz) capacitively coupled discharges
- continuous wave and pulsed modes
  - $t_{\mathrm{on}} = 660\,\mu$s, $t_{\mathrm{off}} = 1340\,\mu$s $\Rightarrow$
  - $f_{\mathrm{puls}} = 500$ Hz, $DC = 33\,\%$
- in CPA/Ar mixtures

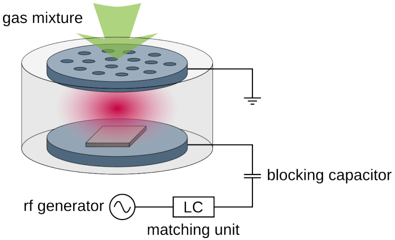


reactor R3, substrate at floating potential



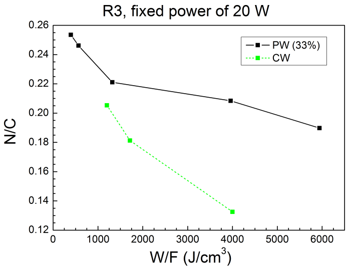
- Ar 28 sccm, CPA 0.1–1.0 sccm
- pressure 120 Pa
- RF power 20–30 W
- electrode diameter 80 mm
- interelectrode distance 185 mm

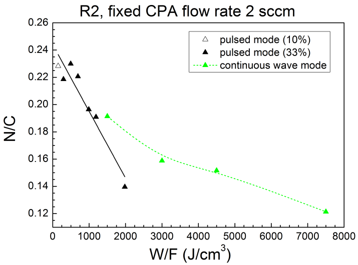
reactor R2, substrate at RF electrode

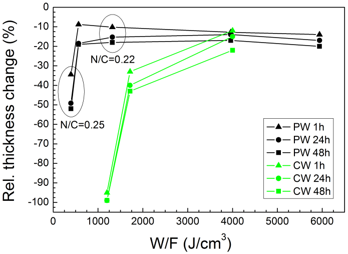


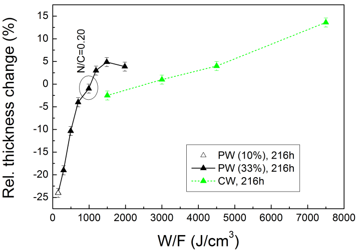
- $Q(\mathrm{Ar}) = 28$ sccm, $Q(\mathrm{CPA}) = 2.0$ sccm
- pressure 50 Pa
- RF power 30–250 W
- electrode diameter 420 mm
- interelectrode distance 55 mm

Comparison of Floating (R3) × RF Biased (R2) Substrate





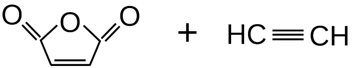




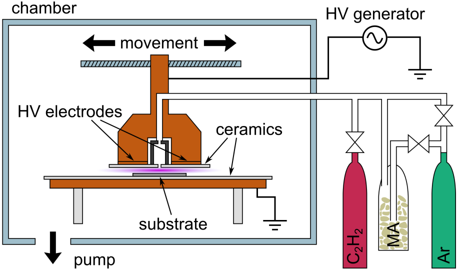
A. Manakhov et al. Plasma Process. & Polym. 11 (2014) 532 & 14 (2017) 1600123

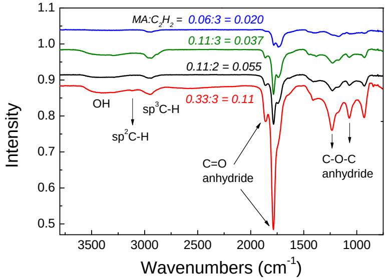
10.5 Anhydride/Carboxyl PPs

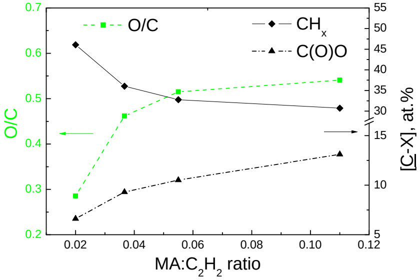
Co-polymerization of maleic anhydride (MA) with C_2H_2 in Ar dielectric barrier discharge (DBD) at atmospheric pressure



L. Zajíčková et al. Plasma Phys. Control. Fusion 59 (2017) 034003
A. Obrusník et al. Surf. Coat. Technol. 314 (2017) 139

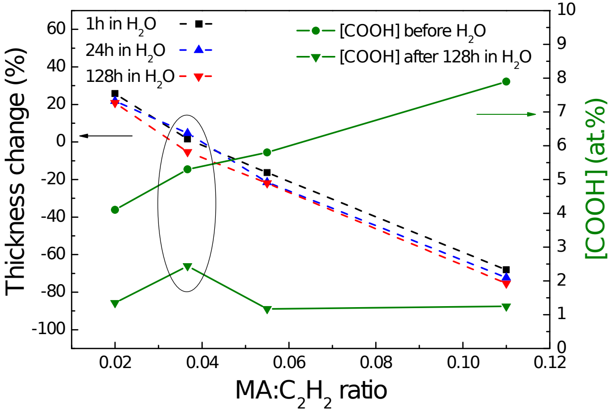






[COOH] by Chemical Derivatization and Water Stability

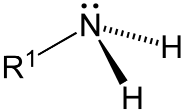
Increasing MA ⇒ ↑ C1s peak at 289.1 eV, i.e. carboxyls (COOH) / esters (COOR).
⇒ **important to quantify „true“ concentration of COOH** - derivatization with trifluoroethanol

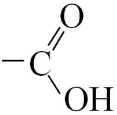


A. Manakhov et al. Surf. Coat. Technol. 295 (2016) 37-45

10.6 Plasma Polymers in Immunosensing

Reactivity of primary amine and carboxyl groups

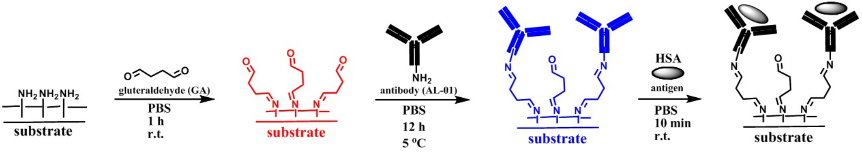




is important for

- **immobilization of biomolecules for immunosensing**

Human serum albumin (HSA) chosen for the demonstration of immunosensing application:

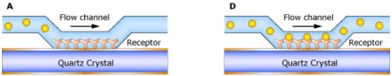


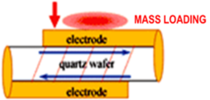
gold electrode coated with CPA-PP, covalent attachment of antibody AL-01 by 3 coupling methods, the most robust being glutaraldehyde (GA)

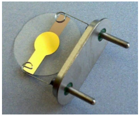
Immunosensing - Two Principles, Same Material Needs

Different principles/transducers but same material is needed
- gold electrode coated with a functional film

Quartz crystal microbalance





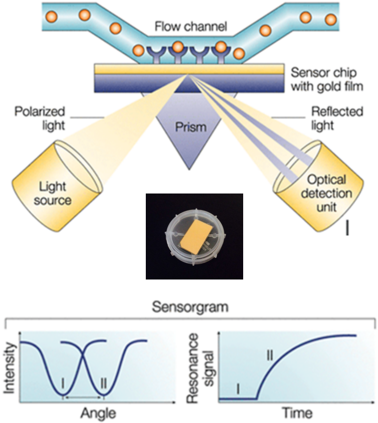


Sauerbrey equation for
change of oscillator frequency

$$\Delta f = 2.26 \times 10^{-6} f^2 \Delta m / A$$

f resonant frequency, A electrode area,
Δm mass change

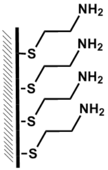
Surface plasmon resonance



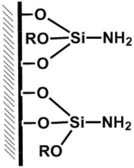
**change of resonance angle /
reflectance at given angle**

Chemically Prepared Amine Films versus Plasma Polymers

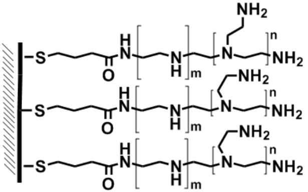
SAM of cysteamine



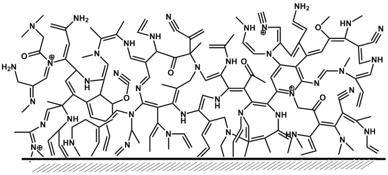
(3-Aminopropyl)triethoxysilane (APTES)



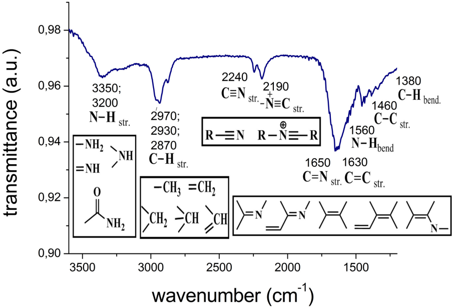
Polyethyleneimine (PEI)



Plasma polymerization - alternative to the conventional methods



Example of plasma polymerized cyclopropylamine optimized for sensing performace

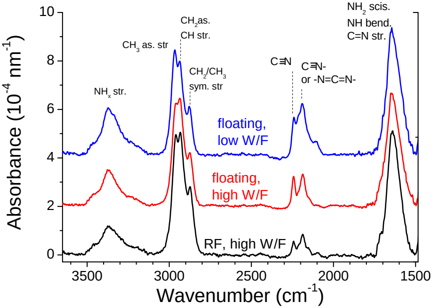


Selected Films for Immunosensors

CPA/Ar mixtures, $Q_{\mathrm{Ar}} = 28\,\mathrm{sccm}$
pulsed RF discharges: $t_{\mathrm{on}} = 660\,\mathrm{ms}$, $t_{\mathrm{off}} = 1340\,\mathrm{ms} \Rightarrow f_{\mathrm{puls}} = 500\,\mathrm{Hz}$, $DC = 33\,\%$

conditions	C [at%]	N [at%]	O [at%]	C-NH$_x$ [at%]	NH$_x$ [at%]	NH$_3^+$ [at%]	[NH$_2$] [at.%]	$\Delta d/d$ [%]
floating, ↓ W/F	78.3	20.1	1.6	18.9	5.1	2.6	**3.4**	-53
floating, ↑ W/F	79.5	19.0	1.5	22.8	6.4	0	**1.5**	-18
RF biased, ↑ W/F	80.3	17.2	2.5	16.2	4.6	0	**1.3**	-2

⇒ difference in atomic composition relatively small but water stability quite different



- IR spectra reflect different film structure
- SIMS analyses reveal different degree of film cross-linking
- confirmed by different stability in water

Solving the Baseline Drift for CPA PPs

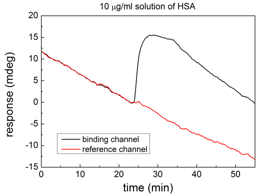
QCM immunosensing with CPA PPs:

1. 5% glutaraldehyde in PBS, 1 h at room temperature
2. 100 μg/ml AL-01 in PBS, **18 hours** at 4 ℃

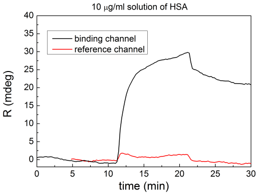
$\Rightarrow$ baseline stable for both the CPA PPs (↑ W/F, floating & RF)

SPR immunotests with optimized PP-CPA (↑ W/F, floating) sensor:
immersed in PBS prior to activation by GA and immobilization of antibody:

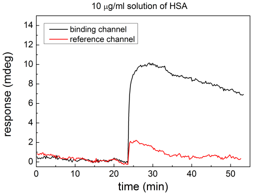
1 hour in PBS



18 hours in PBS



18 h in antibody/PBS solution



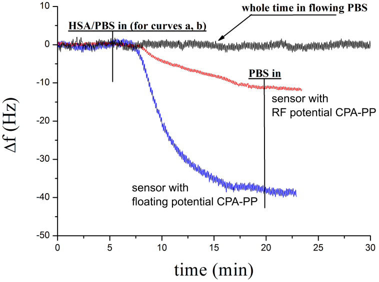
- longer immersion in PBS improved baseline stability while keeping sensor performace
- longer immersion in antibody/PBS also improves baseline stability but detection of antigen is not efficient

Sensitivity of CPA PPs

Is a perfect water stability of film thickness necessary for succesful immobilization of biomolecules and surpression of drifts?

sensor	reactor	W/F	$\Delta d/d$ [%]	[NH_2] [at.%]	NH_x [at.%]	C≡N [at.%]
a	**R3, floating**	**high**	18	1.5	6.4	11.8
b	**R2, RF driven**	**high**	2	1.3	4.6	8.2

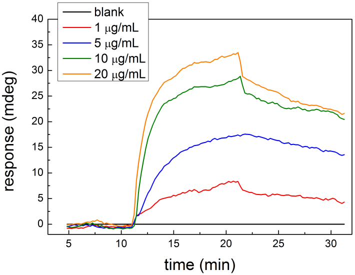
Response of QCM sensors with films (a) and (b) to HSA (film thickness 40 nm):



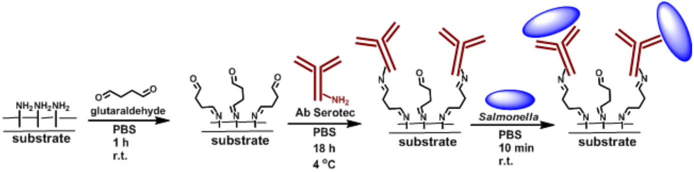
E. Makhneva et al. Surf Coat. Technol. 290 (2016) 116

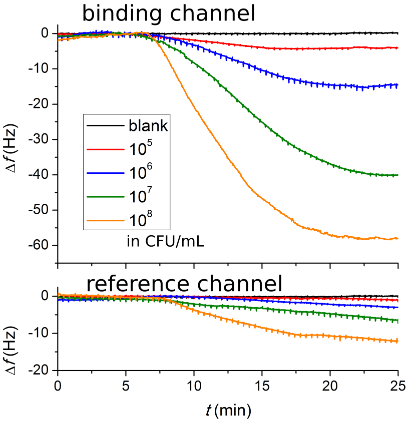
⇒ **Better response for the sensor (a)**

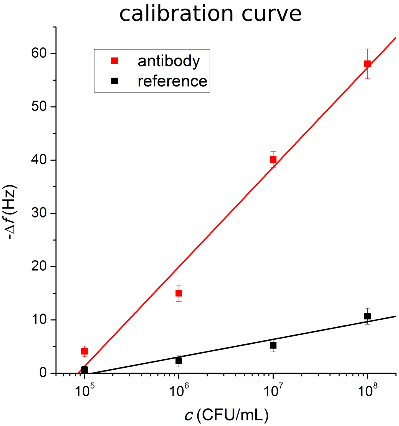
Response of SPR sensor with film (a) - thickness 40 nm



Real Immunosensing with PP-CPA - QCM Detection of Salmonella







10.7 Plasma Coating of Polymer Nanofibers

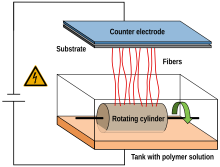
. . . combination leading to **novel nanomaterials**

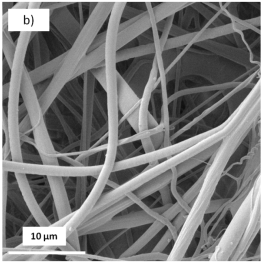
- electrospinning of polymer nanofibers
- + plasma processing

Plasma coating of polymer micro/nanofibers can bring additional functionality for

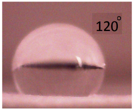
- smart textiles
- filtration of liquids/gases
- battery separators
- tissue engineering
- drug delivery

Nozzle-less electrospinning by Nanospider$^{\mathrm{TM}}$ from ELMARCO (Czech Rep.) and plasma processing of polymer nanofibers

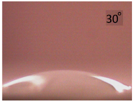




water contact angle before

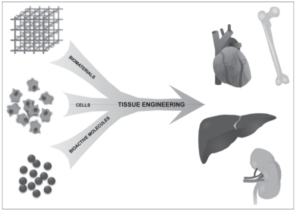


after

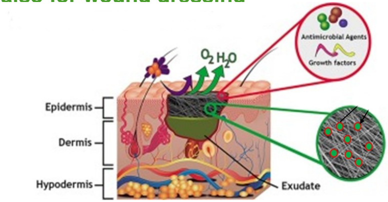


PP-Coated Nanofibers in Health Care

tissue eng. requires suitable scaffold



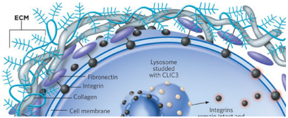
nanofibrous polymer mats are ideal also for wound dressing



[*S.P. Miguel et al., Colloids & Surf. B 2018*]

Electrospun polymer nano/microfibers

- can be prepared in the form of flexible foil
- from biodegradable polymers
- provide moist environment
- allow gas exchange
- avoid bacteria infiltration
- resembles the structure of extracellular matrix (ECM)

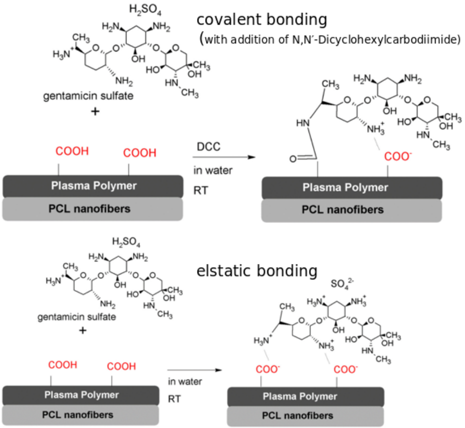


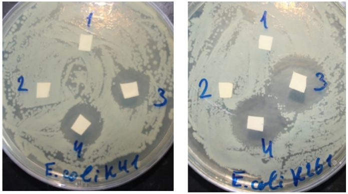
- **deliver bioactive molecules** - high surface area but a need of surface modifications creating reactive groups

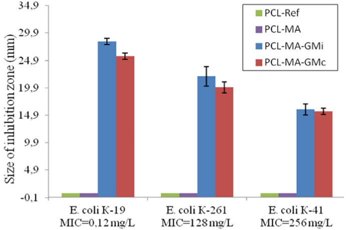
Bonding of Antibiotics onto COOH PPs-coated Nanofibers

Plasma co-polymerization of maleic anhydride and C_2H_2 in atmospheric pressure plasma
$\Rightarrow$ films with anhydrides (6.3 % rel. to total C) spontaneously creating -COOH at air.

Two different approaches for gentamicin bonding were tested:



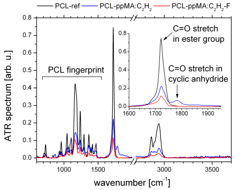


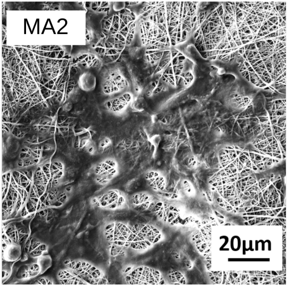


E. Permyakova et al. Antibacterial biocompatible PCL nanofibers modified by COOH-anhydride plasma polymers and gentamicin immobilization, Materials & Design 153 (2018) 60.

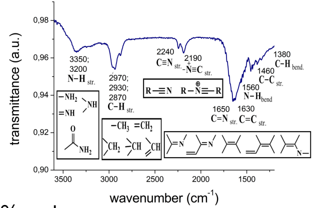
Cells on PCL Mats with PPs

anhydride/carboxyl PP

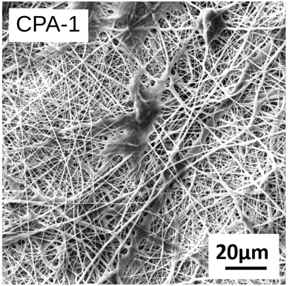




amine PP

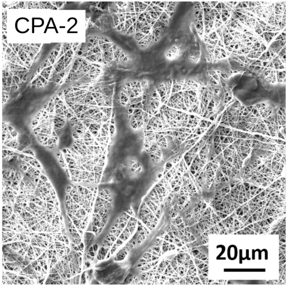


$P_{\rm av} = 10\,{\rm W}$ (18% water soluble, N/C=0.22)



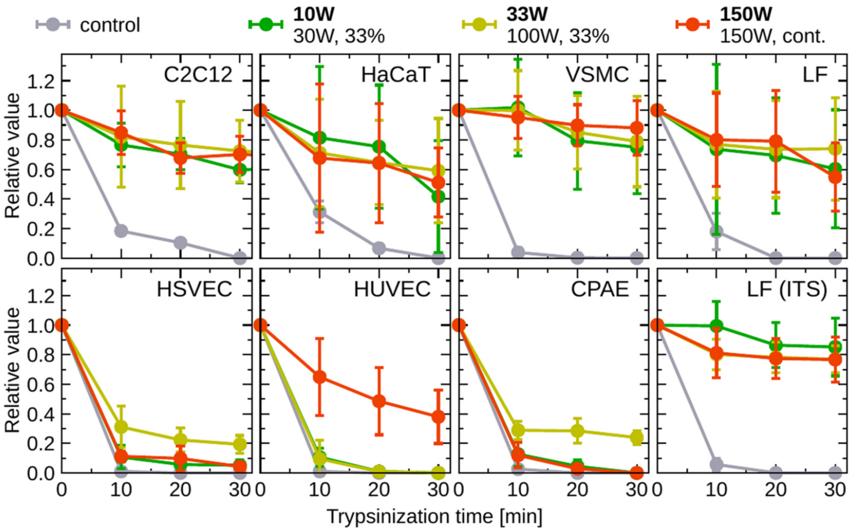
$P_{\rm av} = 150\,{\rm W}$

(5% water swelling, N/C=0.15)



A. Manakhov et al. Materials & Design 132 (2017) 257–265

Cell-Type Specific Adhesion to Amine PPs

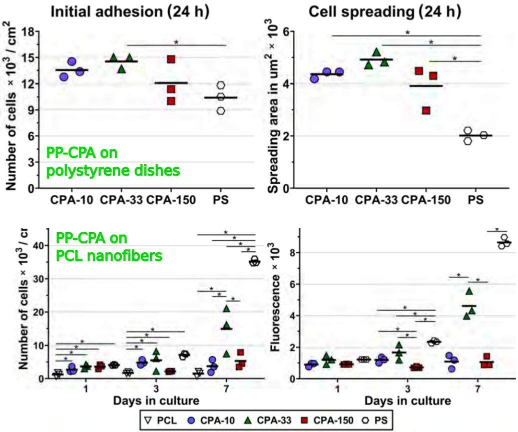


⇒ Adhered non-endothelial cells cannot be removed by trypsin

P. Černochová et al. Sci. Reports 10 (2020) 9357

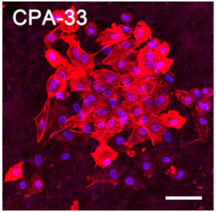
Optimization of Surfaces for Vascular Grafts

Vascular smooth muscle cells (VSMC) on polystyrene culture dishes (PS), polycaprolactone nanofibers (PCL) and amine-PP coated surfaces (CPA-10, 33, 150)



I. Nemcakova et al. Int. J. Mol. Sci. 2020

VSMCs can be utilized for reconstruction of the tunica media.



Morphology of VSMC cells on amine-PP coated PCL (optimized PP - CPA 33W)

PCL mats coated with CPA-33 PP: excellent support for VSMC cultivation (desirable moderate proliferation rate, continuous proliferation of VSMCs during 7-day-long cultivation, no signs of immunogenicity).