

F4280 Technology of Thin Film Deposition & Surface Treatments

10. PECVD

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MUNI

Outline

- 10. PECVD

 - 10.4 Plasma Polymerization

 - Understanding the Plasma Polymerization

 - Plasma Polymerization in Pulsed RF Discharges

 - Amine Plasma Polymers

 - Carboxyl Plasma Polymers

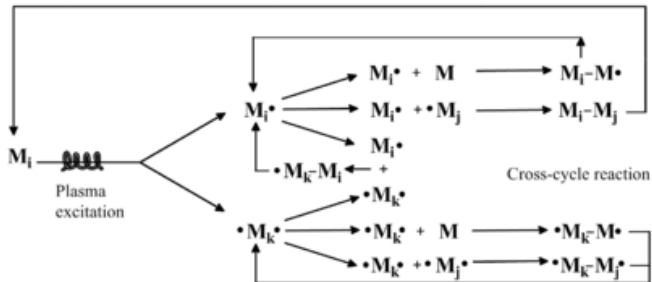
10.4 Plasma Polymerization

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:

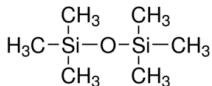


1st pathway (M^\bullet) - similar to a standard free radical polymerization mechanism,
 2nd pathway ($\bullet M^\bullet$) - difunctional mechanism, “polymer” can grow in multiple directions by multiple pathways off one species \Rightarrow a very rapid step-growth polymerization:

Different Types of Plasma Polymers

Organosilicon plasma polymers

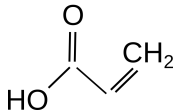
hexamethyldisiloxane



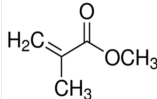
- ▶ barrier and protective coatings
- ▶ hydrophilic/hydrophobic surface
- ▶ cross-linking improvement (stabilization of organic functionalities by co-polymerization)

Carboxyl/ester/anhydride films

acrylic acid

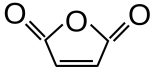


methyl methacrylate

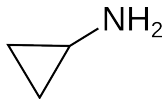
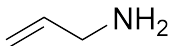


- ▶ interfacial adhesion,
- ▶ grafting of molecules with specific functionalities (reverse adhesion),
- ▶ improvement of cell colonization (tissue engineering),
- ▶ immobilization of biomolecules (biosensors, drug delivery systems).

maleic anhydride



Amine films



- ▶ interfacial adhesion,
- ▶ improvement of cell colonization (tissue engineering),
- ▶ immobilization of biomolecules (biosensors, drug delivery systems).

10.4.1 Understanding the Plasma Polymerization

Description of plasma polymerization by **macroscopic kinetic approach**

involving a composite (“Yasuda”) parameter W/F (W power, F monomer flow rate) proportional to the **energy delivered per one molecule of monomer in gas phase**

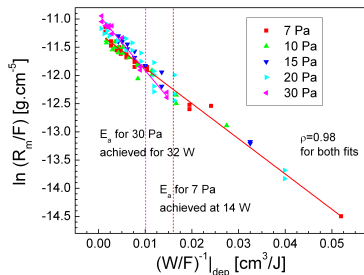
D. Hegemann et al. Plasma Process Polym 7 (2010) 889

$$\frac{R_m}{F} = G \exp\left(-\frac{E_a}{W/F|_{\text{dep}}}\right)$$

$$\frac{W}{F}|_{\text{dep}} = \frac{W}{F} \frac{d_{\text{act}}}{d_{\text{gas}}} \quad (1)$$

mass deposition rate R_m , apparent activation energy E_a , absorbed power density W , gas flow F

Arrhenius plot - describing **gas-phase processes**:



(again for the example of plasma polymerization of HMDSO in CCP)

10.4.1 Understanding the Plasma Polymerization

Effect of ion bombardment (plasma-surface interaction) should not be forgotten, especially for low pressure CCP discharges!

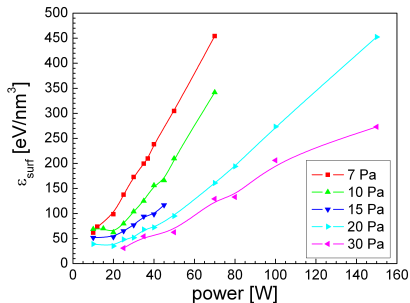
and its not only about the ion energy - **it is about ion energy flux**

Energy dissipated per deposition rate R

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

Γ_i ion flux, E_{mean} mean ion energy

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

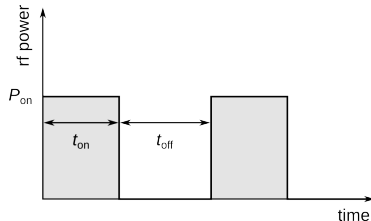


(again for the example of plasma polymerization of HMDSO in CCP)

10.4.2 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

$$P_{aver} = P_{on} \times DC$$

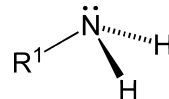
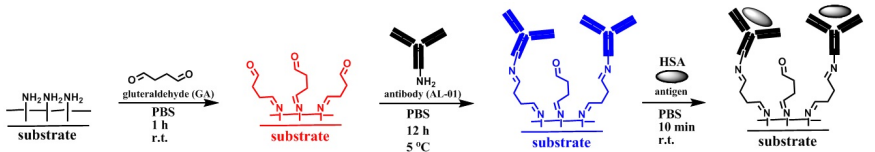
⇒ Macroscopic approach uses P_{aver}

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

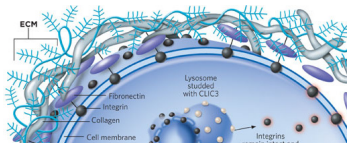
10.4.3 Amine Plasma Polymers

Reactivity of primary amines is important for

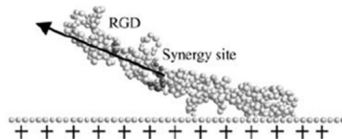
- ▶ adhesion enhancement
- ▶ immobilization of biomolecules (for enzyme electrodes, immunosensors etc.)



- ▶ cells interaction with surfaces (artificial tissue engineering)



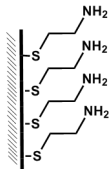
Cells interact with surfaces via extracellular matrix (ECM)



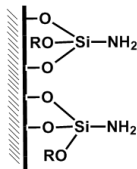
ECM contains proteins like fibronectin that bonds well to protonated surfaces such as NH_2 surfaces at neutral pH.

Various Amine Functional Films

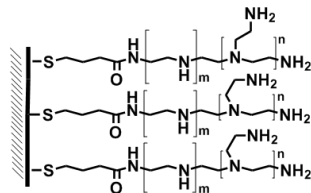
SAM of
cysteamine



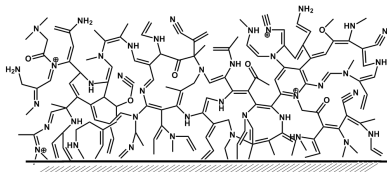
(3-Aminopropyl)triethoxysilane
(APTES)



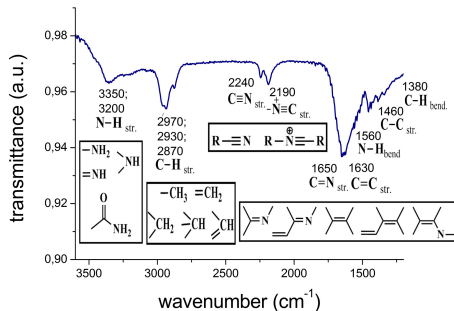
Polyethyleneimine (PEI)



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.

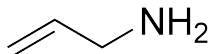
usually in pulsed RF discharges, substrate floating or grounded

Deposition from gas mixtures:

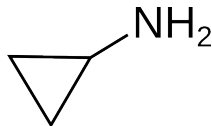
- ▶ NH_3/CH_4
- ▶ NH_3/C_2H_4

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**



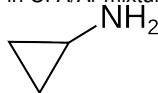
Cyclopropylamine - promising monomer for amine-rich coatings, **non-toxic, vapor pressure of 32 kPa at 25 °C.**



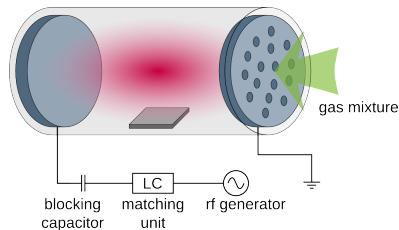
CPA Plasma Polymerization at Low Pressure

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

- ▶ in CPA/Ar mixtures

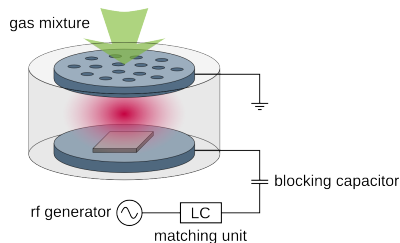


reactor R3, substrate at floating potential



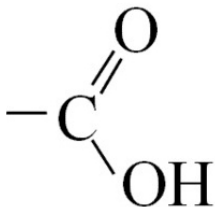
- ▶ Ar 28 sccm, CPA 0.1–1.0 sccm
- ▶ pressure 120 Pa
- ▶ RF power 20–30 W
- ▶ electrode diameter 80 mm
- ▶ interelectrode distance 185 mm

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

10.4.4 Carboxyl Plasma Polymers

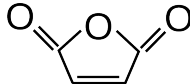
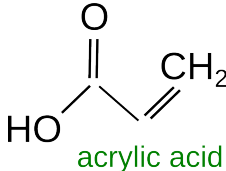


Plasma processing of carboxyl plasma polymers
by **PECVD from simple molecules**

- ▶ 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]



maleic anhydride

- [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. 12 (2015) 1220

COOH-Films Deposited at Atmospheric Pressure

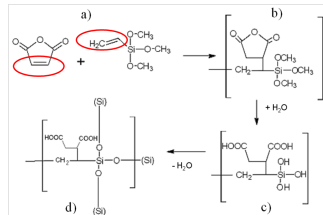
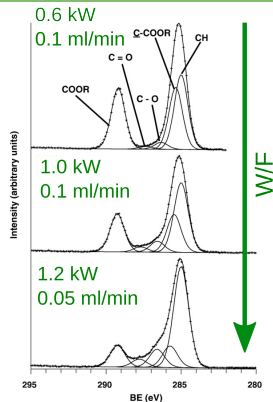
DBD plasma polymerization of acrylic acid in He

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

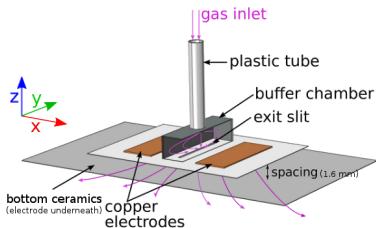
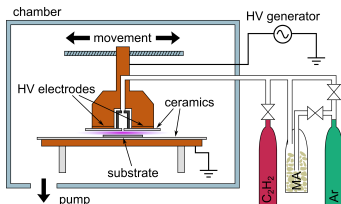
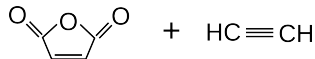
Thomas et al. Plasma Process. Polym. 4 (2007) S475
Manakhov et al. PPP 9 (2012) 435

- 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