Atmospheric-pressure plasma deposited epoxy-rich thin films as platforms for biomolecule immobilization – application for anti-biofouling and xenobiotic-degrading surfaces

G. Camporeale, M- Moreno-Couranjou, S. Bonot, R. Mauchauffé, N. D. Boscher, C. Bebrone, C Van de weerdt, H.-M. Cauchie, P. Favia and P. Choquet

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Introduction

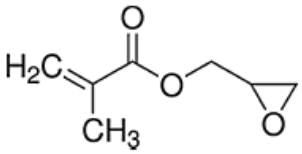
- LP plasma processes have been used for deposition of thin films funcionalized with groups such as amino, carboxylic, or epoxy for covalent bonding of peptides/proteins with biological activity
- APDBD used for fast deposition of epoxy-rich layers
- study of influence of plasma process parameters on the chemical and morphological properties of layer
- two enzymes with different activities (*dispersin*, *laccase*) have been used in order to explore the possibilities of the epoxy-containing layer as a platform for biomolecule immobilization

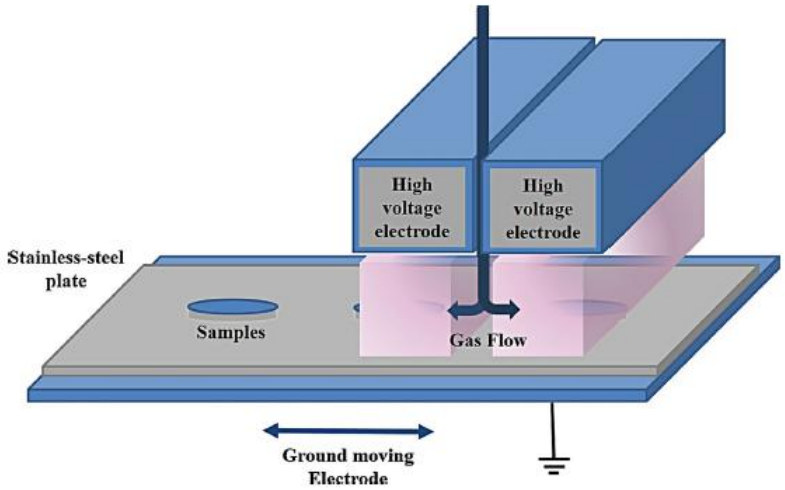
Experiment

- two kinds of substrates
  - mirror-polished stainless steel disks
  - two face-polished silicon (111) wafers

- Ar + GMA (flow 10,5 ml/min)

- plasma was generating using corona source
  - CW and PW discharge mode
  - P = 50 W
  - in PW mode - t_{on} fixed at 10 ms, t_{off} varied from 10 ms to 80 ms





Obr 1: GMA structure and plasma source.

Used characterization methods

- Scanning electron microscopy (SEM)
  - thickness of ppGMA
  - film deposition rate
- Atomic force microcopy (AFM)
- Fourier-transform infrared spectroscopy (FTIR)
- X-ray photoelectron spectroscopy (XPS)

Scanning electron microscopy

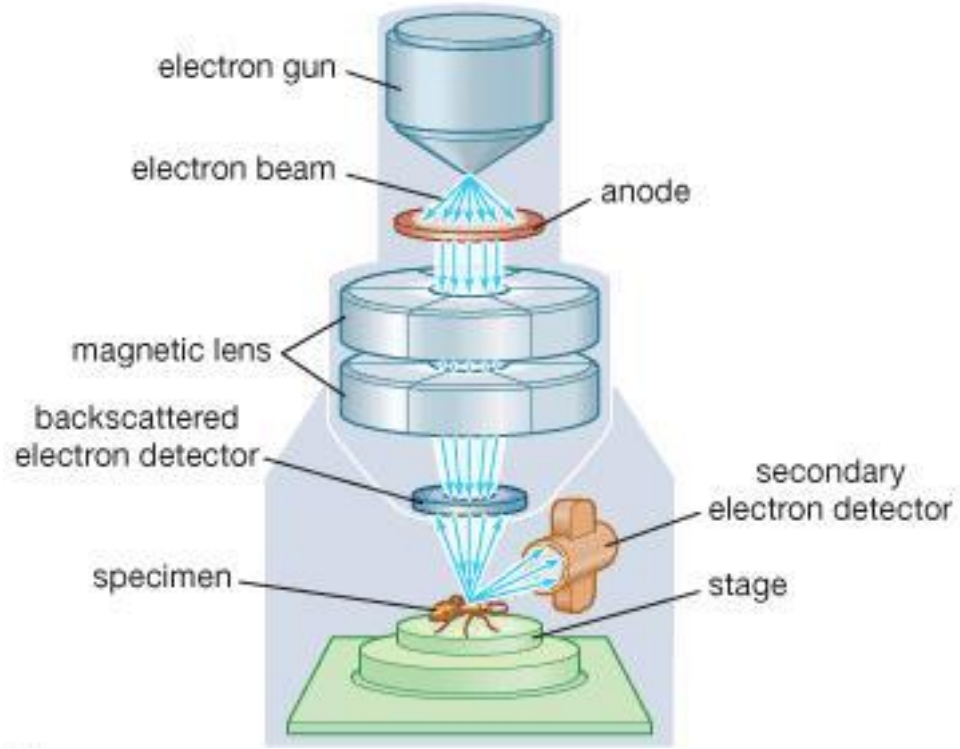
- SEM is based on imaging of sample by scanning it with focused electron beam

- types of signal
  - secondary electrons (SE)
  - SE are emitted from very close to the sample surface (~ 100 nm)
  - SE used for topography imaging (emitted mostly from sharp edges)

  - backscattered electrons (BSE)
  - BSE emerge from deeper locations ((~ 1 um)
  - intensity of BSE signal is related to atomic number
  - BSE provide information about the distirbution of different elements in the sample

  - characteristic x-rays
  - used to identify the composition and measure the abundance of elements in the sample

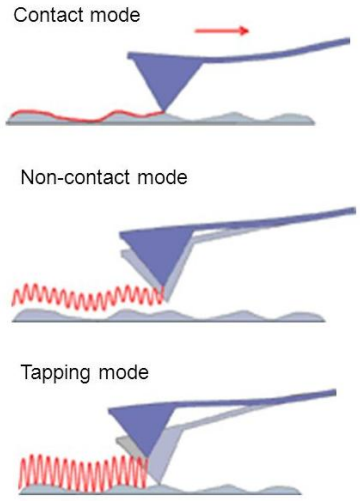
Scanning electron microscopy



Obr 2: Principle od SEM.

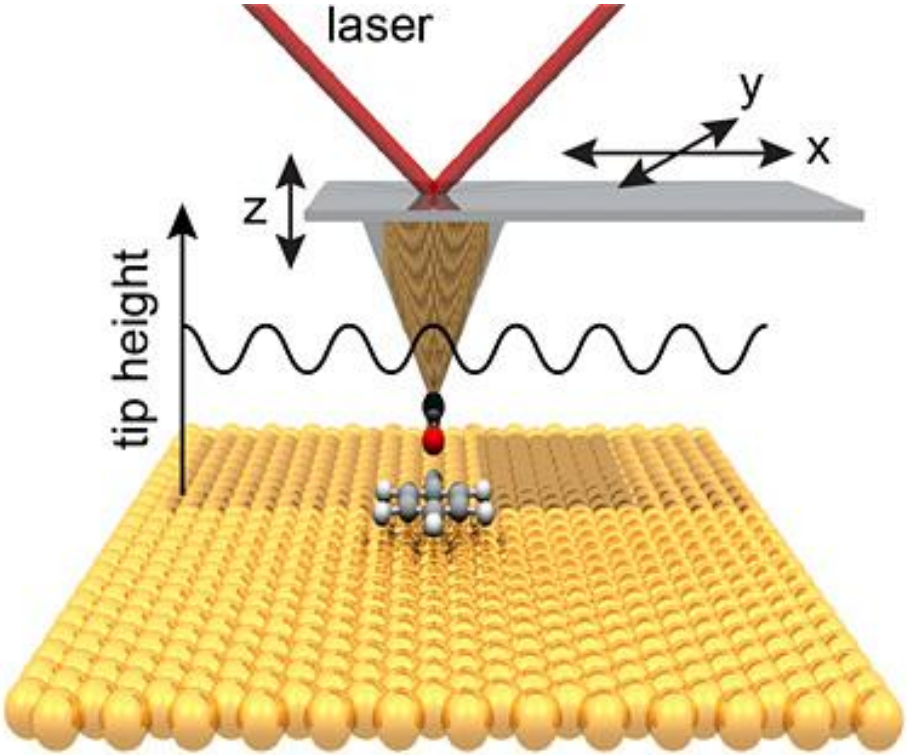
Atomic force microcopy

- AFM is suitable technique for study of the surface of thin solid films
- the cantilever with a sharp tip scans the surface of the analyzed sample
- lateral scanning ensures piezoelectric crystal which moves the probe over the sample
- three possible modes
  - contact
  - non-contact
  - tapping



Obr 3: Principle of AFM.

Atomic force microcopy

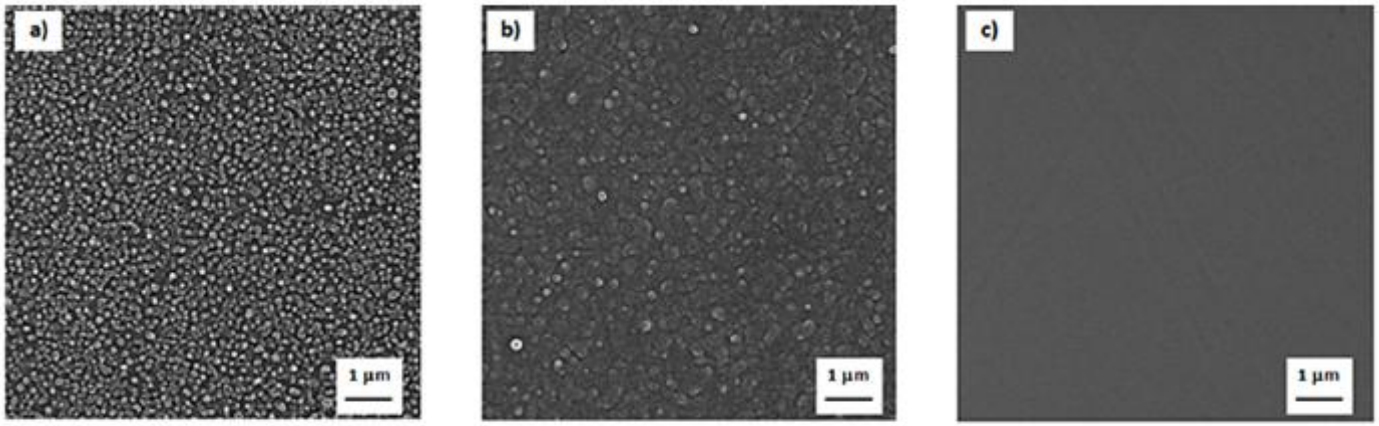


Obr 4: Principle of AFM.

SEM and AFM results

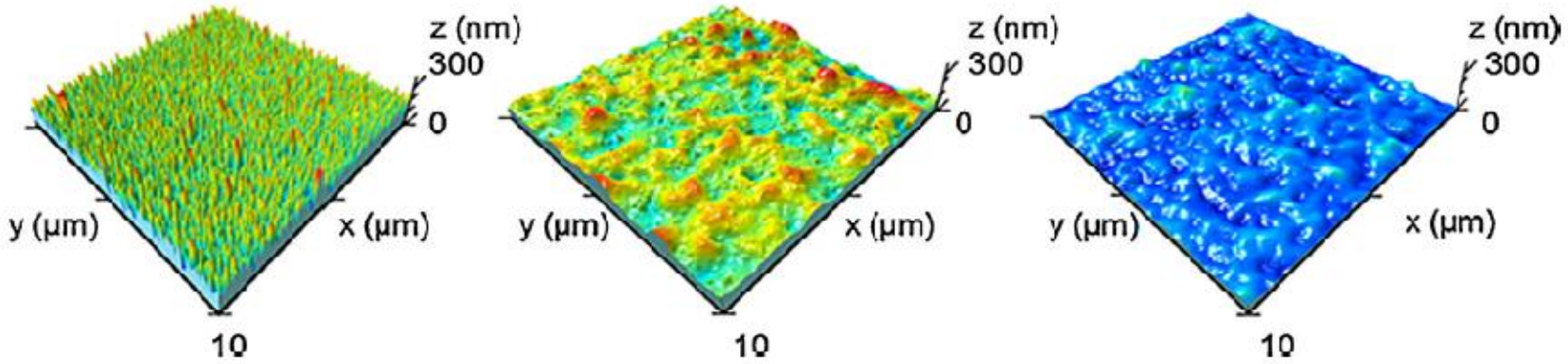
- PW mode leads to higher film rates FR
  - FR (CW) = 1,2 nm/s
  - FR (PW, 10:80) = 1,8 nm/s

- pinhole free coating
- PW mode leads to smoother surface without aggregates



Obr 5: ppGMA layers deposited at 50 W in CW mode (a) and 10:10 ms (b) and 10:80 ms (c) PW modes.

SEM and AFM results



Obr 6: ppGMA layers deposited at 50 W in CW mode (a) and 10:10 ms (b) and 10:80 ms (c) PW modes.

Deposition conditions	Average roughness [Ra, nm]
50 W, CW	148 ± 13
50 W, 10:10 ms	43 ± 8
50 W, 10:80 ms	24 ± 11

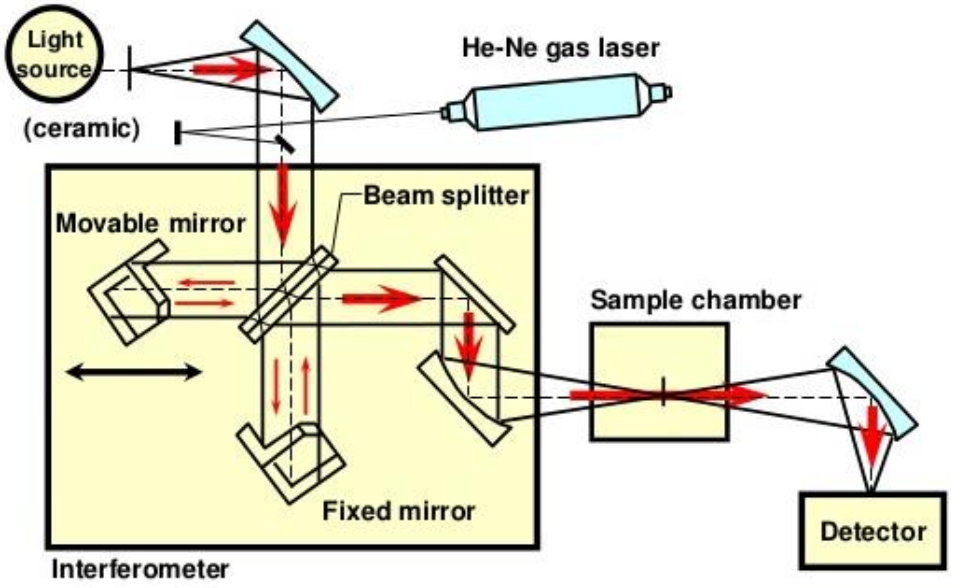
Fourier-transform infrared spectroscopy

- IR spectroscopy is based on absorption of IR radiation which influence vibrational and rotational states of chemical compound
- FTIR use Michelson interferometer includes beamsplitter
- interference signal measured by the detector as a function of the optical pathlength difference is called the interferogram
- IR spectrum is computed from the interferogram by performing a Fourier transform
- quantitative analysis – Lambert-Beer law

$$I = I_0 \exp(-abC)$$

where I_0 is the intensity of incident light, I is intensity of the light transmitted by sample, a is absorption coefficient, b is thickness of the sample and C is the sample concentration.

Fourier-transform infrared spectroscopy



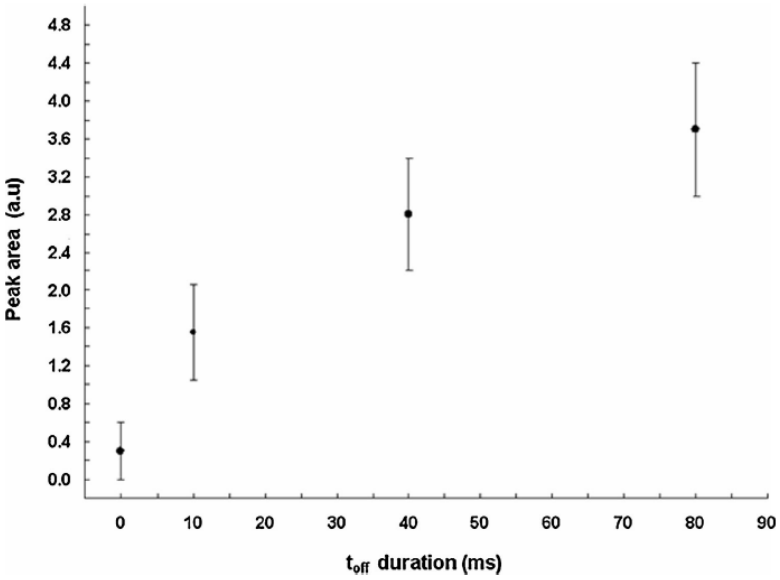
Obr 7: Principle of FTIR.

Fourier-transform infrared spectroscopy

- four characteristic epoxide peaks
  - 3060 cm^{-1} C-H epoxide ring stretching
  - 1258 cm^{-1} epoxide ring breathing
  - 910 cm^{-1} epoxide ring asymmetric deformation
  - 852 cm^{-1} epoxide ring symmetric deformation

- in CW mode, all peaks barely detectable
- increasing t_{off} leads to increasing the epoxide bands intensity

- in PW mode film with high monomer structure retention due to chemical reactions occurring during the t_{off} between intact monomer molecules and surface radical centers generated during the t_{on} period



Obr 7: Area evolution of the assymetric rign deformation band as function of the plasma-off time.

X-ray photoelectron spectroscopy

- XPS is based on irradiation of a material with a beam of Xrays that cause emission of the inner shell electron

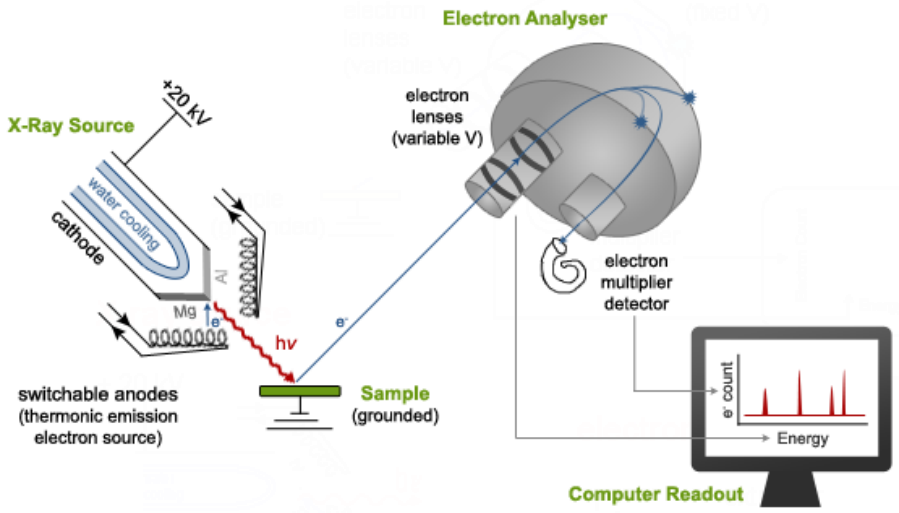
- measurement of the kinetic energy E_k of the emitted electron and determination of elemental composition and chemical and electronic states of the elements

$$E_B = hf - E_k - \phi$$

where E_B is the binding energy,

hf is energy of photon and

ϕ is spectrometer work function.



Obr 8: Principle of XPS.

X-ray photoelectron spectroscopy

- PW mode allows a higher retention of the initial ester and epoxy groups
- increasing the t_{off} leads to an increase of the epoxy surface content

Samples			50 W, CW	50 W, 10:10 ms	50 W, 10:80 ms	50 W, 10:80 ms after 50 days at air	Poly(GMA)
XPS surface composition [at. %]							
		C	77	75	72	73	73
		O	23	25	28	27	27
XPS C1s peak fitting, [%]							
Contribution	**Binding energy [eV]**	**Functional group**					
C1	285.0	C—C	52	36	33	38	42
C2	285.7	C—CO—O	8	11	13	12	11
C3	286.7	C—O	25	25	22	25	8
C4	287.0	Epoxy	0	7	18	9	27
C5	287.8	C=O/C—O—C	5	10	2	4	–
C6	289.1	O—C=O	8	11	13	12	11

What I like

- information about uncertainty related to the XPS measurement (2 at%)
- thickness measurements were carried out on at least three samples for each condition

What I miss

- no information about layer thickness
- FTIR results could be discussed in more details
  - more details about manipulation with background – which method was used?
  - area evolution of other epoxide peaks – is there the same trend?

Thank you for attention!

Šárka Trochtová