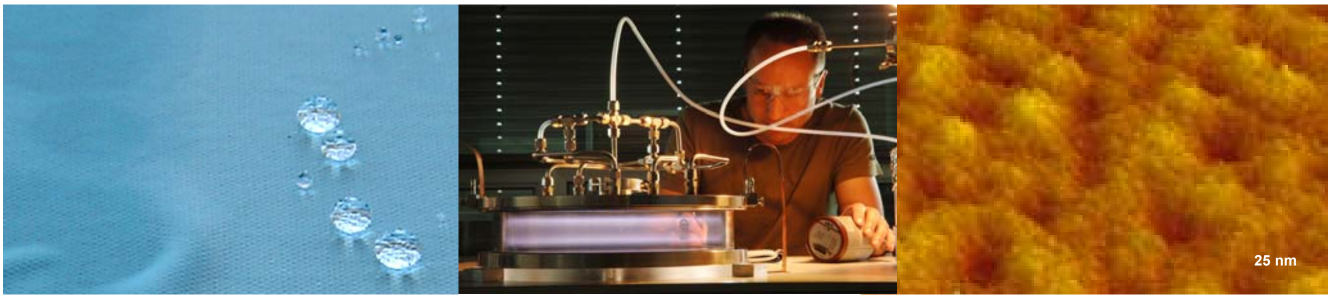
18th Int. Sym. on Plasma Chemistry
August 26-31, 2007, Kyoto, Japan

EMPA
Materials Science & Technology

Control of Plasma Polymerization Processes

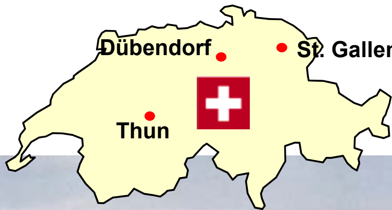


Dr. Dirk Hegemann
Empa, St.Gallen, *Advanced* **Fibers**
dirk.hegemann@empa.ch

Fibers Advanced

Empa, Swiss Materials Science & Technology

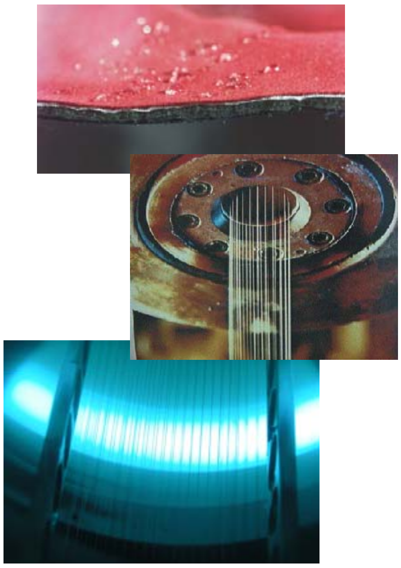
Member of ETH board in Switzerland
865 employees at three sites
→ R&D for (international) SMEs



Empa Laboratory

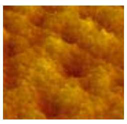
Advanced Fibers

- **Fiber and Textile Chemistry**
  - finishing, wet-chemical treatment
- **Fiber Development**
  - bi-component fiber spinning device
- **Plasma-modified Surfaces**
  - cleaning, activation, deposition



Outline

Control of Plasma Polymerization Processes



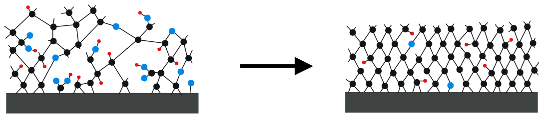
- **Plasma polymerization**
- **Influence of**
  - reactor geometry
  - plasma expansion
  - pressure
  - monomers
  - carrier / reactive gas
- **Nanoporous coatings**
- **Scale-up**

Plasma Polymerization

Different regimes

retention of monomer groups ←

→ fragmentation, cross-linking



hydrogels — e.g. PEO-like

functional density control — e.g. hydrophobic, -COOH, $-NH_2$

permeation control / barrier — e.g. SiO_x, a-C:H

hard coatings — e.g. a-C:H

energy-deficient | *monomer-deficient*

E_a → energy input *S*

D. Hegemann, Indian J. Fibre Text. Res. 31, 2006, 99.

Macroscopic Kinetics

Concept of chemical quasi-equilibria related to plasma

gas flow → **dissociation excitation** | **recombination relaxation** → stable products

e.g. monomer — **active zone** — **passive zone** — e.g. deposition

Macroscopic kinetics: (Becker formula)

$$S = \frac{W\tau_{act}}{pV_{act}} \propto \frac{W}{F} \qquad \tau_{act} = \frac{pV_{act}}{p_0 F}$$

The similarity parameter *S* represents the energy invested per particle of the gas mixture during the flow through the active plasma zone.

H.-E. Wagner, in: Low Temperarure Plasma Physics, ed. Hippler et al., Wiley-VCH, 2001, p. 305.

A. Rutscher, H.-E. Wagner, Plasma Sources Sci. Technol. 2, 1993, 279.

Plasma Polymerization

Evaluation of deposition rates

For radical-dominated discharges the reaction parameter power input per gas flow *W/F* within the active plasma zone determines the mass deposition rate R_m

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

in [g/cm^5]
deposited mass from (per) plasma volume and per area

E_a: (apparent) activation energy

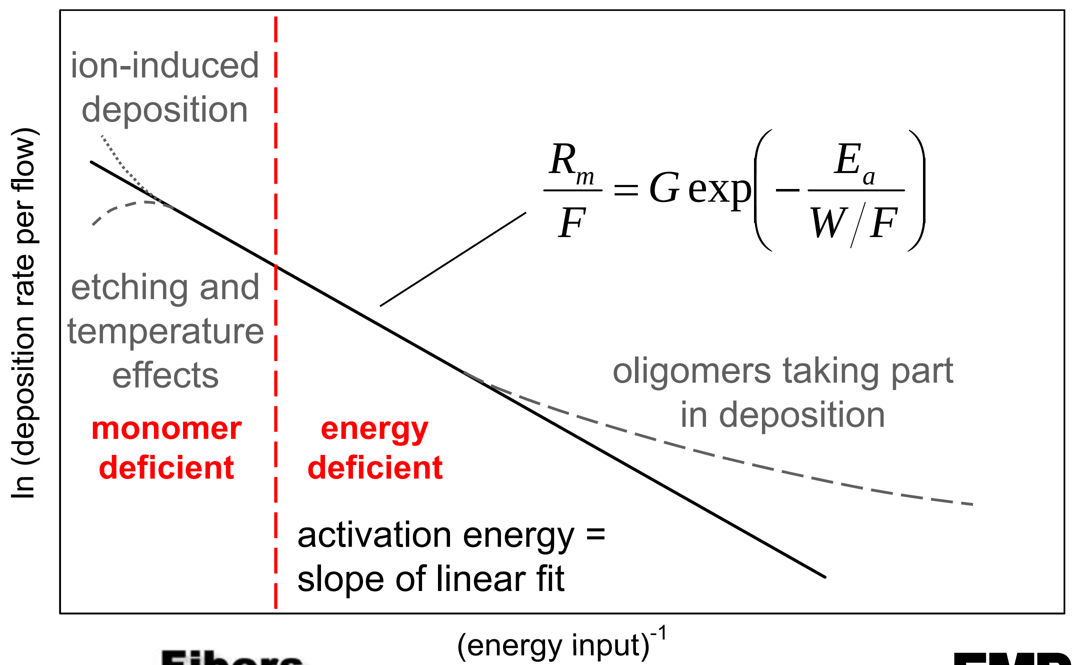
G: geometrical factor

Y.S. Yeh, I.N. Shyy, H. Yasuda, J. Appl. Polym. Sci.: Appl. Polym. Symp. 42, 1988, 1.

D. Hegemann, H. Brunner, C. Oehr, Plasmas Polym. 6, 2001, 221.

Plasma Polymerization

Evaluation of deposition rates

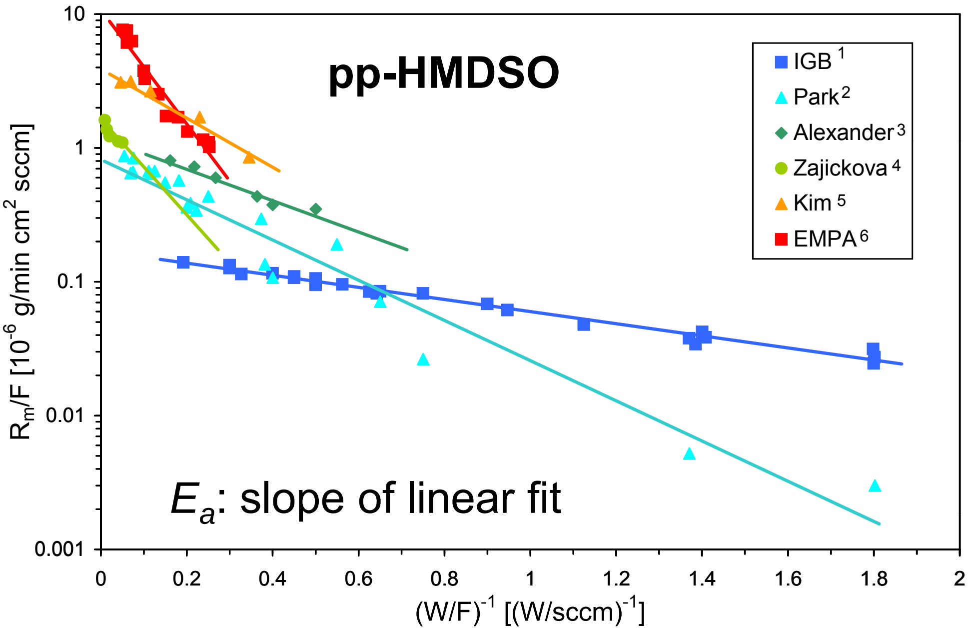


D. Hegemann, M.M. Hossain, Plasma Process. Polym. 2, 2005, 554.

Advanced Fibers
Dirk Hegemann, Plasma Polymerization, ISPC 18
EMPA
Materials Science & Technology

Evaluation of Deposition Rates

Deposited mass for different reactor geometries



[1] Hegemann et al., Plasma Polym. 6, 2001, 221.

[2] Park, N. Kim, J. Appl. Polym. Sci.: Appl. Polym. Symp. 46, 1990, 91.

[3] Alexander et al., Plasma Polym. 2, 1997, 277.

[4] Zajickova et al., Proc. ISPC 14, 1999, 1439.

[5] M.T. Kim, Thin Solid Films 311, 1997, 157.

[6] Hegemann et al., J Vac Sci Technol A23, 2005, 5.

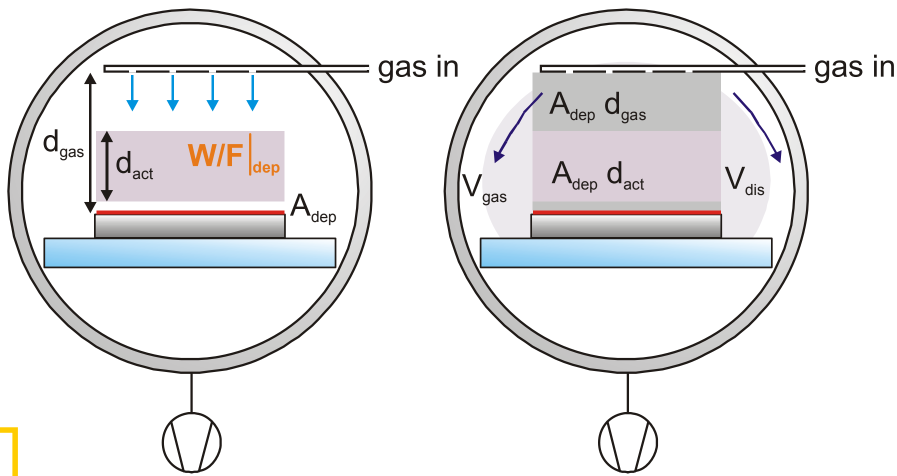
Influence of Reactor Geometry

Plasma deposition in a reaction vessel

$$S = \frac{W}{F}\Big|_{dep}$$

$$W\big|_{dep} = W\,\frac{A_{dep}\,d_{act}}{V_{dis}}$$

$$F\big|_{dep} = F\,\frac{A_{dep}\,d_{gas}}{V_{gas}}$$



$$S = \frac{W}{F}\,\frac{d_{act}}{d_{gas}}\,\frac{V_{gas}}{V_{dis}}$$

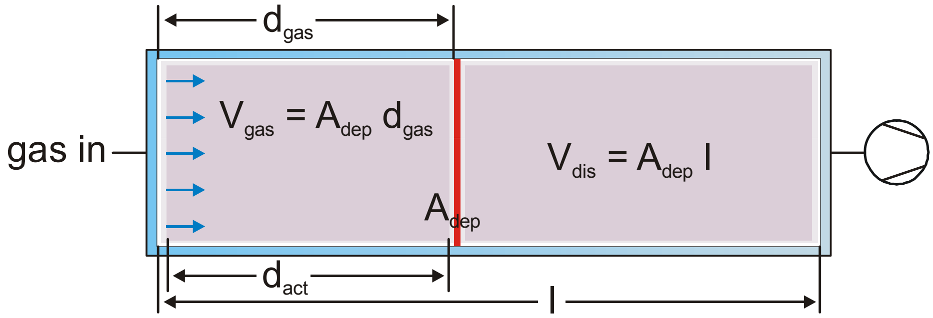
Similarity parameter is related to power and flow that contribute to film deposition.

D. Hegemann et al., Thin Solid Films 491, 2005, 96; Surf. Coat. Technol. 200, 2005, 458.

Influence of Reactor Geometry

Tubular set-up

$$S = \frac{W}{F}\frac{d_{act}}{l}$$



$$S = \frac{W}{p}\frac{\tau_{act}}{V_{dis}} \qquad \tau = \frac{V}{F}\frac{p}{p_0} \quad ; T = \text{const.}$$

Similarity parameter changes with position of substrate within the discharge.
→ Fragmentation increases with distance and residence time

J.M. Kelly, R.D. Short, M.R. Alexander, Polymer 44, 2003, 3173.

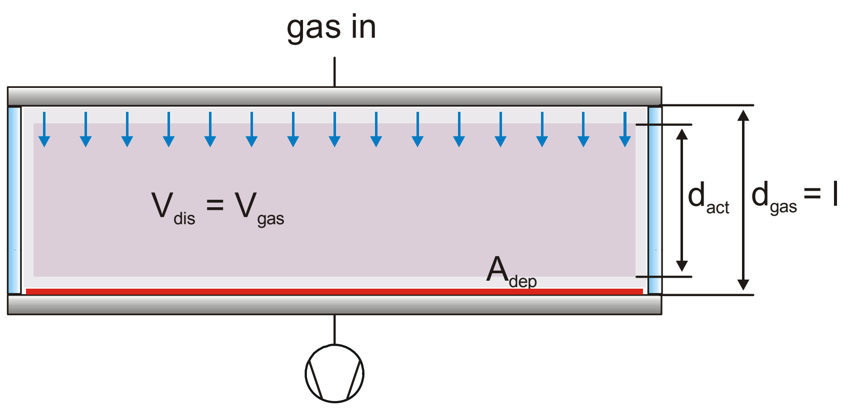
Influence of Reactor Geometry

Symmetric plane parallel set-up

$$S = \frac{W}{F}\frac{d_{act}}{l}$$

$$l = d_{act} + 2d_{sh}$$

$$S = \frac{W}{F}\left(1 - 2\frac{d_{sh}}{l}\right)$$

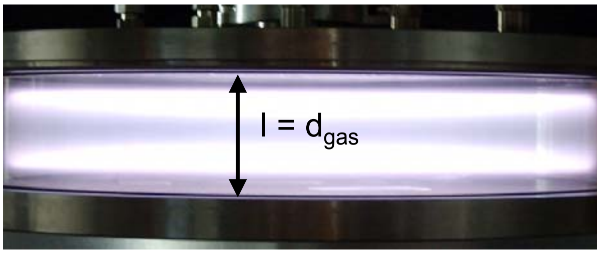


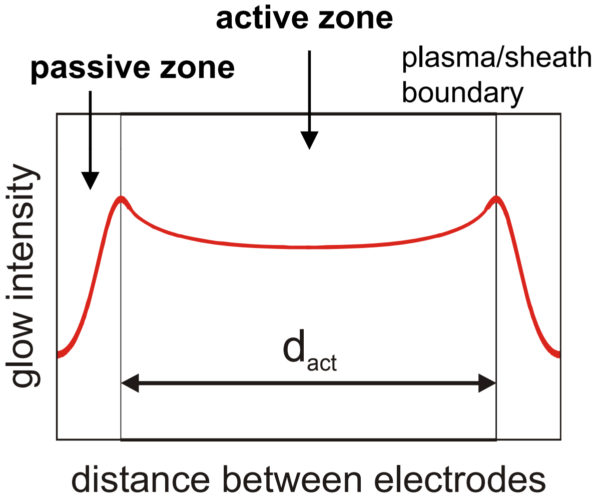
Similarity parameter increases with electrode distance.

D. Hegemann, H. Brunner, C. Oehr, Surf. Coat. Technol. 142-144, 2001, 849.
V. Sciarratta, D. Hegemann, M. Müller, U. Vohrer, C. Oehr, in: Plasma Processes and Polymers, Wiley-VCH, 2005, p. 39.

Symmetric Reactor

Plasma length d_{act}

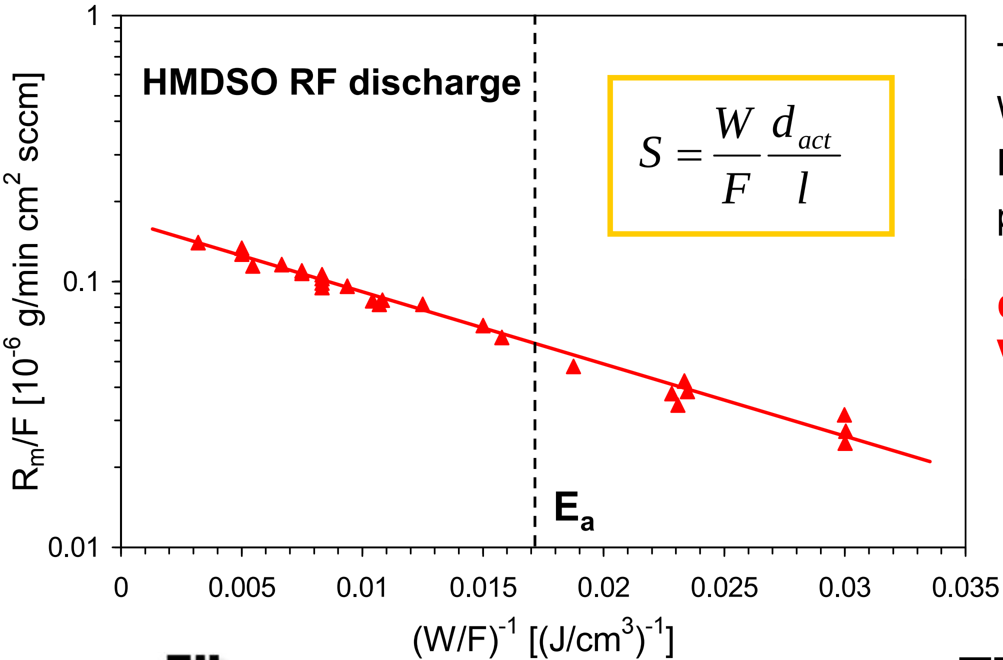




- well defined geometrical conditions
- known gas flow (vertical flow)
- known power adsorption

Symmetric Reactor

Variation of temperature, power, flow, and pressure



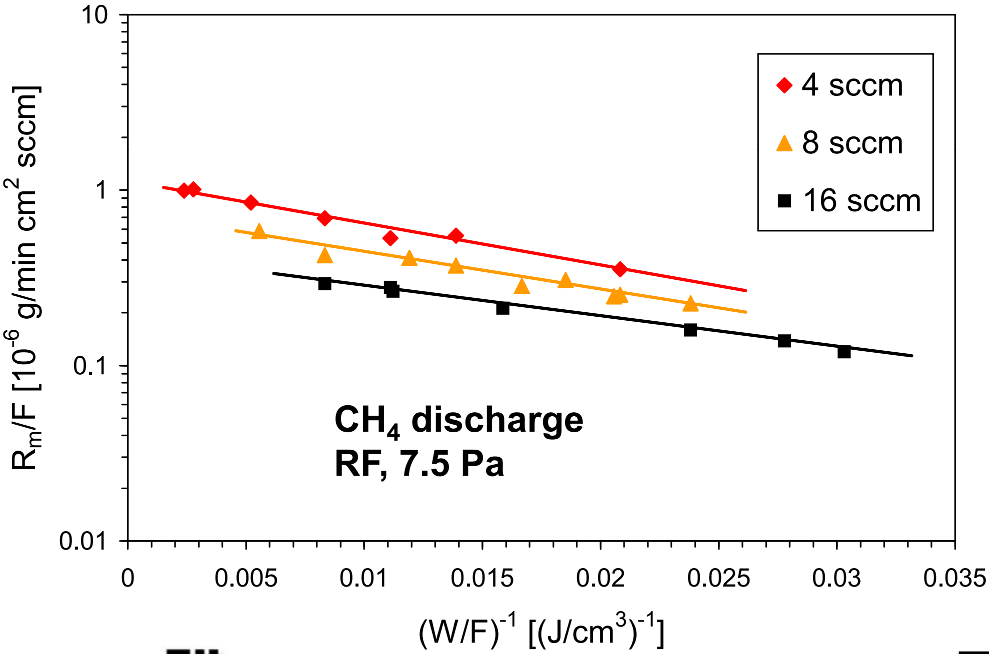
T_S: 30-90° C
W: 50-400 W
F: 50-120 sccm
p: 10-50 Pa

$d_{act} \approx$ const
$V_{dis} = V_{gas}$

D. Hegemann et al., Plasmas Polym. 6, 2001, 221.

Influence of Plasma Expansion

Plasma polymerization within asymmetric discharges

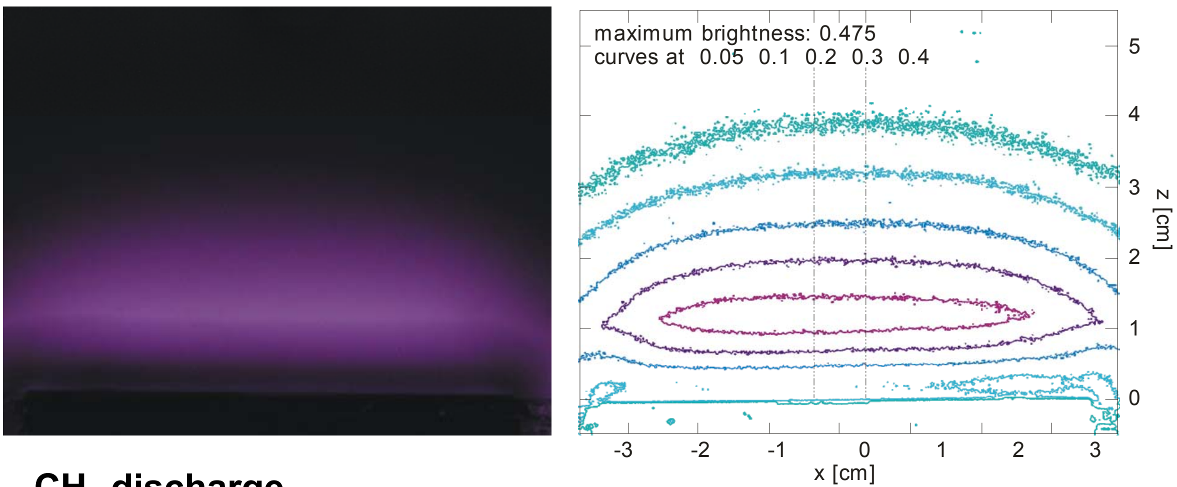


Different activation energies (slopes) were obtained for different gas flows.

D. Hegemann et al., Thin Solid Films 491, 2005, 96.

Influence of Plasma Expansion

Light distribution of plasma in front of RF electrode

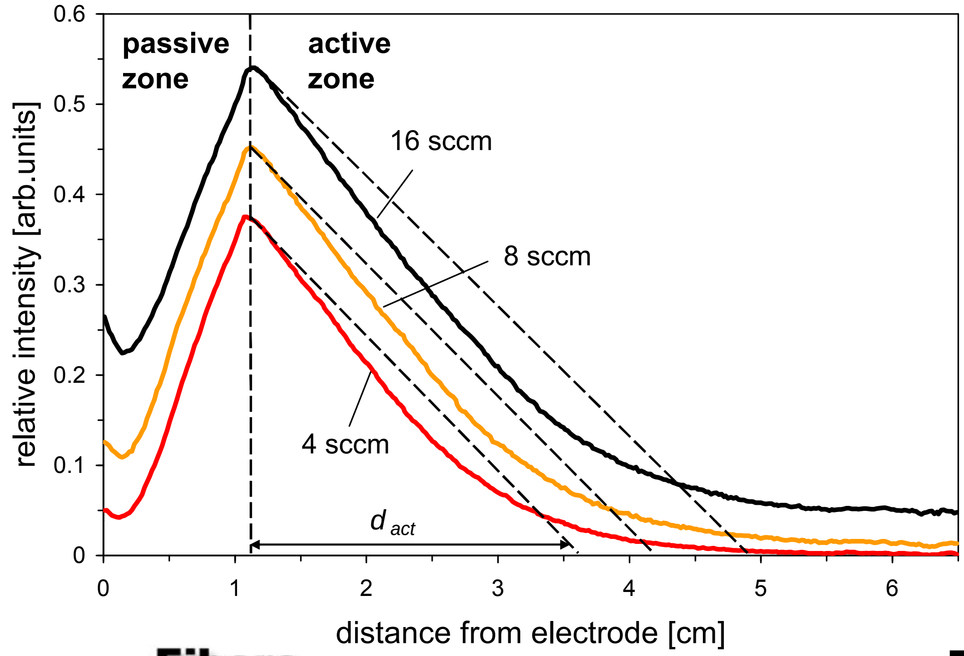


CH_4 discharge
RF, 7.5 Pa

D. Hegemann et al., Thin Solid Films 491, 2005, 96.

Influence of Plasma Expansion

Light distribution of plasma in front of RF electrode

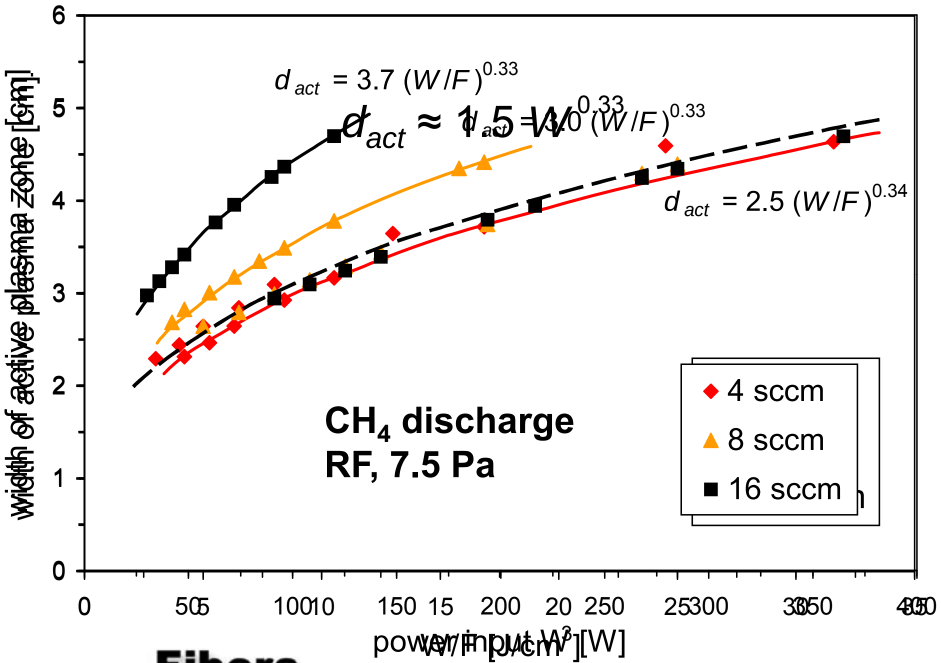


d_{gas} = 6.5 cm

CH_4 discharge
RF, 7.5 Pa

Influence of Plasma Expansion

Expanding plasma zone depending on power and flow

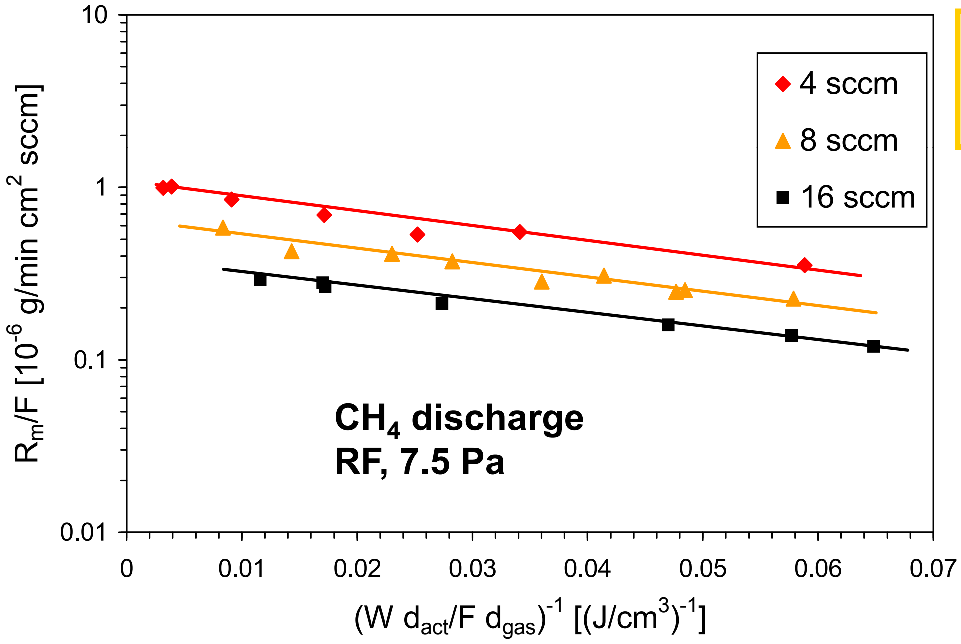


d_{act} only depends on W (independent of different monomer flows)

D. Hegemann et al., Thin Solid Films 491, 2005, 96.

Influence of Plasma Expansion

Consideration of similarity factor



$$S = \frac{W}{F}\frac{d_{act}}{d_{gas}}\frac{V_{gas}}{V_{dis}}$$

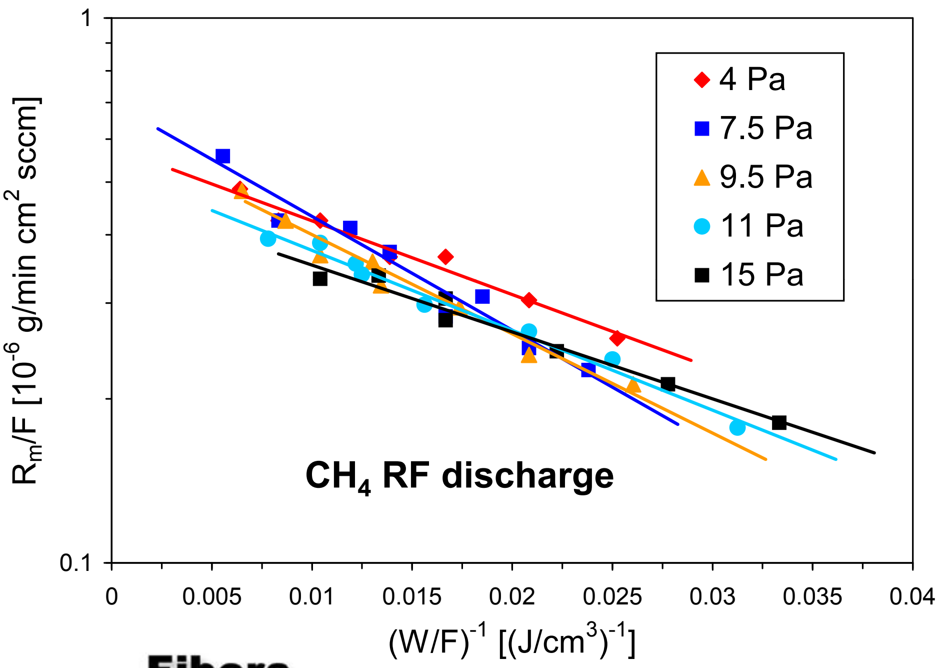
$V_{gas} \approx V_{dis}$

volume-dominated

Introduction of similarity factor yield same activation energy.

Influence of Pressure

Plasma polymerization within asymmetric discharges

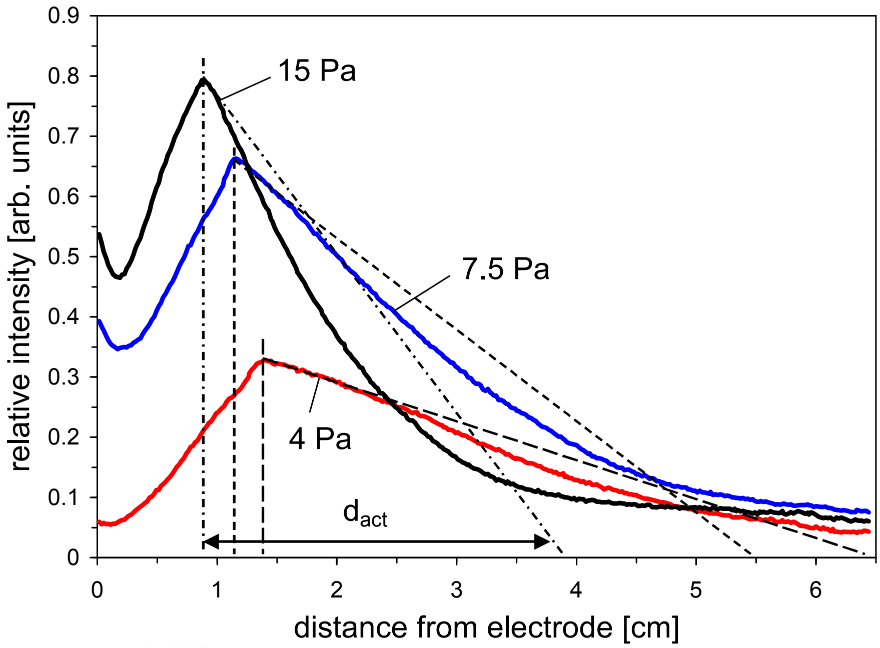


Different activation energies (slopes) were obtained for different pressures.

D. Hegemann, Thin Solid Films 515, 2006, 2173.

Influence of Pressure

Light distribution of plasma in front of RF electrode

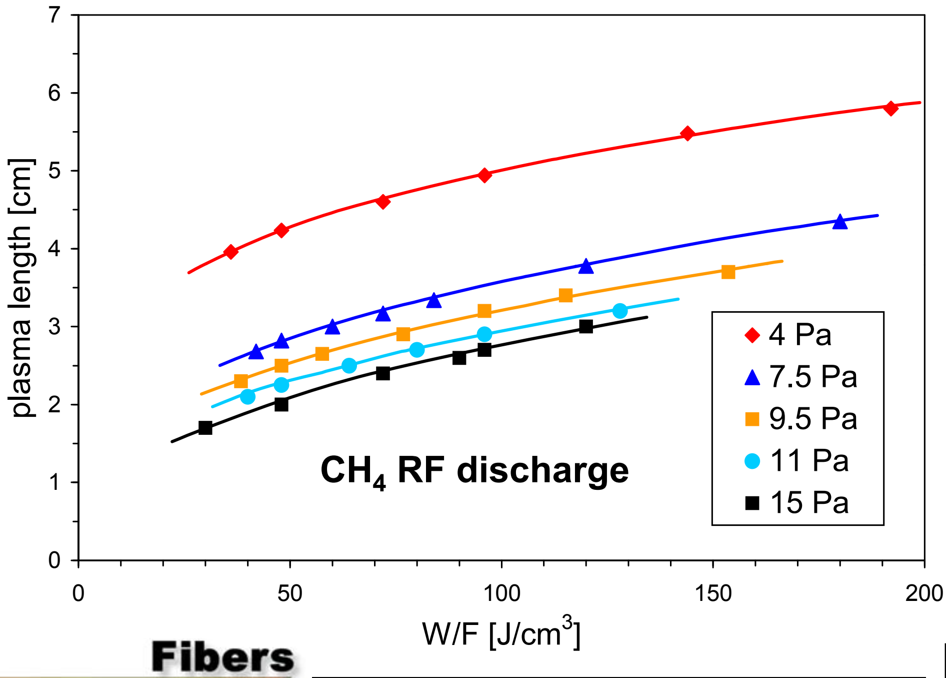


d_{gas} = 6.5 cm

CH_4 RF discharge

Influence of Pressure

Expanding plasma zone depending on energy input

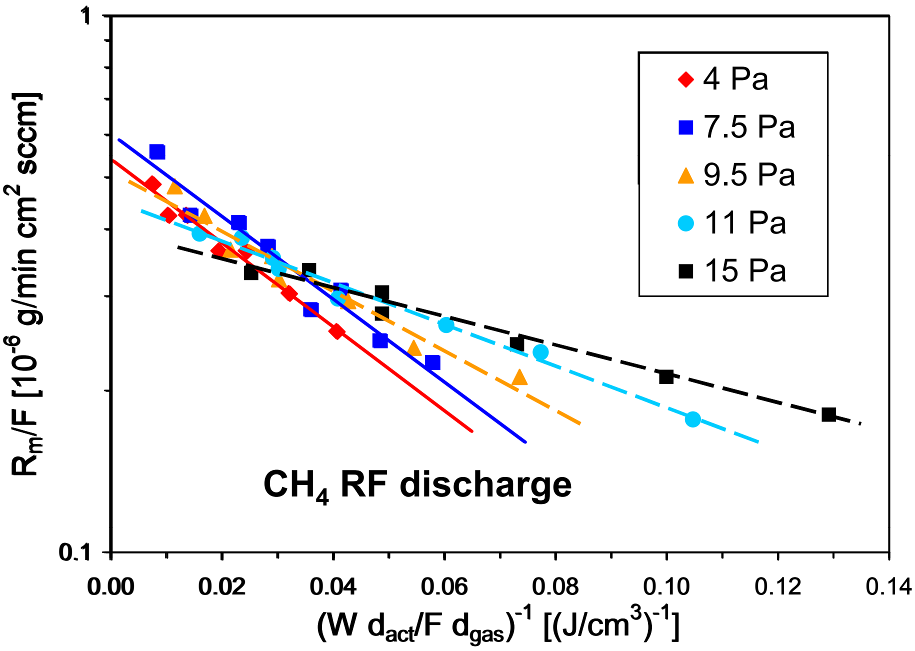


d_{act} increases with decreasing pressure (and power input)

D. Hegemann, Thin Solid Films 515, 2006, 2173.

Influence of Pressure

Consideration of similarity factor



$$S = \frac{W}{F}\frac{d_{act}}{d_{gas}}\frac{V_{gas}}{V_{dis}}$$

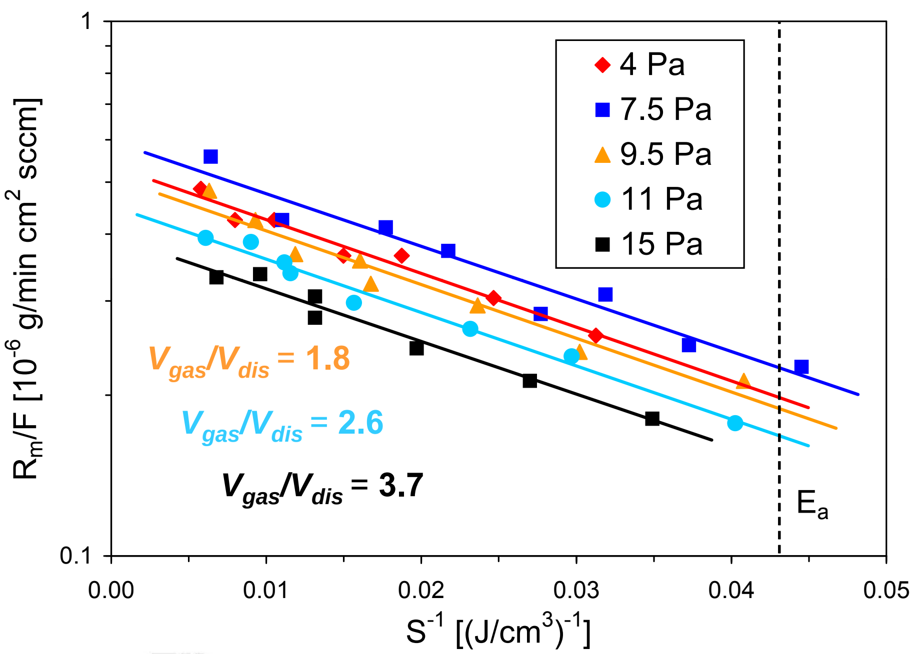
$V_{gas} > V_{dis}$

corner-dominated

Transition from volume- to corner-dominated discharge at a pressure >8 Pa.

Influence of Pressure

Consideration of similarity factor

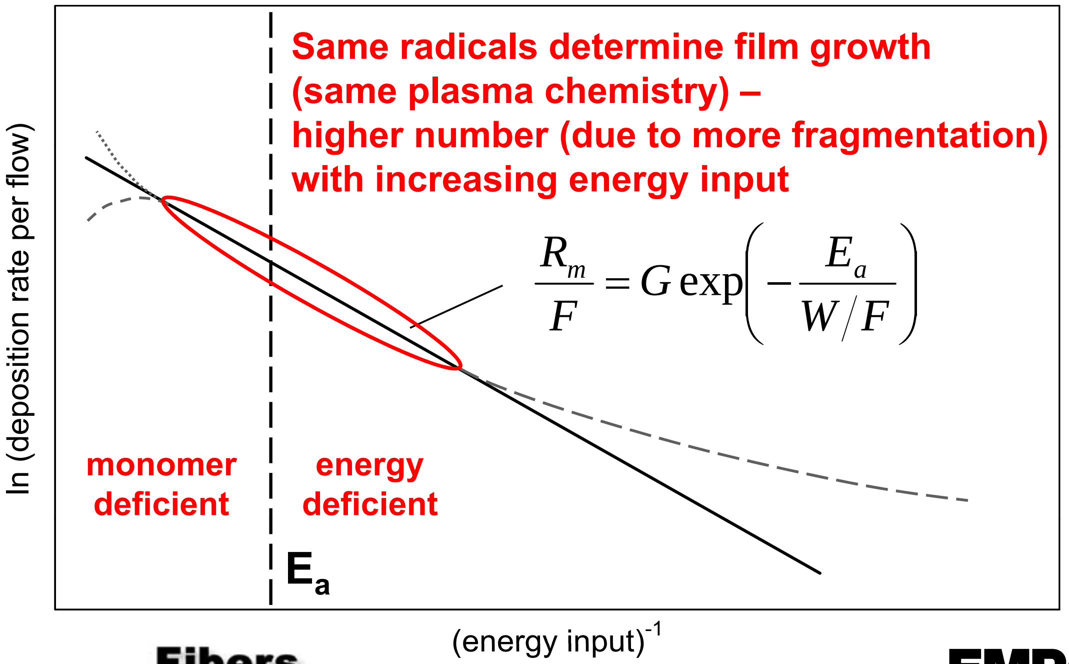


$$S = \frac{W}{F}\frac{d_{act}}{d_{gas}}\frac{V_{gas}}{V_{dis}}$$

Introduction of similarity factor with decreasing discharge volume yield same activation energy.

Plasma Polymerization

Formation of film-forming radicals



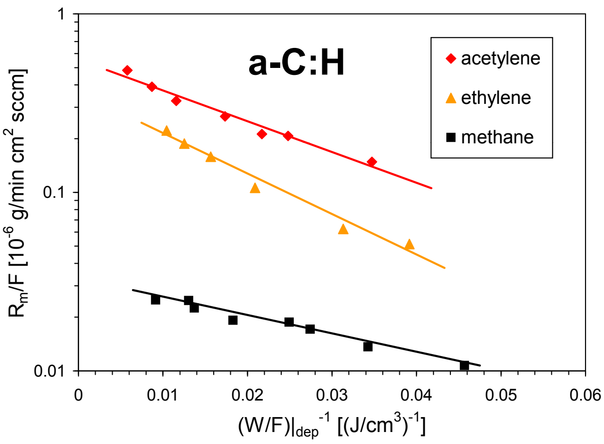
D. Hegemann et al., Plasma Process. Polym. 4, 2007, 229.

Influence of Monomers

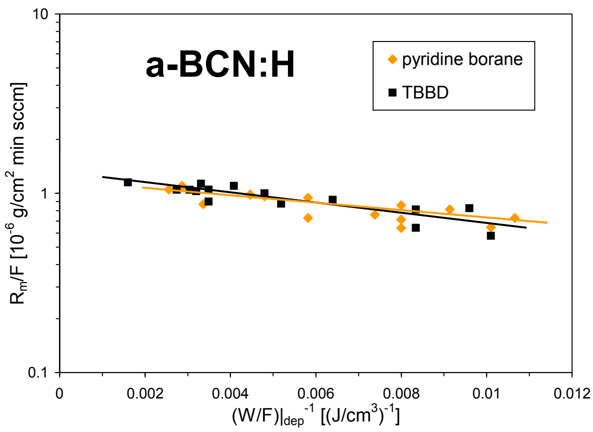
Generalized activation energy

similarity factor enables the finding of a generalized activation energy

$$S = \frac{W}{F}\frac{d_{act}}{d_{gas}}\frac{V_{gas}}{V_{dis}}$$



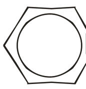
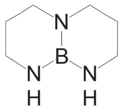
symmetric RF discharge



asymmetric, confined RF discharge

Influence of Monomers

Generalized activation energy of different monomers

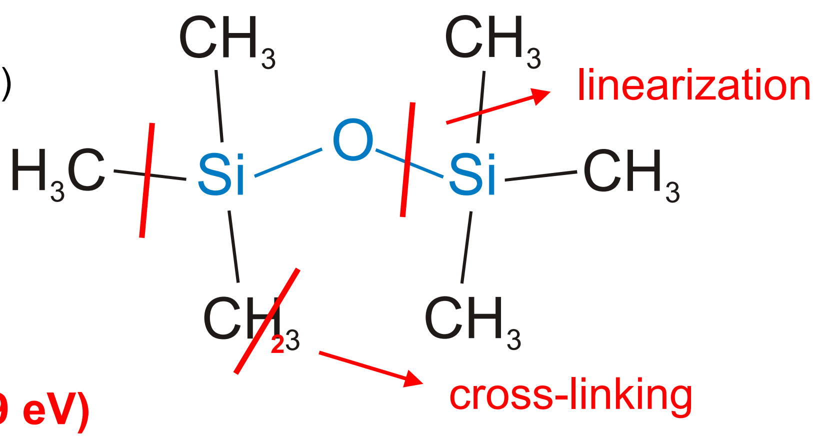
Monomer	Formula	Activation energy	Main dissociation
methane	CH_4	5.3 ± 0.5 eV	C-H, (H-H)
acetylene	C_2H_2	9.0 ± 0.7 eV	C≡C
ethylene	C_2H_4	12 ± 1.2 eV	C=C, C-H (2x)
pyridine borane		12 ± 1.5 eV	C-N, C-C, N:B, C-H
TBBD		15 ± 1.5 eV	C-N (3x), C-C, C-H
HMDSO	$(CH_3)_3$-Si-O-Si-$(CH_3)_3$	12.8 ± 0.7 eV	Si-C, C-H, Si-O

D. Hegemann et al., Plasma Process Polym 4, 2007, 229.

HMDSO Discharge

Initiation of HMDSO plasma polymerization

E_a = 55 J/cm^3
= 7.6 MJ/kg
= 1230 kJ/mol (HMDSO)
= 12.8 eV per molecule



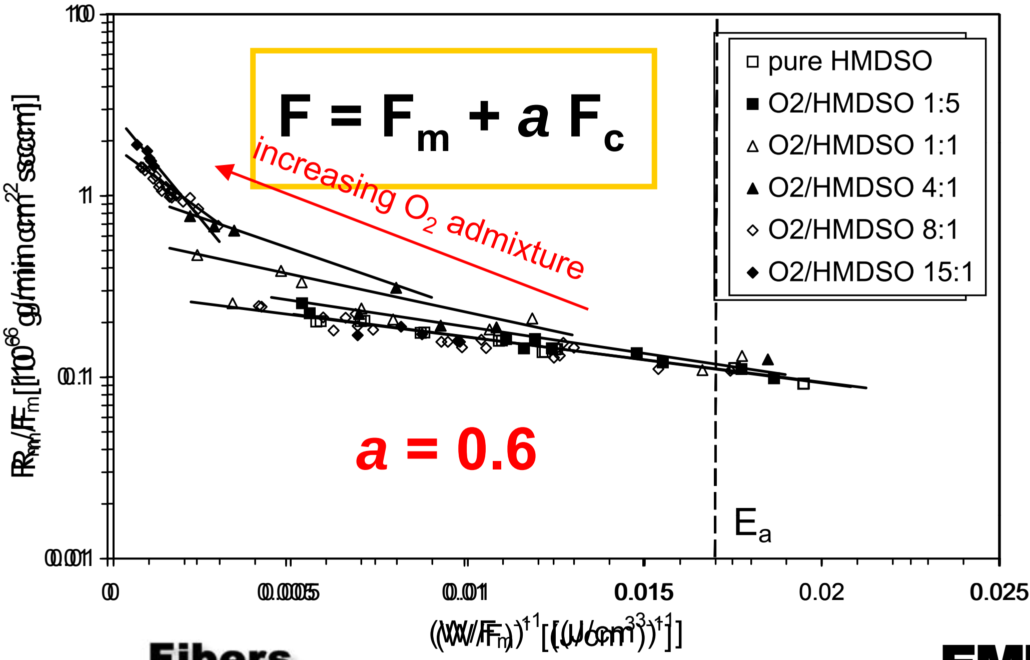
Si-O bond: 452 kJ/mol
Si-C bond: 360 kJ/mol
C-H bond: 435 kJ/mol

→ 1247 kJ/mol (12.9 eV)

The activation energy gives the dissociation energy to obtain the radicals that predominantly lead to plasma polymer growth.

Influence of Carrier / Reactive Gases

Oxygen added to HMDSO discharge



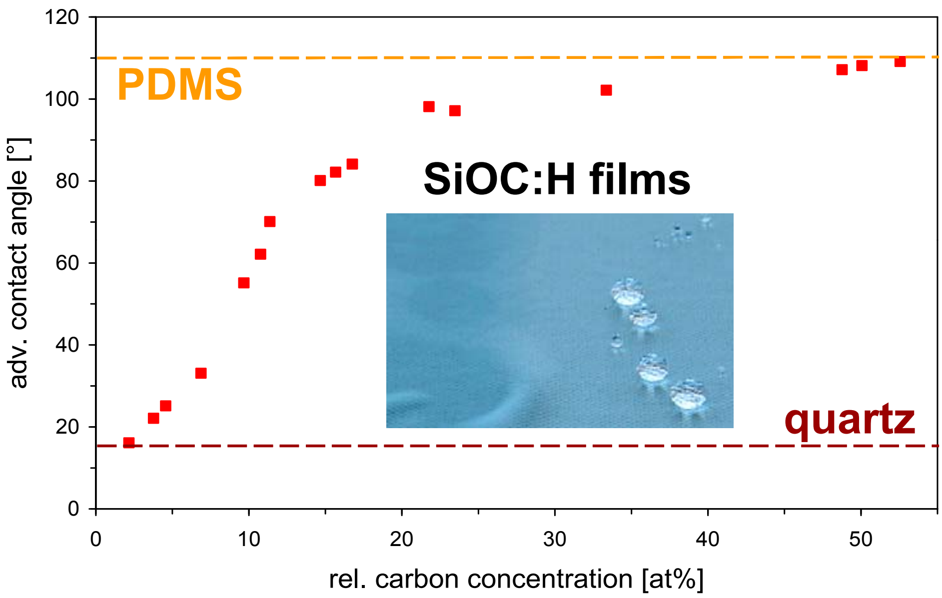
a: reaction crossection

→ energy consumed by carrier gas

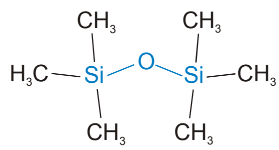
D. Hegemann, M.M. Hossain, Plasma Process. Polym. 2005, 2, 554.

Design of O_2/HMDSO Coatings

Control of wetting properties



O_2/HMDSO



The residual C concentration also scales with the crosslinking and thus the permeability.

Influence of Carrier / Reactive Gases

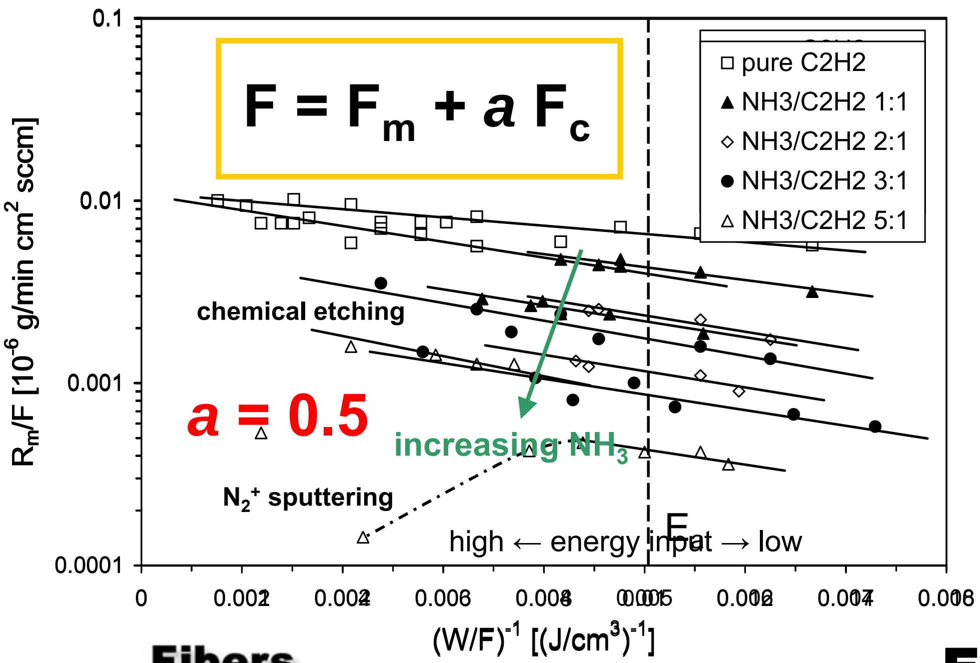
Correction factor for the combined flow $F = F_m + a\ F_c$

Monomer	Added gas	Flow factor *a*
hydrocarbons	Ar, He	0.05-0.1
	H_2	~0.15
	CO_2	~0.15
	N_2	0.35
	NH_3	0.5
HMDSO	O_2	0.6
Acrylic acid	H_2	~0.25

D. Hegemann et al., Plasma Process. Polym. 4, 2007, 229.

Influence of Reactive Gases

Plasma polymerization of hydrocarbon/ammonia



a: reaction crossection

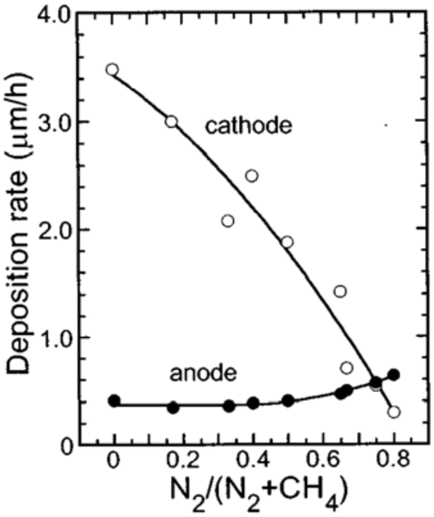
→ energy consumed by carrier gas

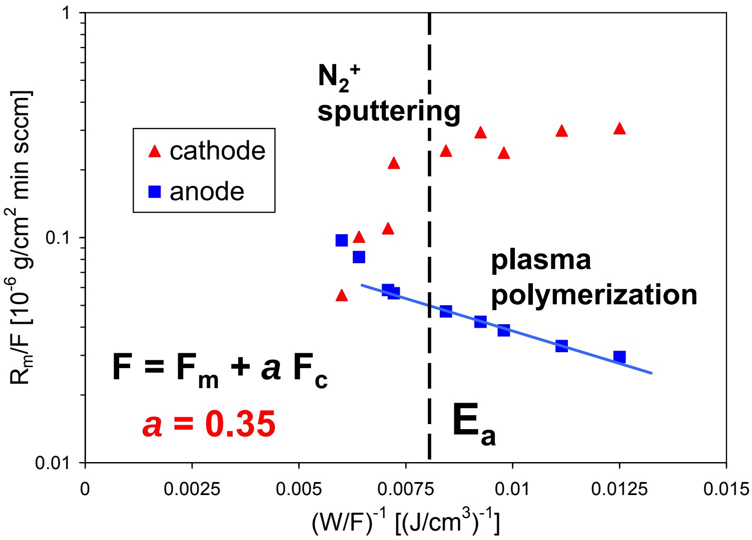
D. Hegemann, M.M. Hossain, Plasma Process. Polym. 2005, 2, 554.

Re-Engineering

Plasma polymerization of asymmetric N_2/CH_4 discharges

RF plasma, 40 Pa, -650 V_{bias}



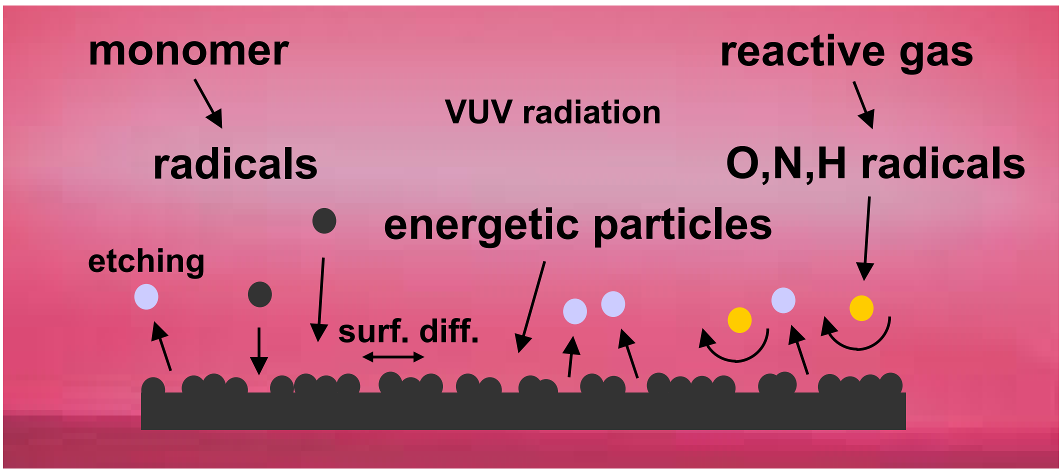


M. Zhang, Y. Nakayama, T. Miyazaki, M. Kume, J. Appl. Phys. 85, 1999, 2904.

Deposition of Nanoporous Coatings

Rivaling deposition/etching processes

plasma polymerization + chem./phys. etching

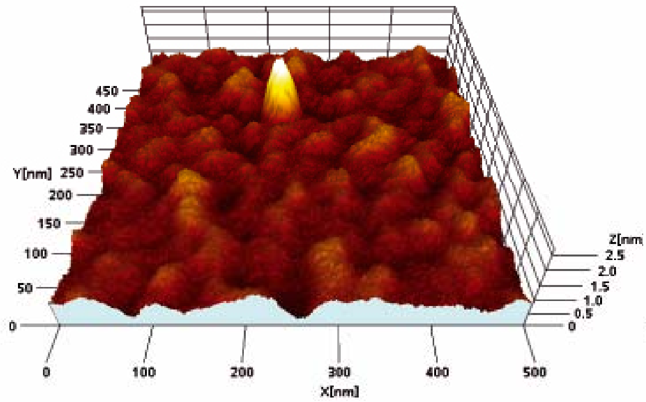


Advanced Fibers
Dirk Hegemann, Plasma Polymerization, ISPC 18
EMPA Materials Science & Technology

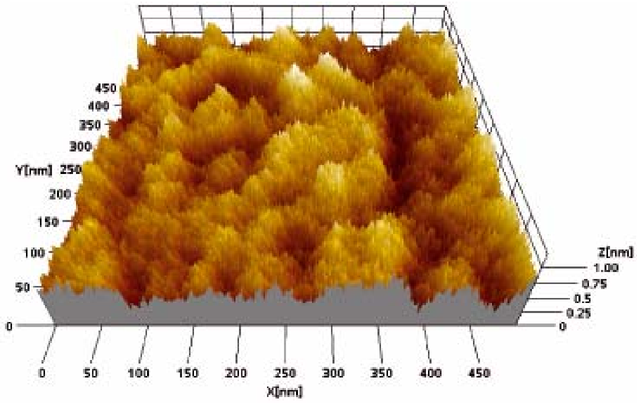
Deposition of Nanoporous Coatings

Hydrocarbon/ammonia RF discharges

Amine-functionalized coatings



porous structure: <30 nm

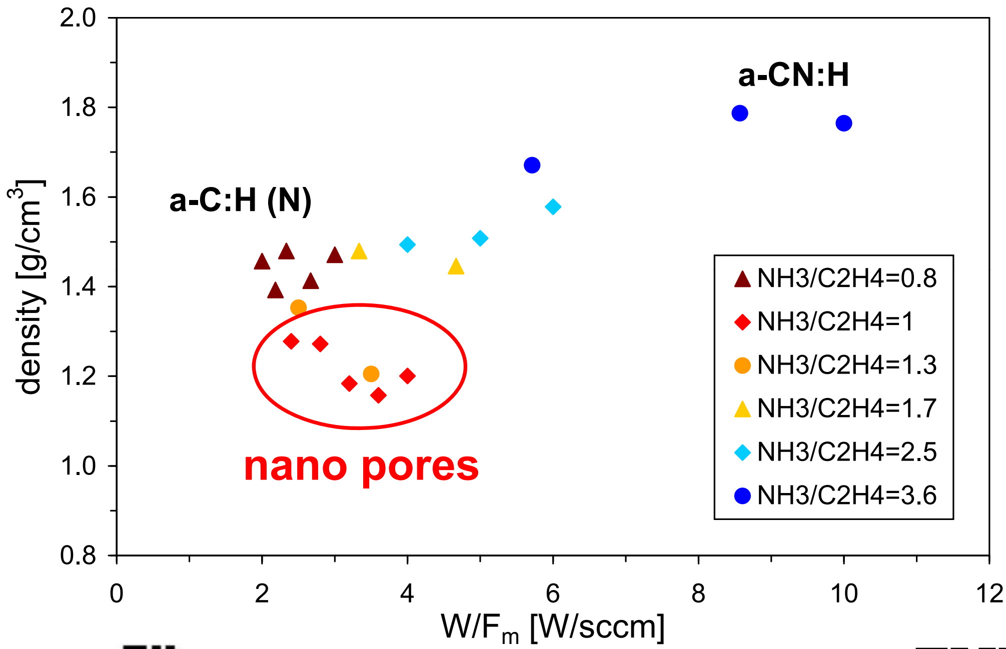


porous structure: <20 nm

D. Hegemann, M.M. Hossain, D.J. Balazs, Prog. Organic Coat. 58, 2007, 237.

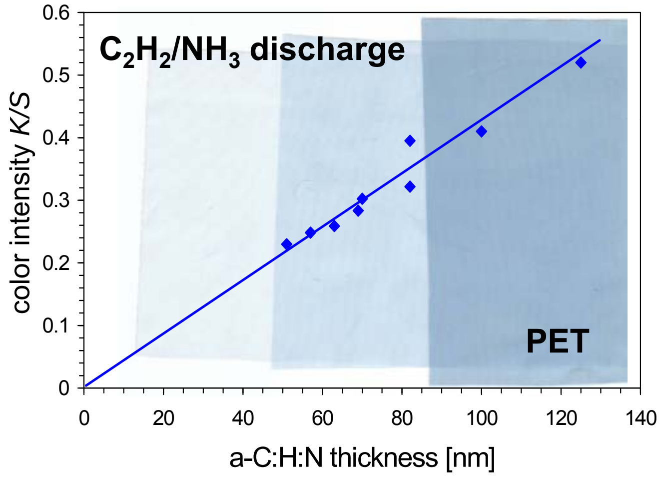
Deposition of Nanoporous Coatings

Film density related to porous structure

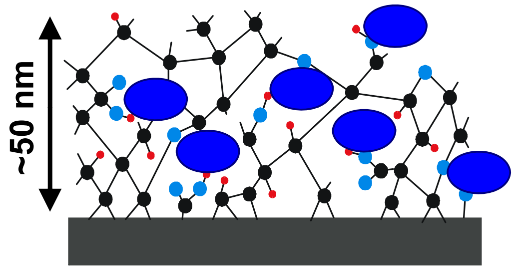


Nanoporous Plasma Coatings

Dyeing of plasma coatings on textile fabrics



dyestuff: C.I. Acid blue 127:1

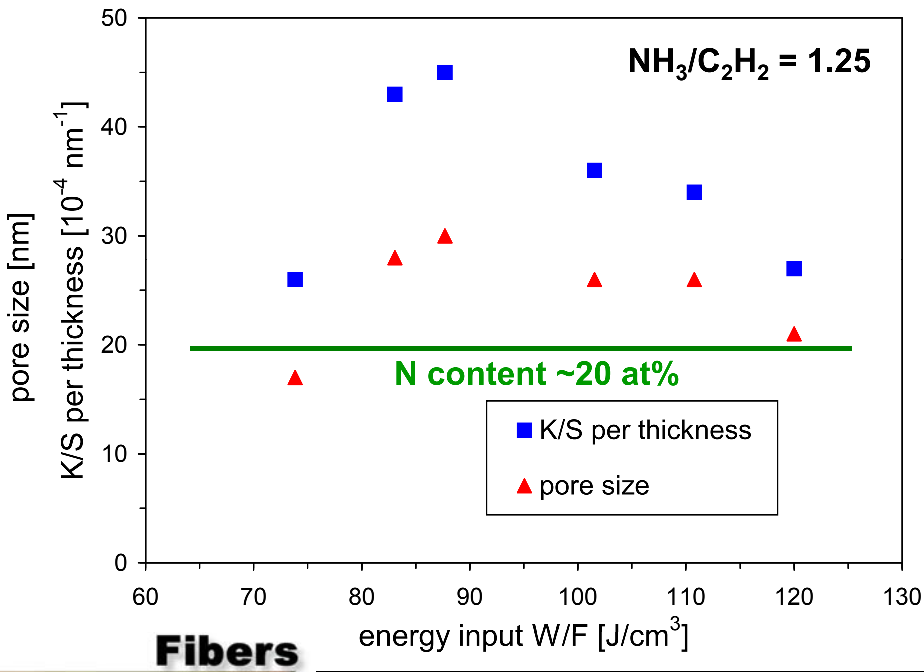


Dye molecules (~3 nm) are able to diffuse into nanoporous structure.

M.M. Hossain, A.S. Herrmann, D. Hegemann, Plasma Process. Polym. 4, 2007, 135.

Nanoporous Plasma Coatings

Dyeability (color intensity K/S) vs. pore sizes



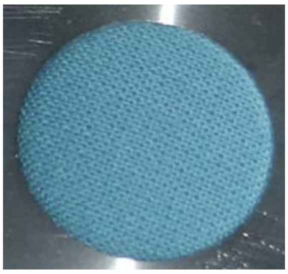
Color intensity correlates with pore sizes, while overall N content is constant for a fixed NH_3/C_2H_2 ratio.

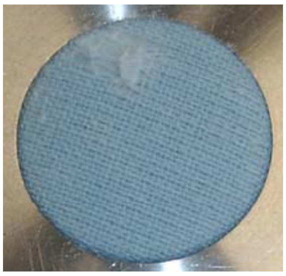
Nanoporous Plasma Coatings

Permanence of dyed plasma coatings on textile fabrics

Martindale | before testing | after 70‘000 cycles

PP multifil



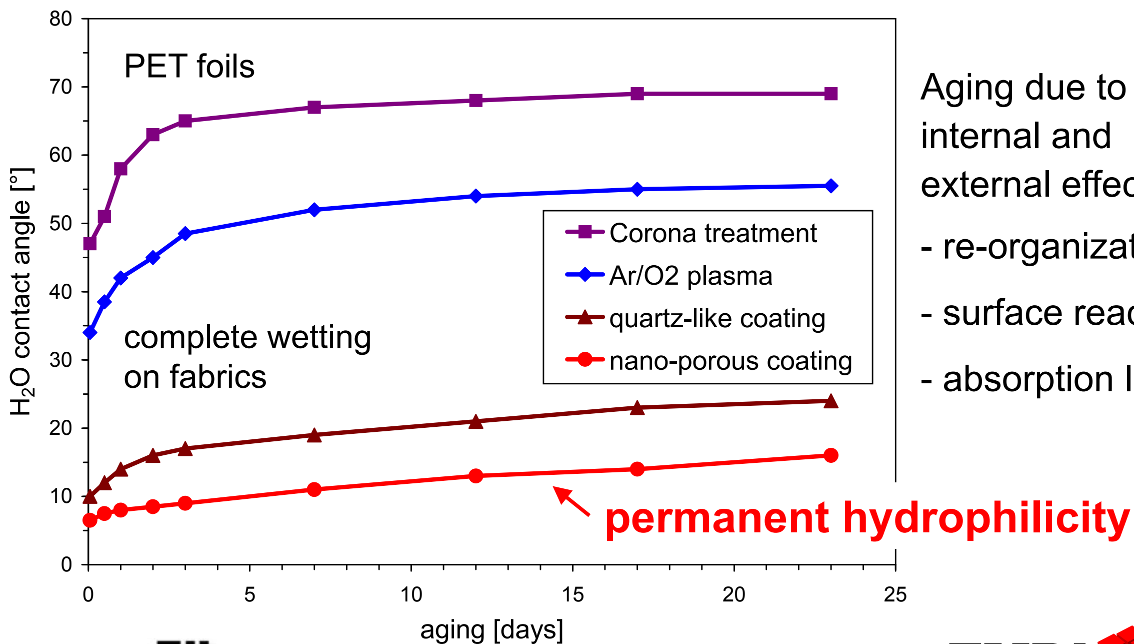


PET monofil

dyestuff: C.I. Acid blue 127:1

Nanoporous Plasma Coatings

Hydrophilic treatment – hydrophobic recovery



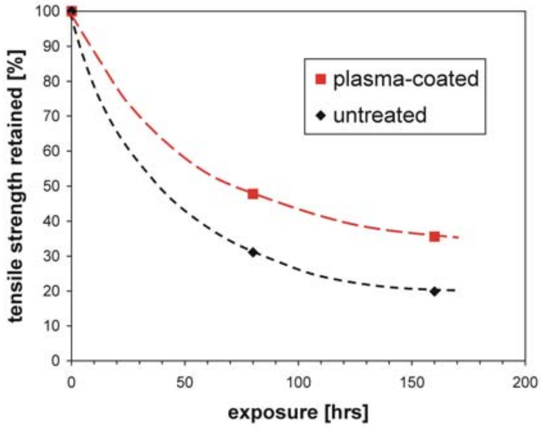
Aging due to internal and external effects:

- re-organization
- surface reactions
- absorption layers

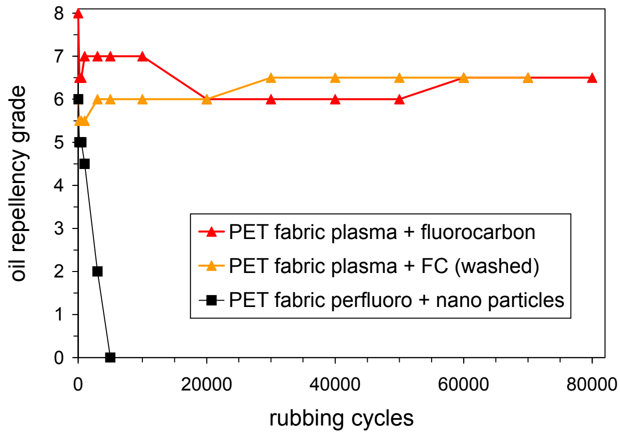
Nanoporous Plasma Coatings

Loading with wet chemicals

UV absorber



Fluorocarbon



UV exposure of aramid fabrics

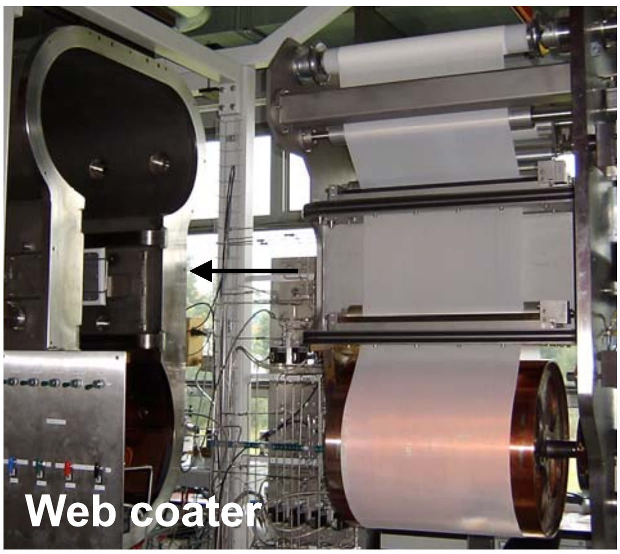
Martindale abrasion test

Transfer of Plasma Polymerization

Scale-up to Web Coater

Continuous processing of textiles, membranes, foils, bands, and papers

width = 65 cm
velocity = 0.1..100 m/min
A_{dep} = 10‘000 cm^2

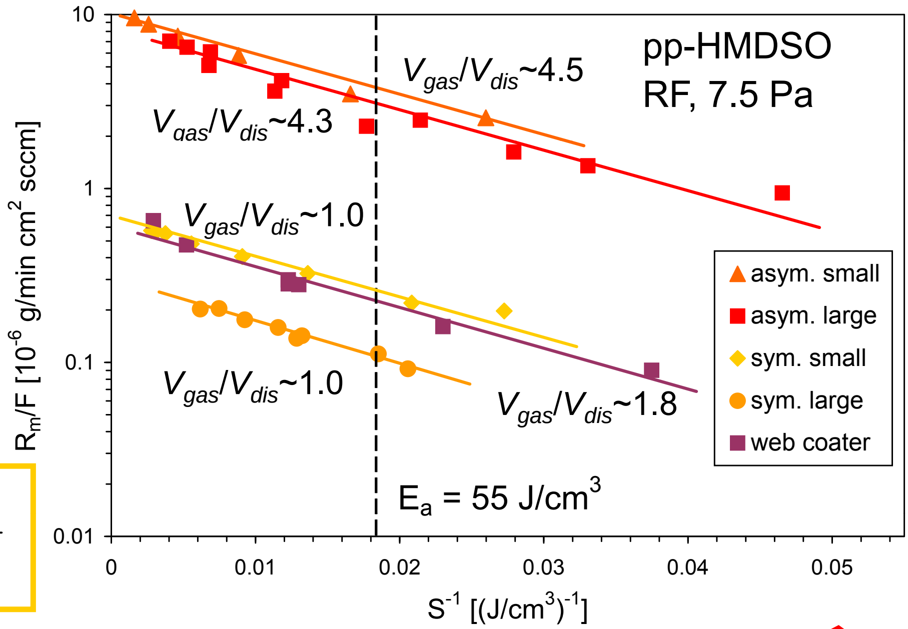


Transfer of Plasma Polymerization

Different reactor geometries

Scale-up can be performed succesfully using the identified similarity parameter

$$S = \frac{W}{F} \frac{d_{act}}{d_{gas}} \frac{V_{gas}}{V_{dis}}$$

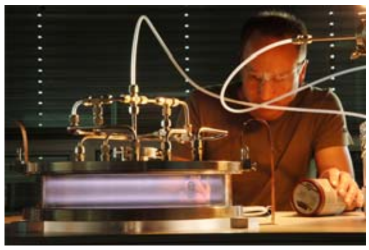


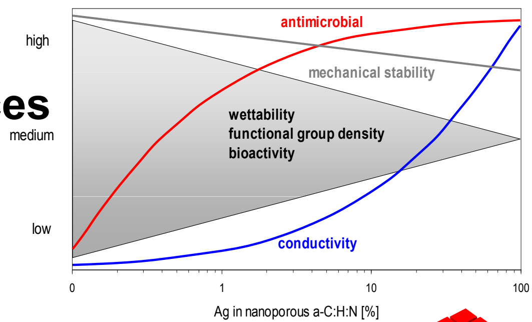
Outlook

Control of Plasma Polymerization Processes

control / design of

- plasma reactors
- nano-scaled coatings
- nanoporous coatings
- multifunctional (textile) surfaces
- transfer into industry





Acknowledgement

Laboratory of *Advanced* Fibers

- **Plasma group**

contact
dirk.hegemann@empa.ch

D. Balazs, M. Hossain, E. Körner, U. Schütz, M. Amberg, S. Guimond

- **Chemistry group**: M. Heuberger, A. Ritter, F. Reifler
- **CTI Bern (funding)** KTI/CTI