

F4280 Technologie depozice tenkých vrstev a povrchových úprav

7.5.4 Plasma Polymers

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Outline - Functional plasma polymers

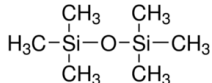
- Functional Coatings
- Why Amine Surfaces/Films?
- Low Pressure Amine Plasma Polymers
- Plasma Polymerization of Cyclopropylamine
- Carboxyl Plasma Polymers
- COOH Plasma Polymers at Atmospheric Pressure
- Co-polymerization of MA and C₂H₂

Functional Coatings

Many types of **functional coatings successfully prepared in atmospheric pressure DBD**, homogeneous mode is preferred

SiO_x and organosilicon films

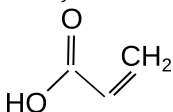
hexamethyldisiloxane



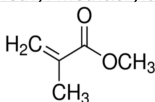
- ▶ barrier and protective coatings
- ▶ hydrophilic/hydrophobic surface
- ▶ cross-linking improvement (stabilization of organic functionalities by co-polymerization)

Carboxyl/ester/anhydride films

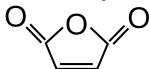
acrylic acid



methyl methacrylate



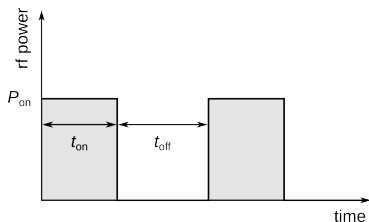
maleic anhydride



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

Plasma Polymerization in Pulsed RF Discharges

Retaining monomer structure for highly functional films \Rightarrow **pulsed discharges**



pulse repetition frequency

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

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

mean RF power $P_{\text{aver}} = P_{\text{on}} \times DC$

Macroscopic approach for simplified understanding of the process:

- ▶ Composite parameter W/F proportional to the **energy delivered per one molecule of monomer in gas phase**

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

Q - monomer flow rate

- ▶ Energy dissipated per deposition rate R due to ion bombardment

$$\varepsilon_{\text{surf}} = \frac{\Gamma_i E_{\text{mean}}}{R}$$

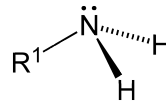
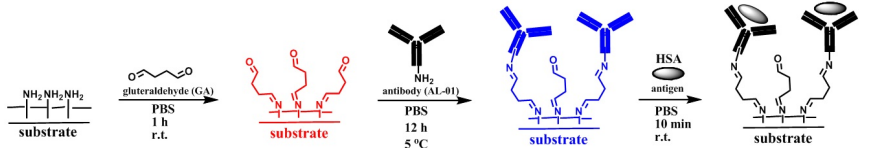
Γ_i ion flux, E_{mean} mean ion energy

D. Hegemann et al. Appl. Phys. Lett. 101 (2012) 211603

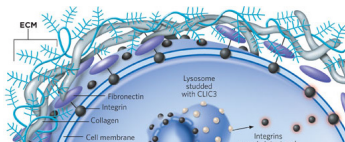
Why Amine Surfaces/Films?

Reactivity of primary amines is important for

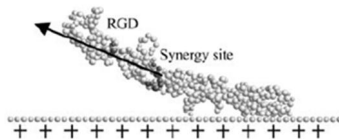
- ▶ adhesion enhancement
- ▶ immobilization of biomolecules (for enzyme electrodes, immunosensors etc.)



- ▶ cells interaction with surfaces (artificial tissue engineering)



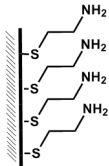
Cells interact with surfaces via extracellular matrix (ECM)



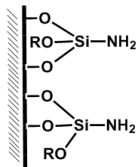
ECM contains proteins like fibronectin that bonds well to protonated surfaces such as NH_2 surfaces at neutral pH.

Various Amine Functional Films

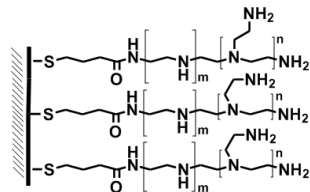
SAM of
cysteamine



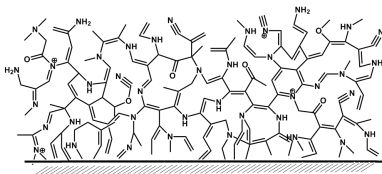
(3-Aminopropyl)triethoxysilane
(APTES)



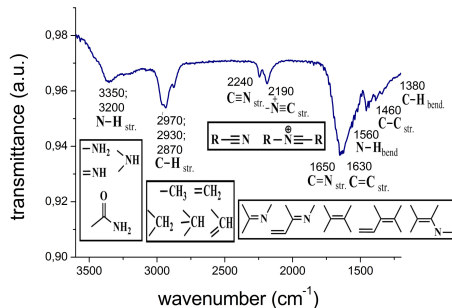
Polyethyleneimine (PEI)



Plasma polymerization - alternative to the conventional methods



Example of plasma polymerized
cyclopropylamine optimized for sensing
performance



Amine Films - Selection of Plasma Process

Surface plasma treatment, e. g. in N_2 or NH_3 discharges \Rightarrow **unstable functionalization of a thin near-surface layer with rather short duration**

Deposition from vapors of amine monomers:

- ▶ allylamine
- ▶ diaminocyclohexane
- ▶ ethylenediamine
- ▶ **cyclopropylamine** (CPA)
- ▶ etc.

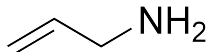
usually in pulsed RF discharges, substrate floating or grounded

Deposition from gas mixtures:

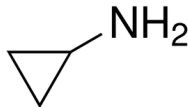
- ▶ NH_3/CH_4
- ▶ NH_3/C_2H_4

usually in continuous wave RF discharges, substrate at RF electrode

Allylamine - commonly used due to presence of vinyl group (free radical polymerization) **but highly toxic flammable chemical compound**



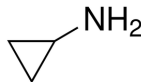
Cyclopropylamine - promising monomer for amine-rich coatings, **non-toxic, vapor pressure of 32 kPa at 25 °C.**



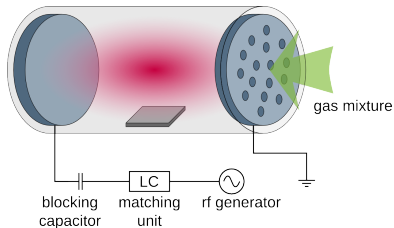
CPA Plasma Polymerization at Low Pressure

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

- ▶ in CPA/Ar mixtures

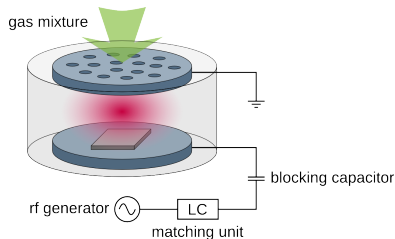


reactor R3, substrate at floating potential



- ▶ 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

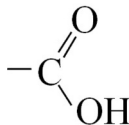


- ▶ $Q(\text{Ar}) = 28 \text{ sccm}$, $Q(\text{CPA}) = 2.0 \text{ sccm}$
- ▶ pressure 50 Pa
- ▶ RF power 30–250 W
- ▶ electrode diameter 420 mm
- ▶ interelectrode distance 55 mm

Carboxyl-rich coatings

Carboxyl-rich coatings are of high interests due to their wide application potential:

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

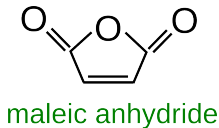
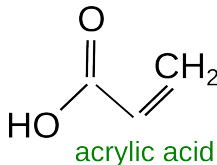


Plasma processing of carboxyl surfaces by PECVD from simple molecules

- ▶ H₂O / CO₂ [1]
- ▶ C₂H₄ / CO₂ [2]

by plasma (co-)polymerization of COOH-based monomers

- ▶ acrylic acid (AA) [2,3,4]
- ▶ maleic anhydride (MA) [5,6]



[1] N. Medard, J.-C. Soutif, F. Poncin-Epaillard, *Langmuir*, 2002, 18, 2246

[2] D. Hegemann, E. Koerner, S. Guimond *Plasma Process. Polym.* 2009, 6, 246

[3] L. Detomasso, R. Gristina, G. Senesi, R. d'Agostino, P. Favia, *Biomaterials* 2005, 26, 3831

[4] A. Fahmy, R. Mix, A. Schonhals, J. Friedrich *Plasma Process. Polym.* 2011, 8, 147

[5] A. Manakhov, M. Moreno-Couranjou, N. D. Boscher et al., *Plasma Process. Polym.* 9 (2012) 435

[6] M. M. Brioude, M.-P. Laborie, A. Airoudj et al., *Plasma Process. Polym.* (2015)

COOH-Films Deposited at Atmospheric Pressure

DBD plasma polymerization of acrylic acid in He

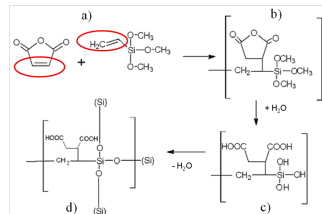
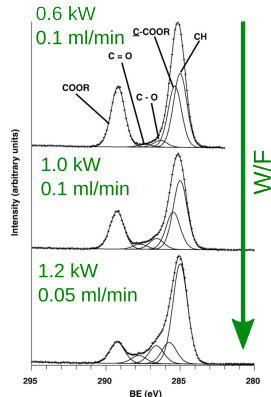
A.J. Beck, R.D. Short, A. Matthews, *Surf Coat Technol* 203 (2008) 822–825:

- ▶ percentage of functional groups by fitting XPS C1s signal (~ 289.3 eV binding energy for $\underline{C}(O)=O$, i.e. carboxyl and ester groups)
- ▶ films with high retention of the monomer structure for low energetic conditions (low W/F) \Rightarrow up to 29.7 % of COOR
- ▶ **Bioapplications** require sufficient **stability in aqueous media** but cross-linking improves the layer stability at expenses of the functional group concentration.
- ▶ **Plasma co-polymerization** offers an additional possibility to tune the film stability and carboxyl functionalization efficiency

Thomas et al. *Plasma Process. Polym.* 4 (2007) S475

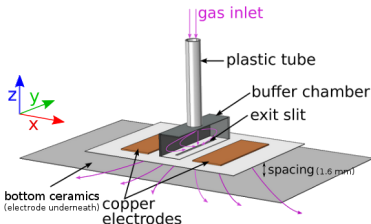
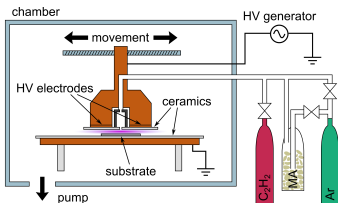
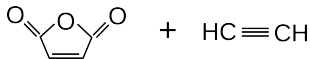
Manakhov et al. *PPP* 9 (2012) 435

- copolymerization of maleic anhydride (MA) and vinyltrimethoxysilane (VTMOS) in DBD



Co-polymerization of MA and C_2H_2

- ▶ **dielectric barrier discharge** at **6.6 kHz, 12 W**
- ▶ distance between dielectrics 1.6 mm
- ▶ top electrode made of two parts, each 55×20 mm, spaced by 20 mm
- ▶ rectangular bottom electrode 150×60 mm
- ▶ central gas inlet, 9 mm in diameter
- ▶ buffer chamber distributing gas flow into a slit, 2 mm wide and 48 mm long



MA : C_2H_2 flow rate ratio varied by changing flow rate of C_2H_2 and Ar through MA.

- ▶ Ar flow rate through MA bubbler $Q_{Ar-MA} = 0.25-1.5$ slm $\Rightarrow Q_{MA} = 0.06-0.33$ sccm
- ▶ C_2H_2 flow rate $Q_{C_2H_2} = 2-3$ sccm
- ▶ total Ar flow rate $Q_{Ar-MA} + Q_{Ar} = 1.5$ slm