Organosilicon Plasma Polymers Prepared On Electrospun Polymer Nanofibers

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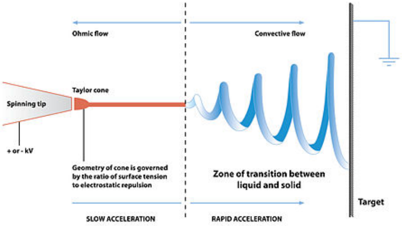
Outline

- Electrospining of Polymer Fibers
- PECVD of Organosilicon Films
- Plasma Sources Used
- Low Pressure CCP
- Atmospheric Pressure Plasma Jet
- Summary

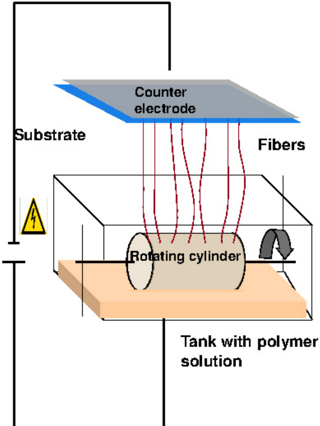
Principle of Electrospinning

Electrospinning of polymer fibers:



Nanospider$^{\mathrm{TM}}$ technology developed by ELMARCO

- High DC voltage between electrodes
- If the electrostatic repelling force overcomes the surface tension of polymer solution or melt, the polymer formed a Taylor cone and is ejected from the surface of electrode and forms a continuous filament.



Electrospinning of PVA and PA6

PVA

PA6

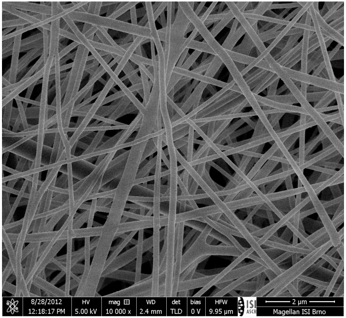
Polyvinylalcohol (PVA)

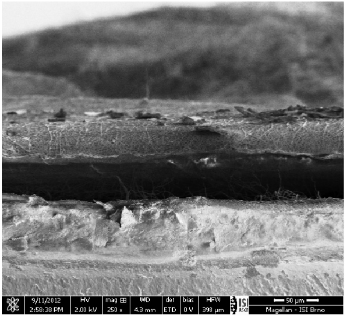
- cylindrical electrode,
- solvent - water,
- $U = 64 - 66$ kV (unstable),
- $I = 0.05A$,
- $v = 12$ mm/min, spin 3 r/min

Polyamide (PA6)

- wired electrode,
- solvent - acetic acid/formic acid (problems of solvent volatility),
- $U = 64$ kV
- $I = 0.04A$,
- $v = 12$ mm/min, spin 2 r/min

Electrospun polymers - highly porous network of micro/nanofibers

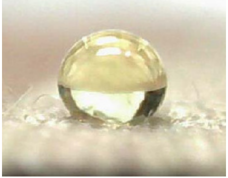




Plasma coating of electrospun polymer micro/nanofibers can bring additional functionality for

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

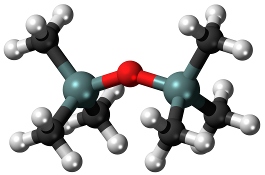
Example of functional coating on complex substrate - hydrophobic/oleophobic surfaces of plasma treated Nomex-based textiles:



M. Klíma *et al.* - cold atmospheric pressure plasma jet

Organosilicon Plasma Polymers and SiO_x Films

Hybrid character of monomers:
source of Si-O and C-H groups

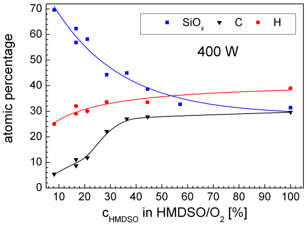


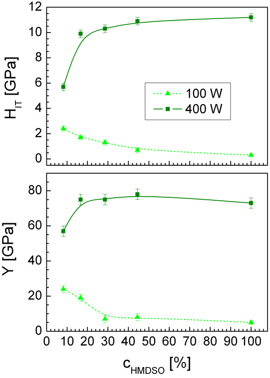
hexamethyldisiloxane (HMDSO)
$Si_2OC_6H_{12}$

Functional coatings:

- **transparent protective films on plastics**
- **(ultra)hydrophobic / (ultra)hydrophilic coatings**
- **intermediate adhesive layers on metals**

Example for
low pressure CCP
in $HMDSO/O_2$

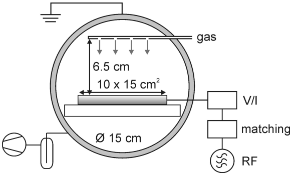


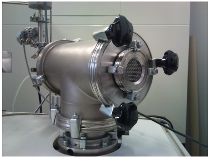


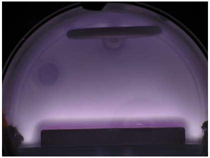
Zajíčková et al. Plasma Sources Sci. Technol. 16 (2007) S123

Low and Atmospheric Pressure Discharges

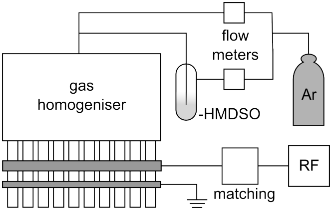
- RF capacitively coupled discharge (13.56 MHz) at EMPA

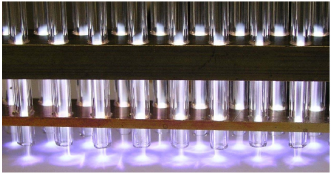






- cold atmospheric pressure RF plasma multijets (13.56 MHz) at MU Brno

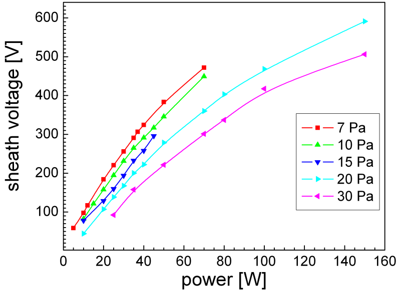




Low Pressure CCP - Variation of Deposition Parameters

- Ar + HMDSO 1:1 mixture
- total flow rate 6 sccm
- pressure p 7–30 Pa
- power W 5–150 W
- dc bias-voltage at RF (substrate) electrode $U_{\rm b}$ varied with W and p

Sheath voltage at substrate electrode
$V_{\rm sh} = 0.39 V_0 + 0.73 U_{\rm b}$



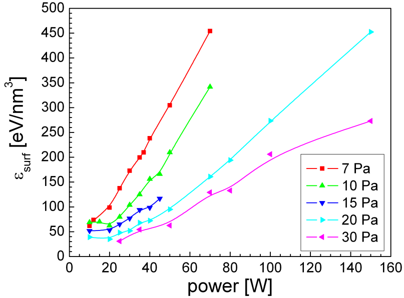
- Gas phase processes
  - energy input $W/F|_{\rm dep}$
- Effect of ion bombardment:

Energy dissipated per deposition rate R

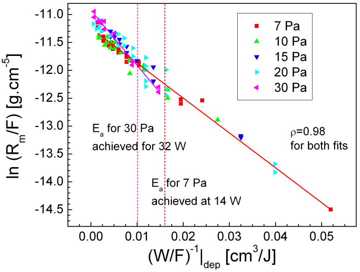
$$\varepsilon_{\rm surf} = \frac{\Gamma_i E_{\rm mean}}{R} \qquad (1)$$

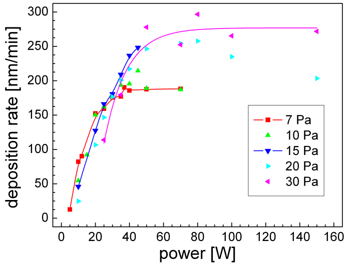
Γ_i ion flux, $E_{\rm mean}$ mean ion energy

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



Understanding Deposition Process



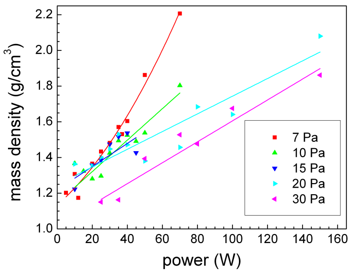


$$\frac{R_\mathrm{m}}{F} = G \exp\left(-\frac{E_\mathrm{a}}{W/F|_\mathrm{dep}}\right) \qquad (2)$$

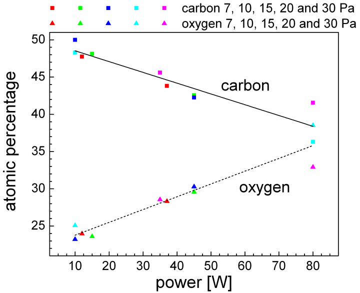
$$\frac{W}{F}\Big|_\mathrm{dep} = \frac{W}{F}\frac{d_\mathrm{act}}{d_\mathrm{gas}} \qquad (3)$$

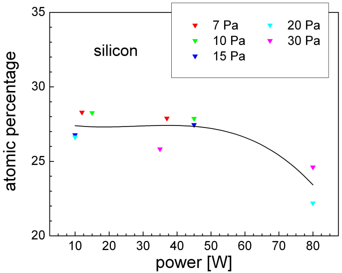
mass deposition rate R_m, apparent activation energy E_a, absorbed power density W, gas flow F

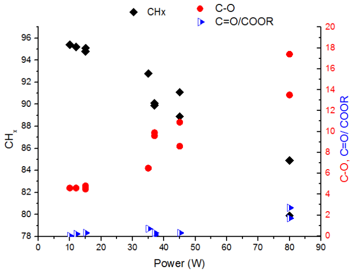
D. Hegemann et al. Plasma Process Polym 7 (2010) 889



Chemical Structure of Films by XPS

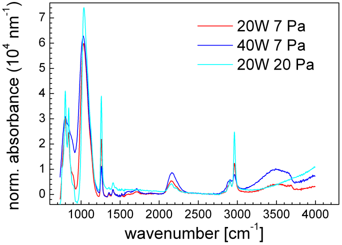


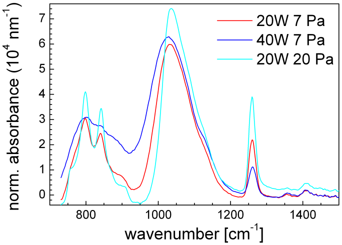




- no obvious difference for different pressures for few selected samples
- oxidation of products from Ar/HMDSO mixture with increased power, i.e. dissociation of monomer
- occurance of C=O, COOR due to oxidation of CH groups and incorporation of the products into films

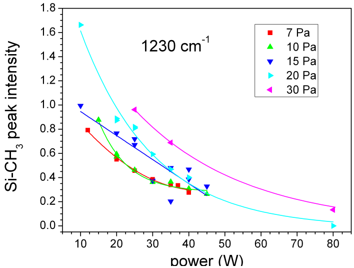
Chemical Structure of Films by FTIR

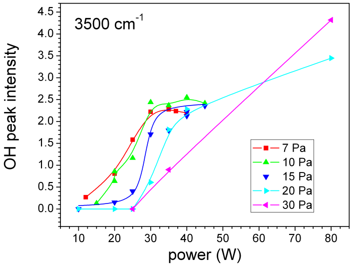


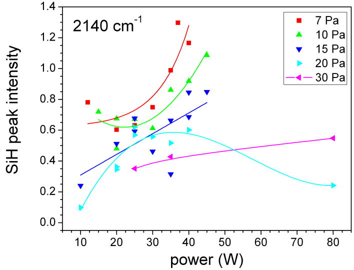


σ (cm^{-1})	Mode	Comment
CH_x correlated peaks		
2960	$\nu^{a}_{CH_3}$	
2900	$\nu^{s}_{CH_3}$	
2925	$\nu^{a}_{CH_2}$	
2855	$\nu^{s}_{CH_2}$	
1460	$\delta^{a}_{CH_2}$	
$Si - CH_2$ correlated peaks		
1360	δ_{CH_2}	in Si-CH_2-Si
1400	δ_{CH_2}	in Si-$(CH_2)_2$-Si
$Si - CH_3$ correlated peaks		
1410	$\delta^{a}_{CH_3}$	in Si-Me_x
1260	$\delta^{s}_{CH_3}$	in Si-Me_x
845	ρ_{CH_3}, ν_{SiC}	in Si-Me_3
760	ρ_{CH_3}, ν_{SiC}	in Si-Me_3
885	ρ_{CH_3}, ν_{SiC}	in Si-Me_2
805	ρ_{CH_3}, ν_{SiC}	in Si-Me_2
775	ρ_{CH_3}, ν_{SiC}	in Si-Me_1
$Si - H$ correlated peaks		
2140	ν_{SiH}	

Chemical Structure of Films by FTIR

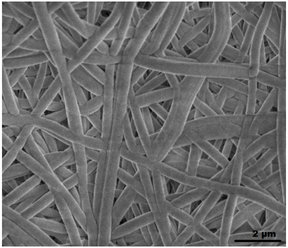


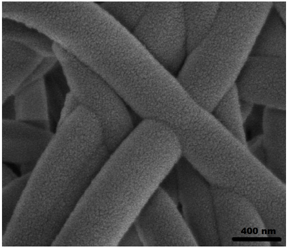




- higher retention of monomer structure ($Si\text{-}CH_3$ groups) at lower power and higher pressure
- general trends are in agreement with XPS
- more details for pressure changes (due to higher amount of samples?)

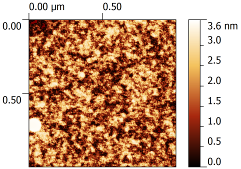
Smooth Films by Low Pressure PECVD

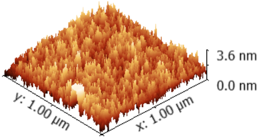




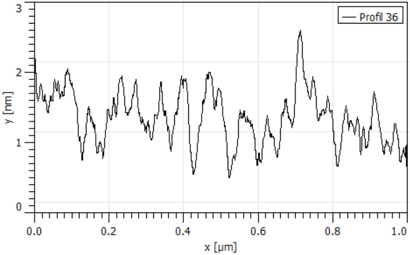
with 5 nm of sputtered Au film

Typical example for 20Pa and 100W



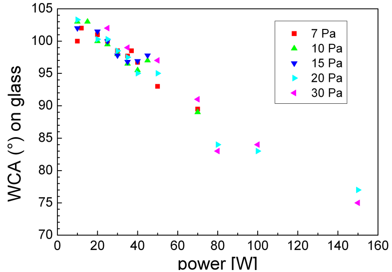


Rms roughness on Si - 0.50 nm

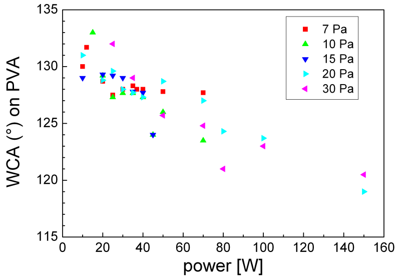


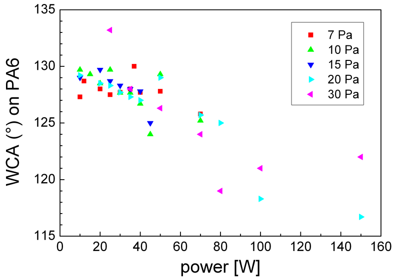
Film thickness on Si substrate 493 nm, on PVA 140 $\pm$ 60 nm (PVA diameter 210 $\pm$ 40 nm).

Water Contact Angle



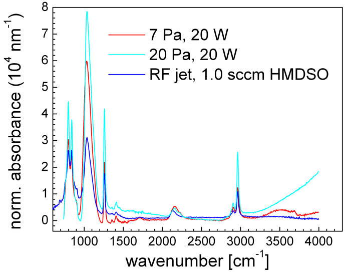
- **hydrophobic films**
- decrease of water contact angle due to increased oxidation
- nanostructure of electrospun fibers causes an increase of CA
- fibers are well protected by the films because water CA could be measured on PVA (normally dissolved in water)





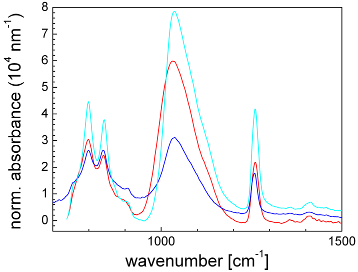
Films Deposited by RF Jets

- atmospheric pressures,
- 20 moving nozzles,
- 10 W per nozzle,
- 3.2 slm of Ar,
- 0.8–1.2 sccm of HMDSO per nozzle (Ar bubbler),
- speed of sample movement - 60 cm/min,
- 4 or 10 passages over substrate

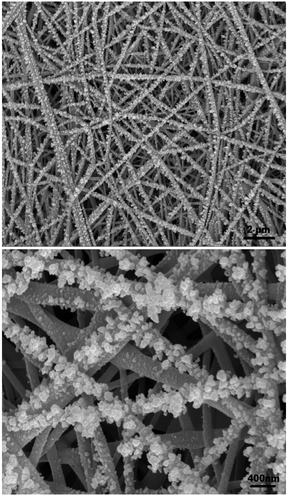


water contact angle on coated nanofibers:
141 – 149 °

- higher value than 130° for low pressure although the film chemistry is similar

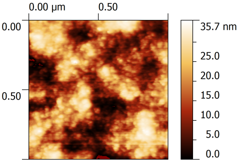


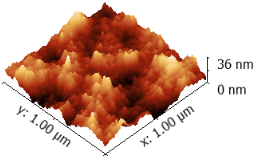
Nanostructured Organosilicon Films



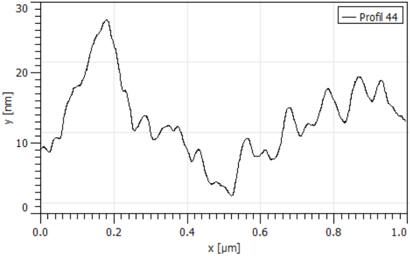
with 10 nm of sputtered Au film

Typical example for 0.8 sccm HMDSO and 4 passages





Rms roughness on Si - 5.15 nm



Maximum film thickness on Si 280 nm.
Thickness of coated PVA nanofibers 210 ± 40 nm (PVA diameter 210 ± 40 nm)

Summary

- PVA and PA6 nanofibrous textiles **can be plasma-coated in Ar/HMDSO without their damage using both**
  - low pressure CCP discharge, fibers on RF electrode (ion bombardment)
  - atmospheric pressure plasma jet (thermal load)
- **Organosilicon coatings protected PVA fibers against water** even for the nanostructured films made by RF multijets.
- **Variable surface structure** achieved due to **different discharges** used
  - low pressure coatings - very low roughness (Rms around 0.5 nm)
  - atmospheric pressure coatings - Rms of 5 nm on flat Si, nanoparticles on polymer fibers.
- **Variation of water contact angle** achieved by **surface chemistry and morphology**
  - low pressure coatings - shift from about 102° to 75° (on flat substrate) due to decrease of $-CH_3$ groups and increase of OH
  - WCA on low pressure plasma-coated nanofibers increased to 130–115°
  - 141–149° was achieved for nanostructured coatings on nanofibers deposited by RF plasma multijets.

Full texts of our publications:

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Our webpage:

http://www.ceitec.eu/programs/advanced-nano-and-microtechnologies/plasma-technologies