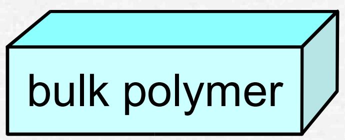
polymer surfaces

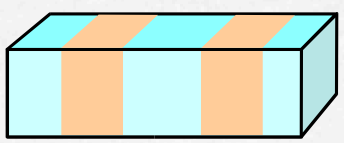
Classes of Polymer Surfaces

1) as substrate:



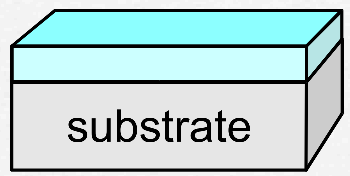
"external" surface

block copolymer



"internal" surface
→ **interface**

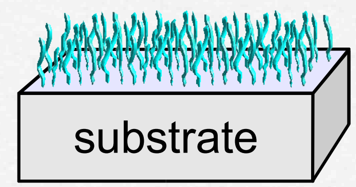
2) as surface layer:



surface & interface

(→ adhesion and cohesion important parameters)

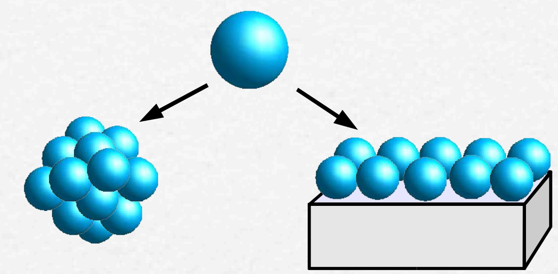
3) as surface molecules:



individual molecules share surface & interface

(→ large gradient of external influence on single molecule possible)

4) as discrete particles:



aggregate

surface layer

often very large surface-to-volume ratio

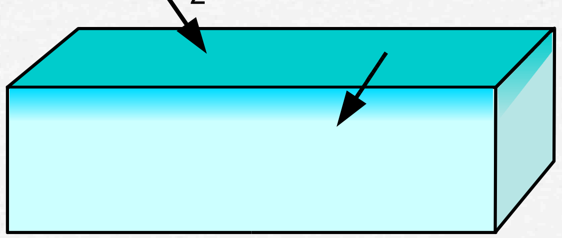
(→ substantially different behavior to bulk material)

General Modification Strategies

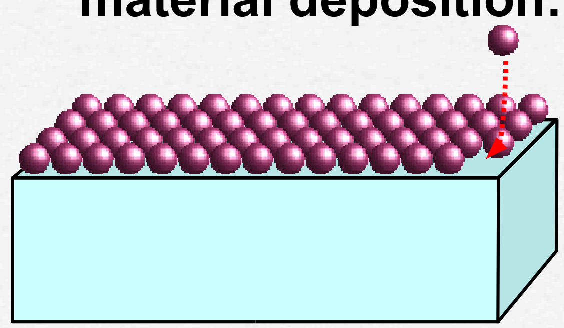
- surface transformation:

reagents (e.g. O_2)

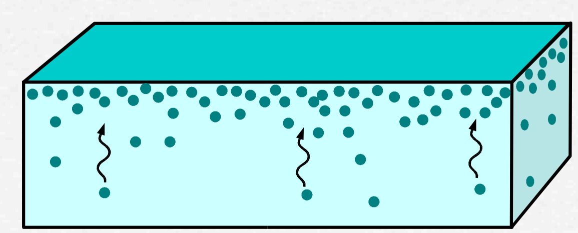
energy (e.g. $h\nu$, γ, kT)



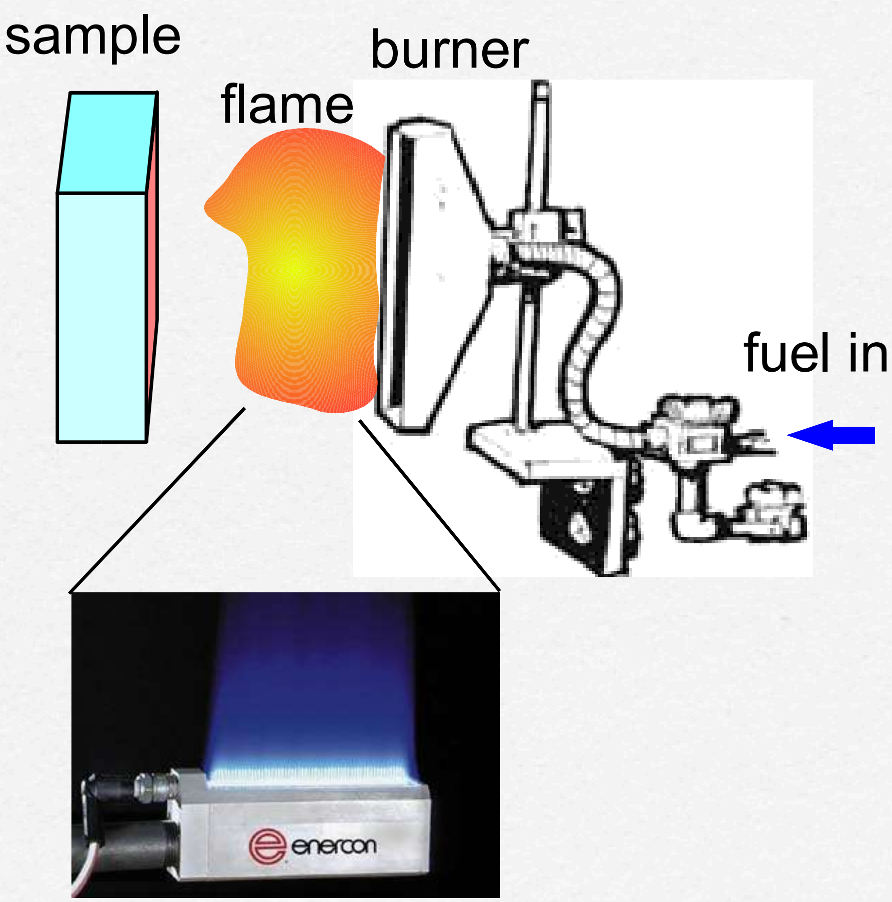
- film formation by material deposition:



- surface segregation:



Flame Treatment



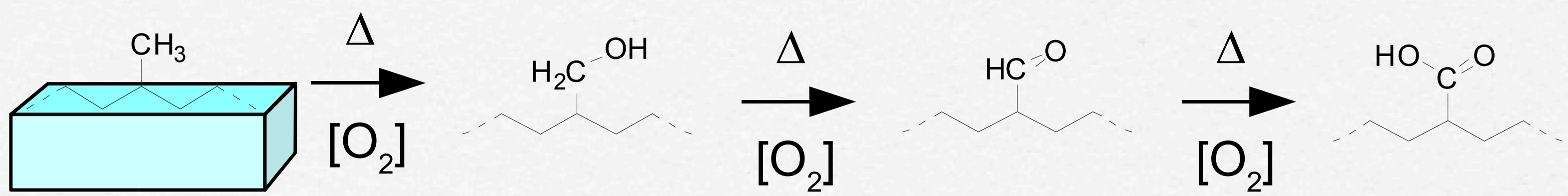
the polymer surface (often polyolefins) is treated with a burner flame (1000-2000°C, 0.2-0.3 s)

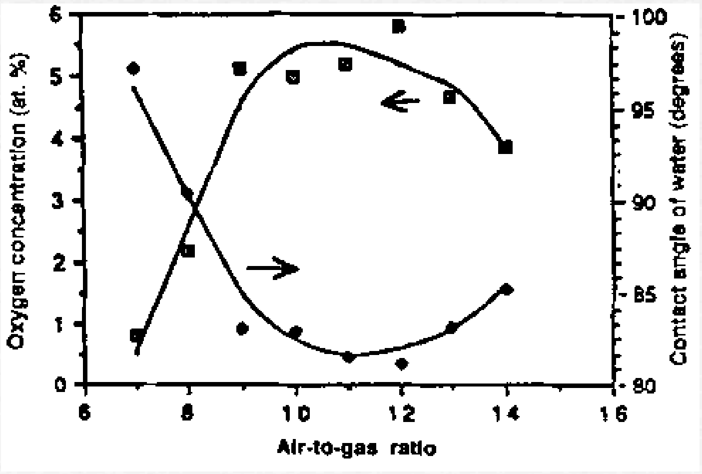
process parameter:
type of gas, air-to-gas ratio, flow rates, position of flame to object, treatment time

→ heat and reactive components of the flame cause chemical modification of the surface

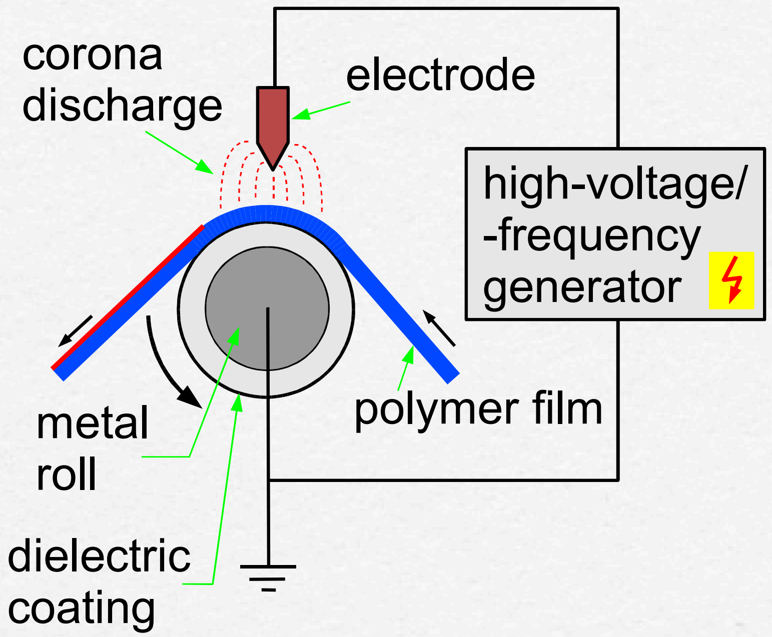
→ promotes adhesion (for gluing or printing) and wetting

surface reactions:

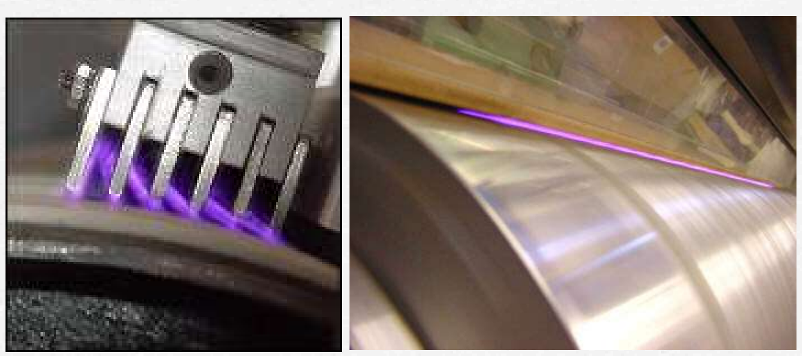




Corona Discharge Treatment



corona discharge glow:



the polymer surface (often polyolefins) is treated with the products (normal pressure plasma) from a corona discharge in ambient atmosphere (about 4000-35000 J m^2)

the workpiece (usually thin polymer film) is placed between an electrode an a grounded metal roll

electrons are ejected from the electrode by strong electric field

→ these electrons collide with air molecules and the polymer surface to generate **free radicals, ions, photons, excited and reactive intermediates**

→ reactions at the polymer surface can lead to:
a) **chain scission**,
b) **cross-linking**, and
c) introduction of **functional groups** (oxidation)

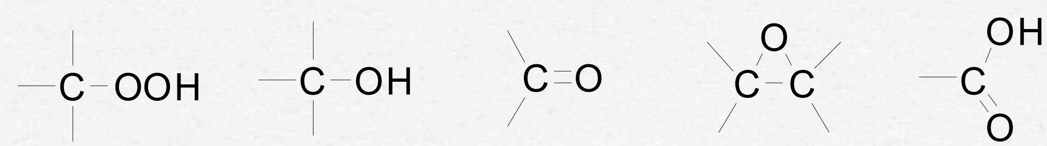
→ promotes adhesion (for gluing or printing) and wetting

chemical reactions:

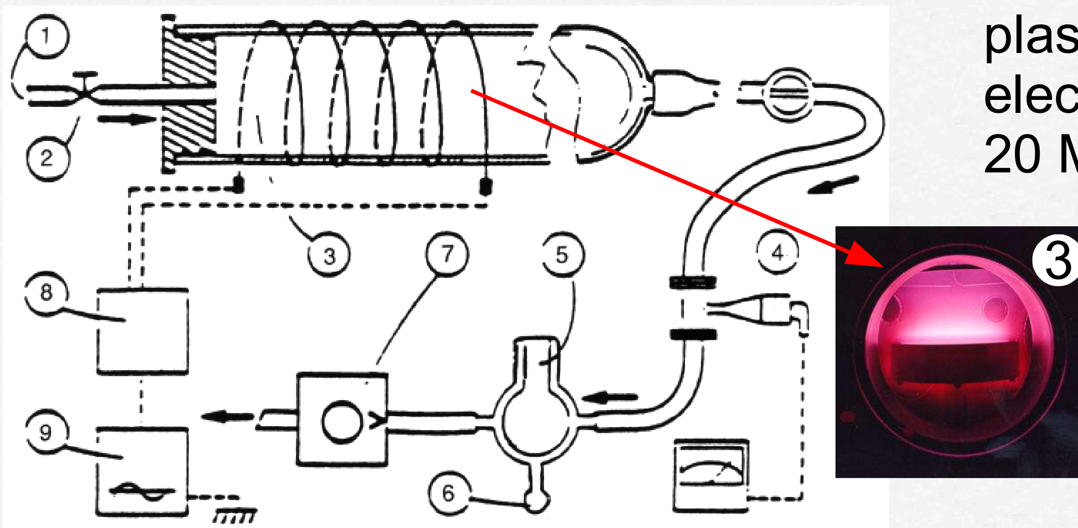
R-H → R• + H•

R-R' → R• + R'•

R• + O_2 → R-O-O• → ...



Plasma Treatment



1) gas inlet   2) valve   3) plasma + sample
4) pressure gauge   5) liq. N_2 6) trap
7) vac. pump   8,9) matching, RF gen.

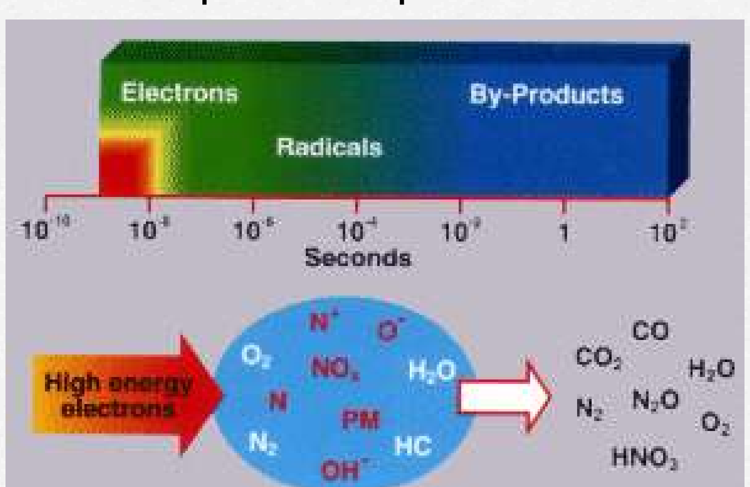
plasma generation in vacuum / low gas pressure *via* electro-magn. high frequency (RF) field (100 kHz, 10-20 MHz, 2.45 GHz) → glow discharge (RFGD)

→ the generation of **functional groups** at the polymer surface can be controlled by the choice of plasma **gas** (e.g. H_2O, O_2, Ar, N_2, F_2, CO_2, NH_3)

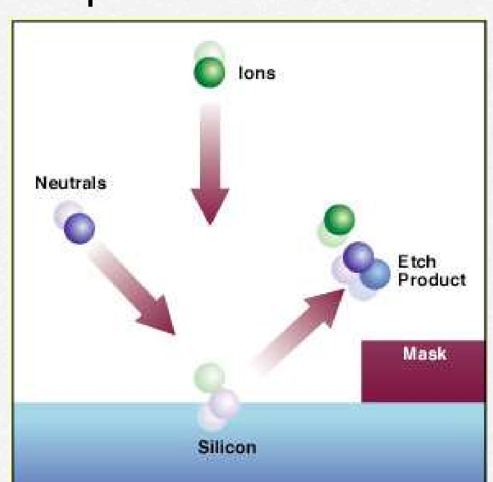
→ free electrons, ions, radicals, and vacuum UV are reactive species (penetration depth few 10 nm)

→ functional group generation, material ablation, chain scission, cross-linking

reaction cascade in a pulsed normal pressure plasma



plasma ablation



process parameter:
- type of gas, pressure, flow rate,
- excitation power, exc. frequency,
- time of treatment, pulse duration / pause, temp. of substrate
- geometric factors (reactor, sample)

→ improved adhesion (metal films and printing)

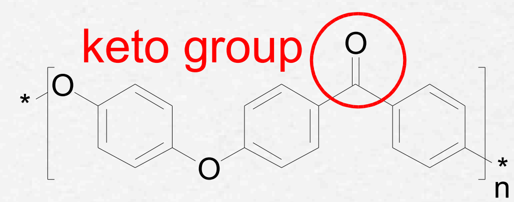
(Wet) Chemical Treatment

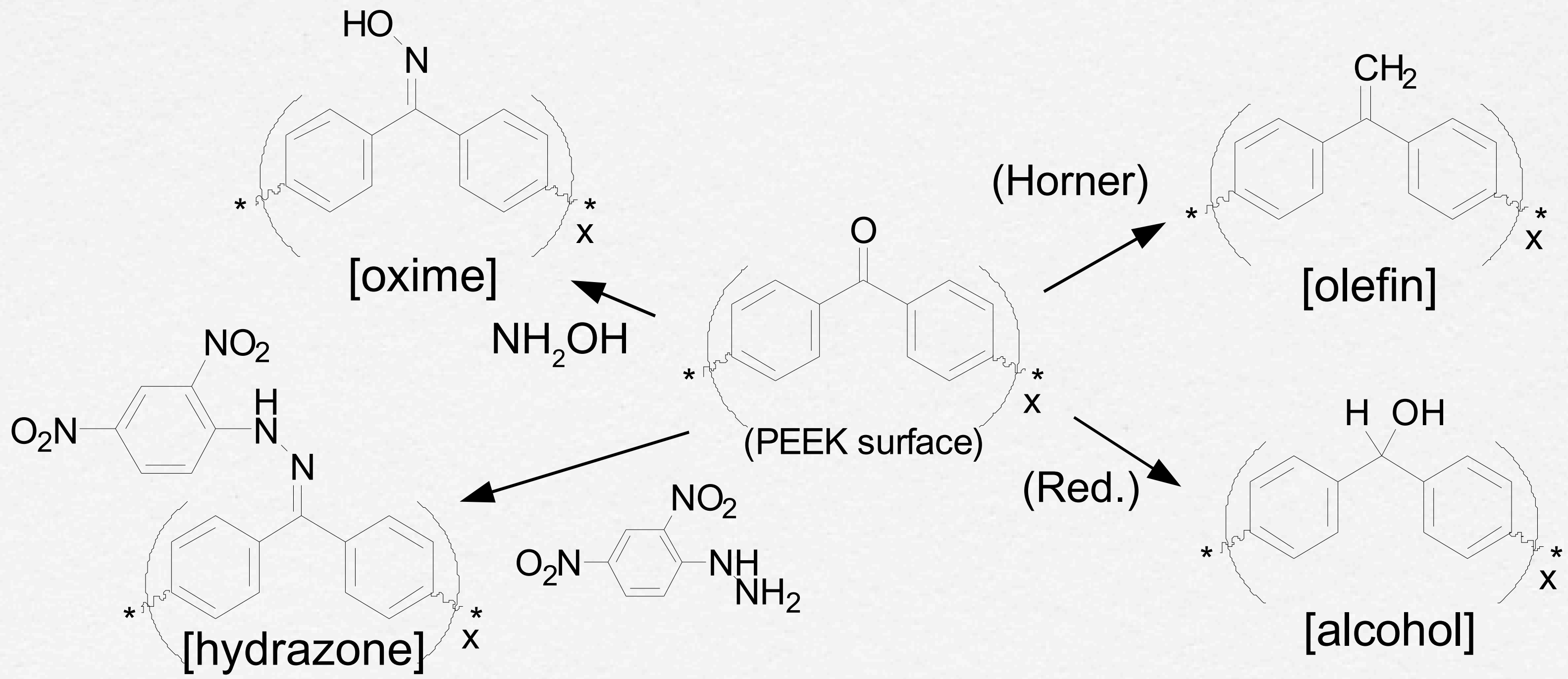
chemical **transformation**, **etching** and **dissolution** of polymer surfaces by active reagents (often oxidizers like H_2SO_4, $KMnO_4$, CrO_3 / H_2CrO_4, or transformation of -COOH or -OH with SO_2Cl_2)

→ often differentiation between **amorphous** (more reactive) and **crystalline** (more inert) regions - enhanced by solvent treatment

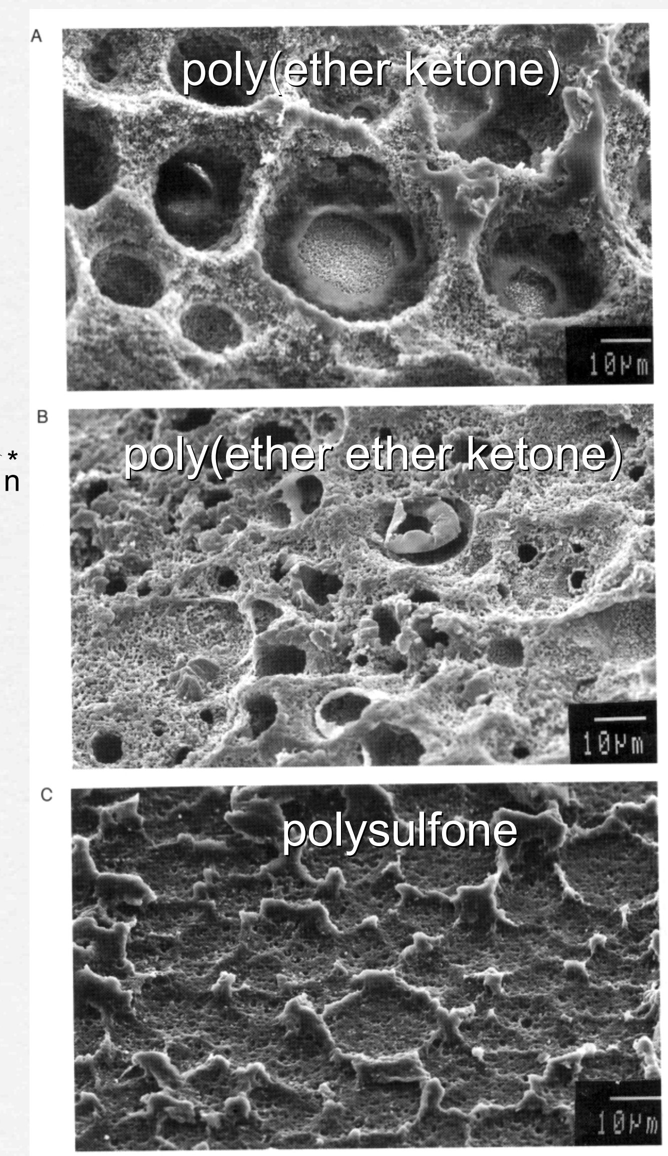
→ improves roughness and adhesion of metal film in plating

example: specific **chemical transformation** of poly(ether ether ketone) PEEK:



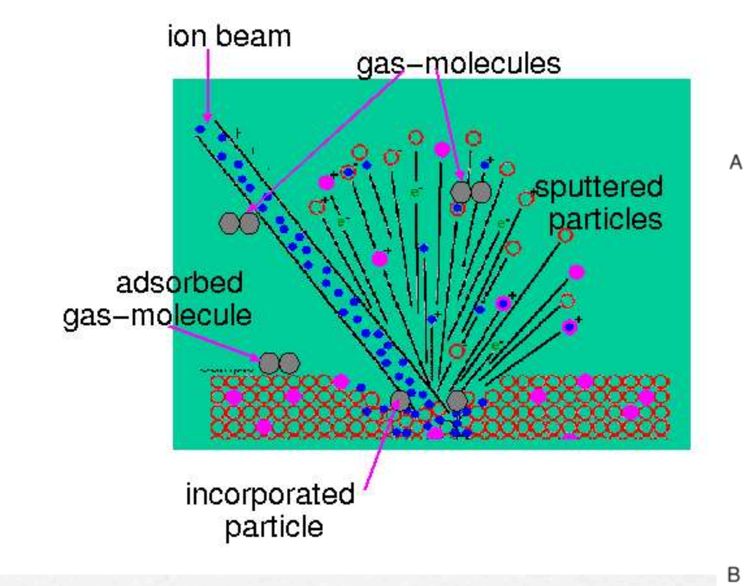


modification of **surface morphology** by wet chemical etching with H_2SO_4

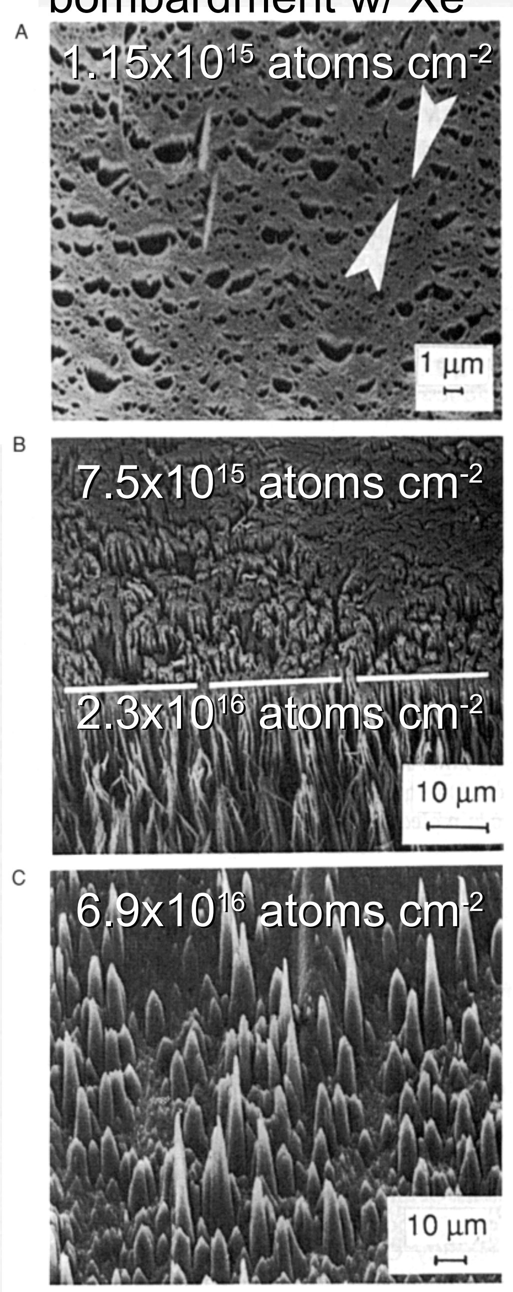


Ion-Beam Modification

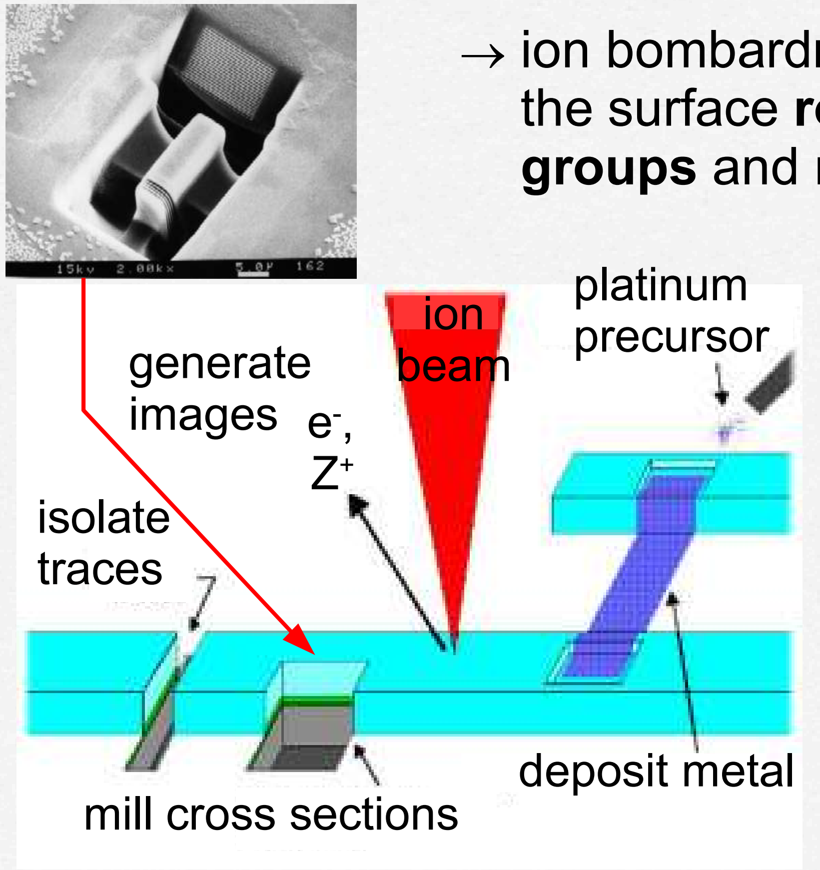
polymer surface is bombarded with **ions** (often focused as beam) to **ablate / mill** the substrate material or to **deposit** new material
→ by **scanning** the focused ion beam **3D structures** with >10 nm resolution can be generated



surface morphology of PTFE after ion bombardment w/ Xe



ion-milled semiconductor



→ ion bombardment of the polymer surface increases the surface **roughness**, generates new **functional groups** and may increase **conductivity**

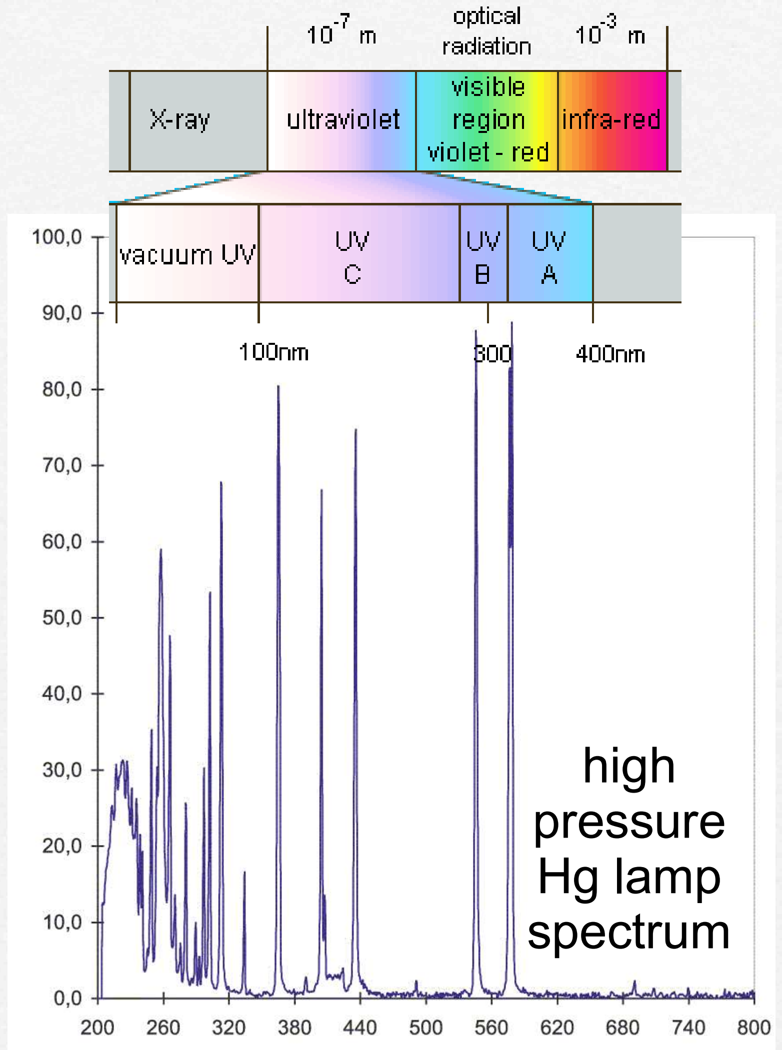
process parameter:
type of ions, ion energy, beam dose
type of polymer

→ **reactions** at the polymer surface:
a) reduction
b) oxidation
c) chain fragmentation
d) cross-linking
e) loss of heteroatoms & aromaticity

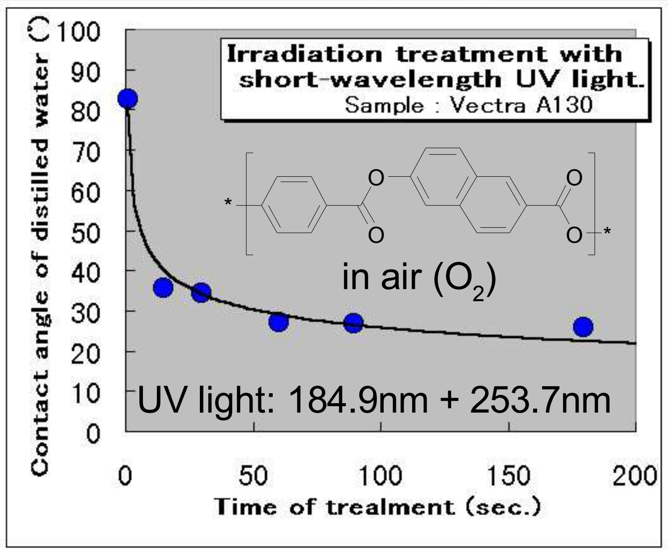
T6) UV-Irradiation

"UV cross-linker"

irradiation treatment with **short-wavelength UV** light (~180-250 nm) to **activate** polymer surfaces, or to **decompose** dirt on the surface



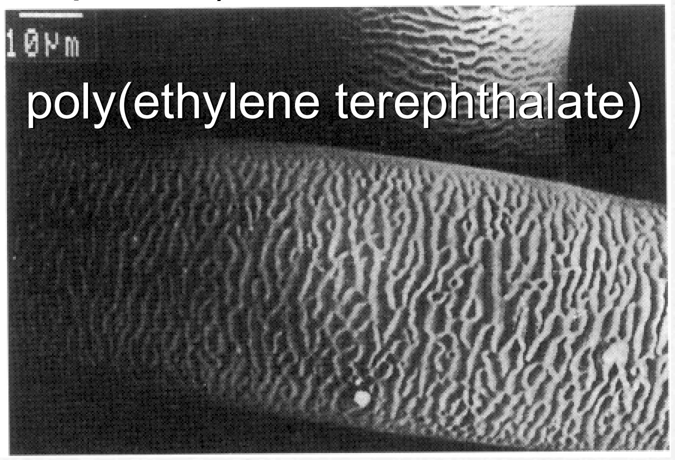
→ **energy** of light induces **chemical reaction** in and near the surface (structuring by irradiation through photomask possible)



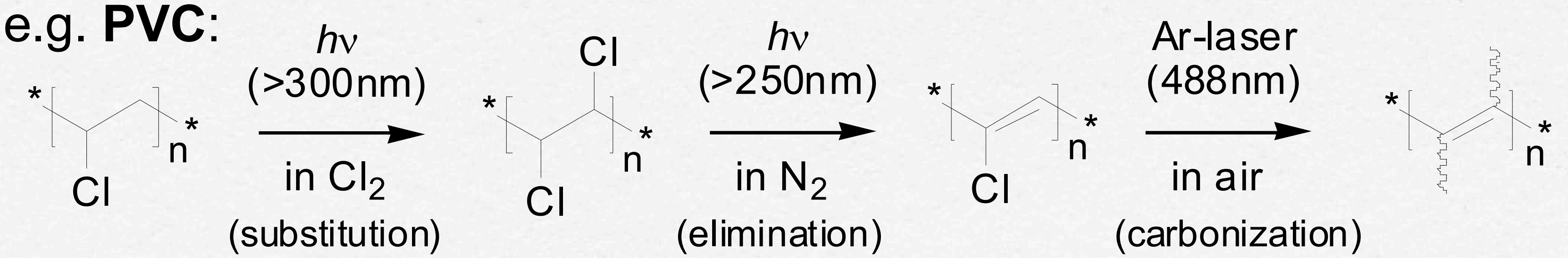
process parameter:
wavelength (photon energy), dosis (energy per area), surrounding species / medium

→ possible **reactions**:
a) ablation (e.g. activation of oxygen to ozone → volatile ox. prod.)
b) surface group transformation (e.g. elimination)
c) introduction of functional groups by photochemical reaction with species from the environment / medium (e.g. -COOH by ox.)

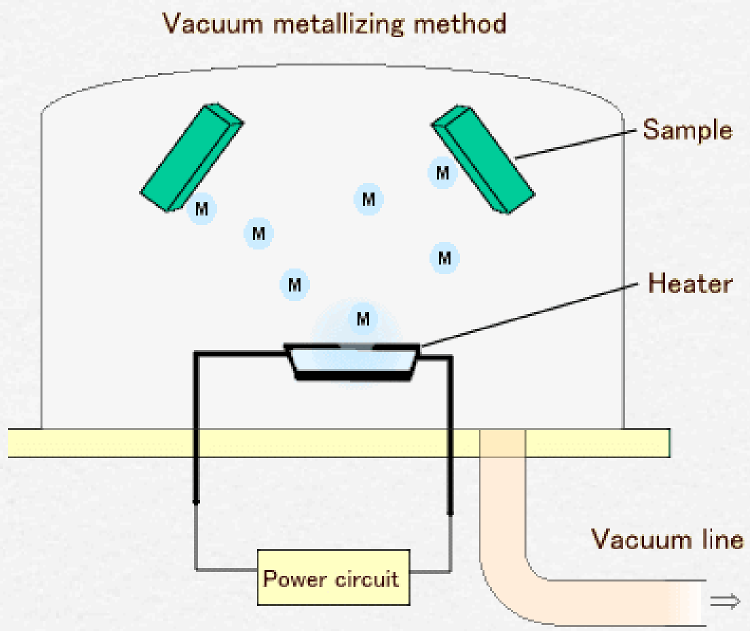
UV laser (248 nm, 60 mJ cm^{-2}, 10 pulses)



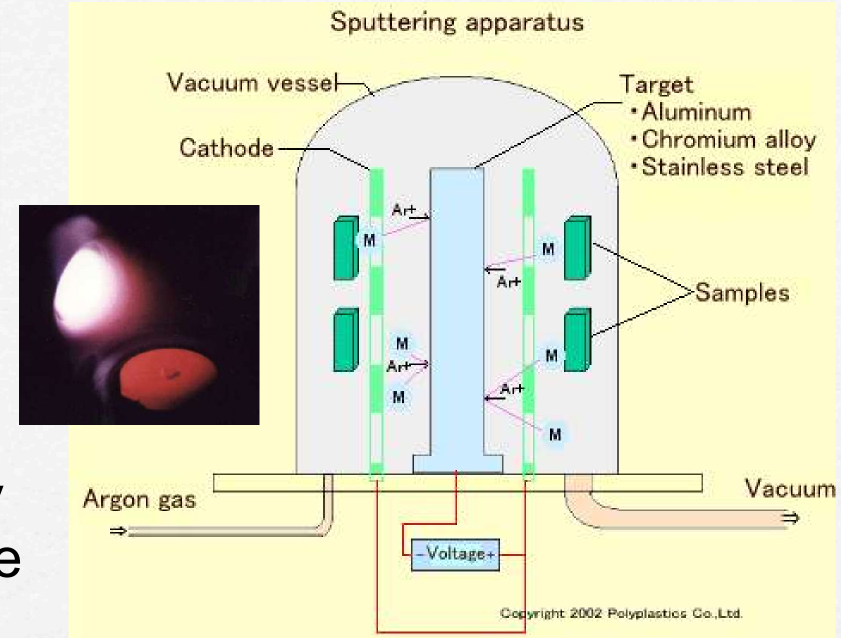
e.g. **PVC**:



Material Deposition: D1) Metalization

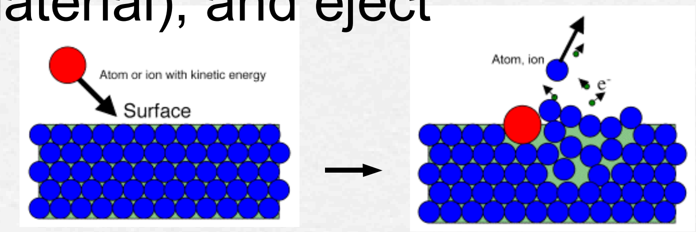


a) metal **evaporation** and **sputtering**:



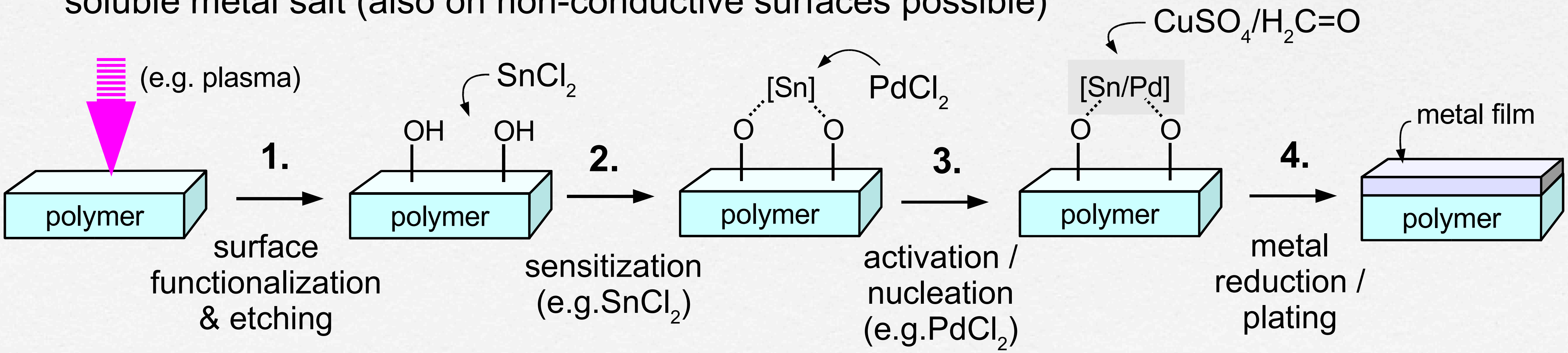
metal evaporation in vacuum by heat, e$^-$-beam, or glow discharge

"**sputtering**": high voltage across a low-pressure gas (e.g. Ar, 5 millitorr) creates plasma (glow discharge), energized plasma ions strike "target" (coating material), and eject atoms from target which travel to and bond with the substrate



b) electroless / **chemical** metal deposition (plating):

usually deposition of a metal film (e.g. Cu, Ni, Co, Au, Ag, Pd, Pt) by chemical reduction of a soluble metal salt (also on non-conductive surfaces possible)

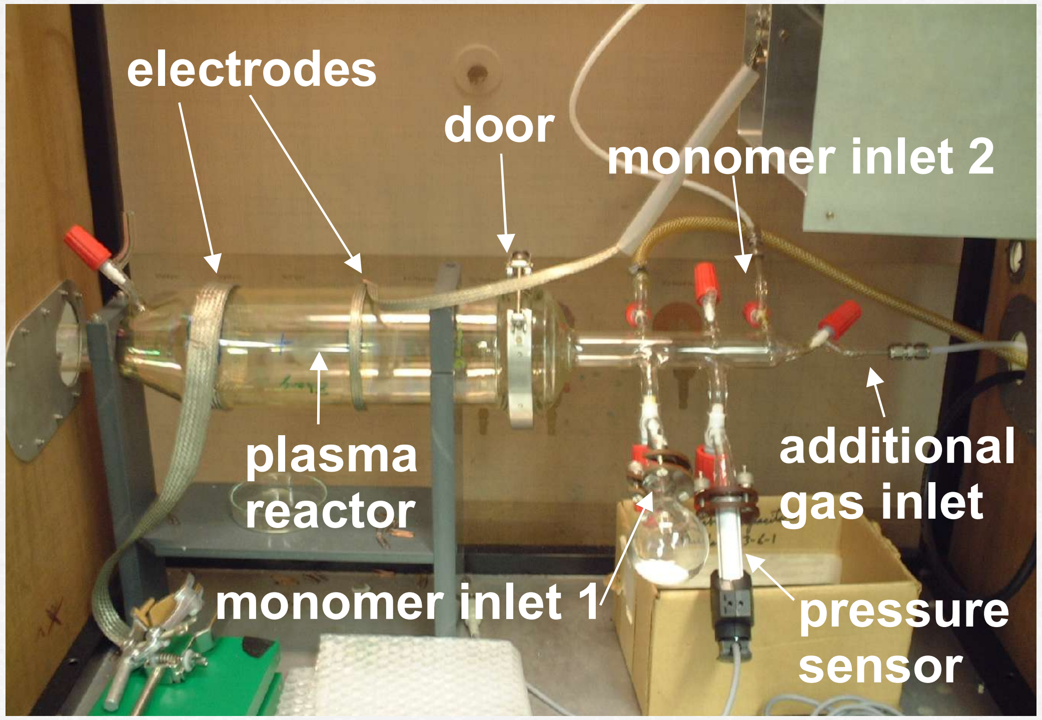


D2) Plasma Polymerization

plasma polymerization or **plasma enhanced chemical vapor deposition** (PECVD) utilizes a similar setup as shown in T3) "Plasma Treatment", but **addition** of **monomer** through gas phase to generate a **polymer film** at the **substrate surface**

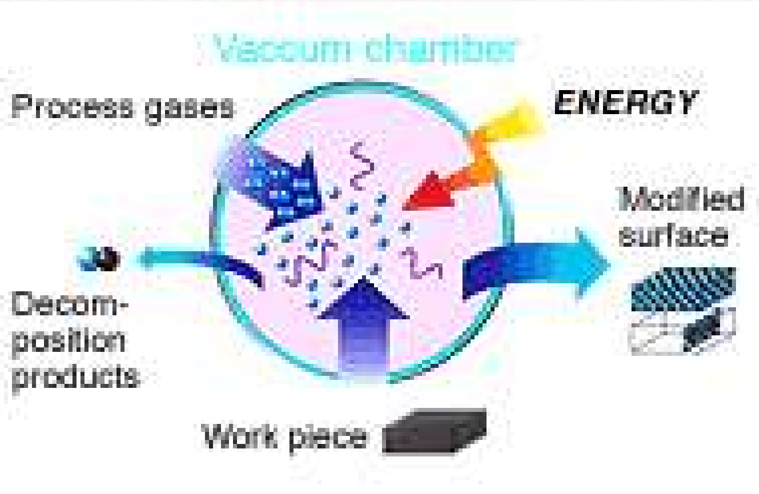
→ **CAP-mechanism** (competitive ablation and polymerization: **parallel** processes of **ablation** (material removal) and **polymerization** (material deposition) in plasma of monomer at low gas pressure

→ can generate **homogeneous**, highly **cross-linked** polymer films with thicknesses of up to 1 μm (~10 nm min^{-1})

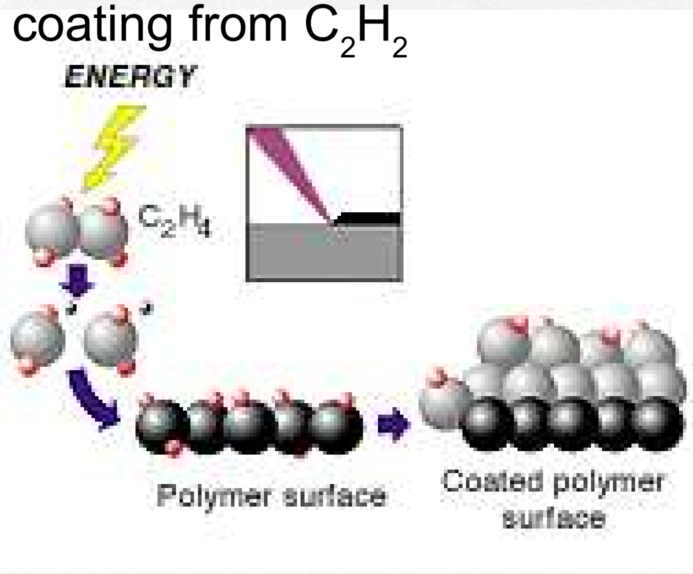


monomer types:

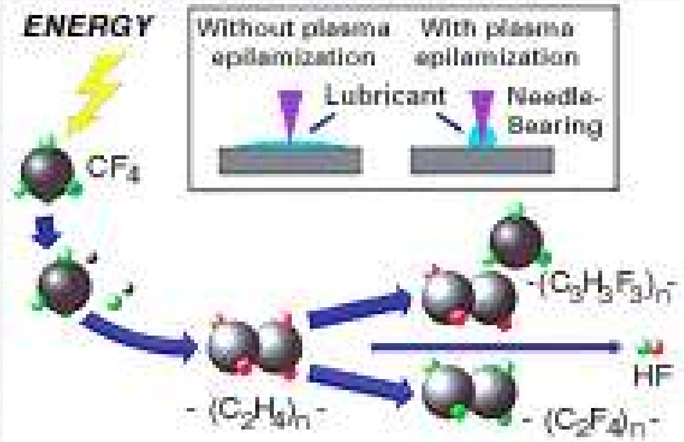
- type I: -C C-, aromatic
- type II: >C=C<, cyclic
- type III: aliphatics (excluded by I & II)
- type IV: O-containing (alcohols, ethers, esters)



generation of **diamond-like** coating from C_2H_2



generation of **hydrophobic** coating from CF_4



Growth mechanism of plasma polymerization

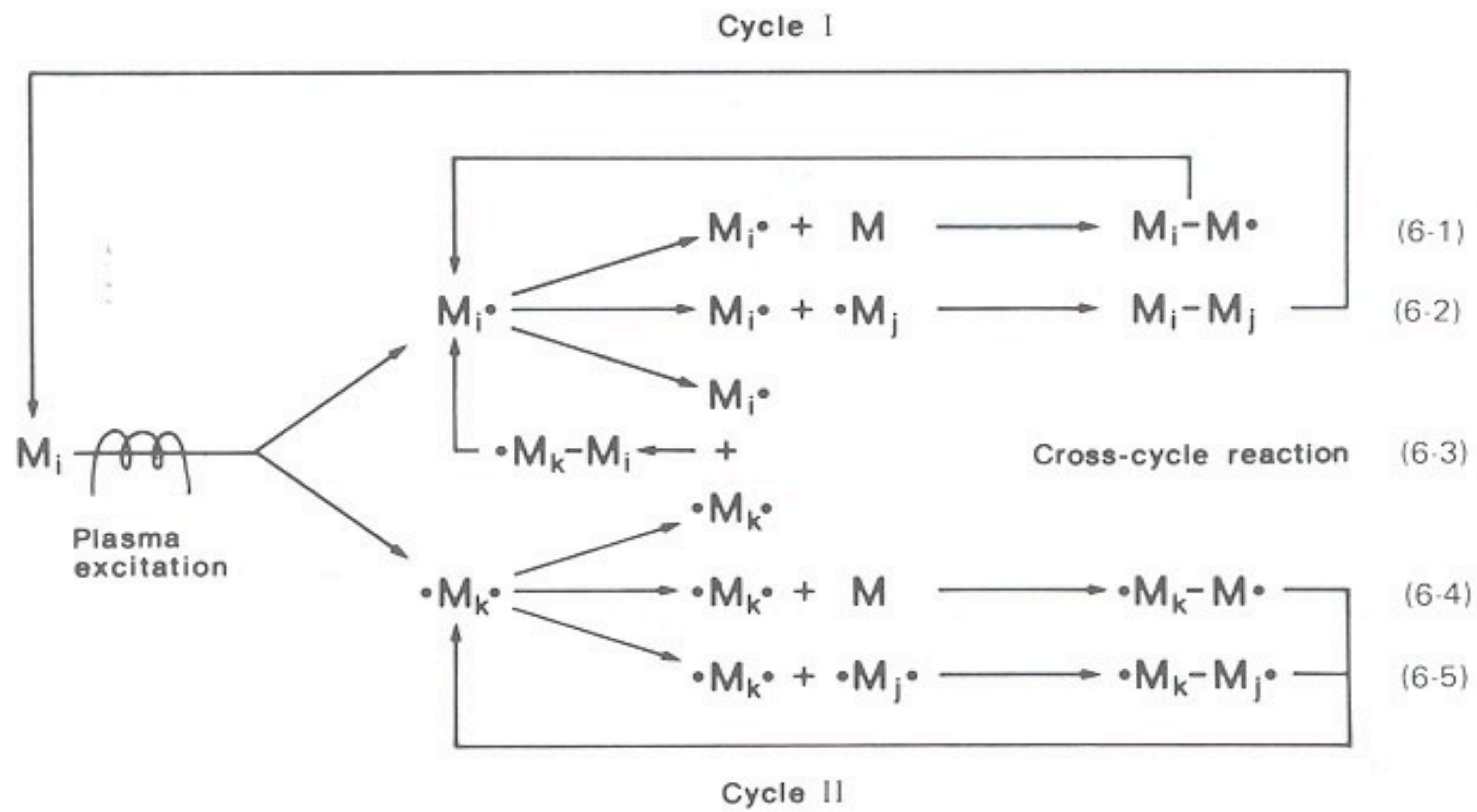


Fig. 6.1 Schematic representation of bicyclic step-growth mechanism of plasma polymerization.

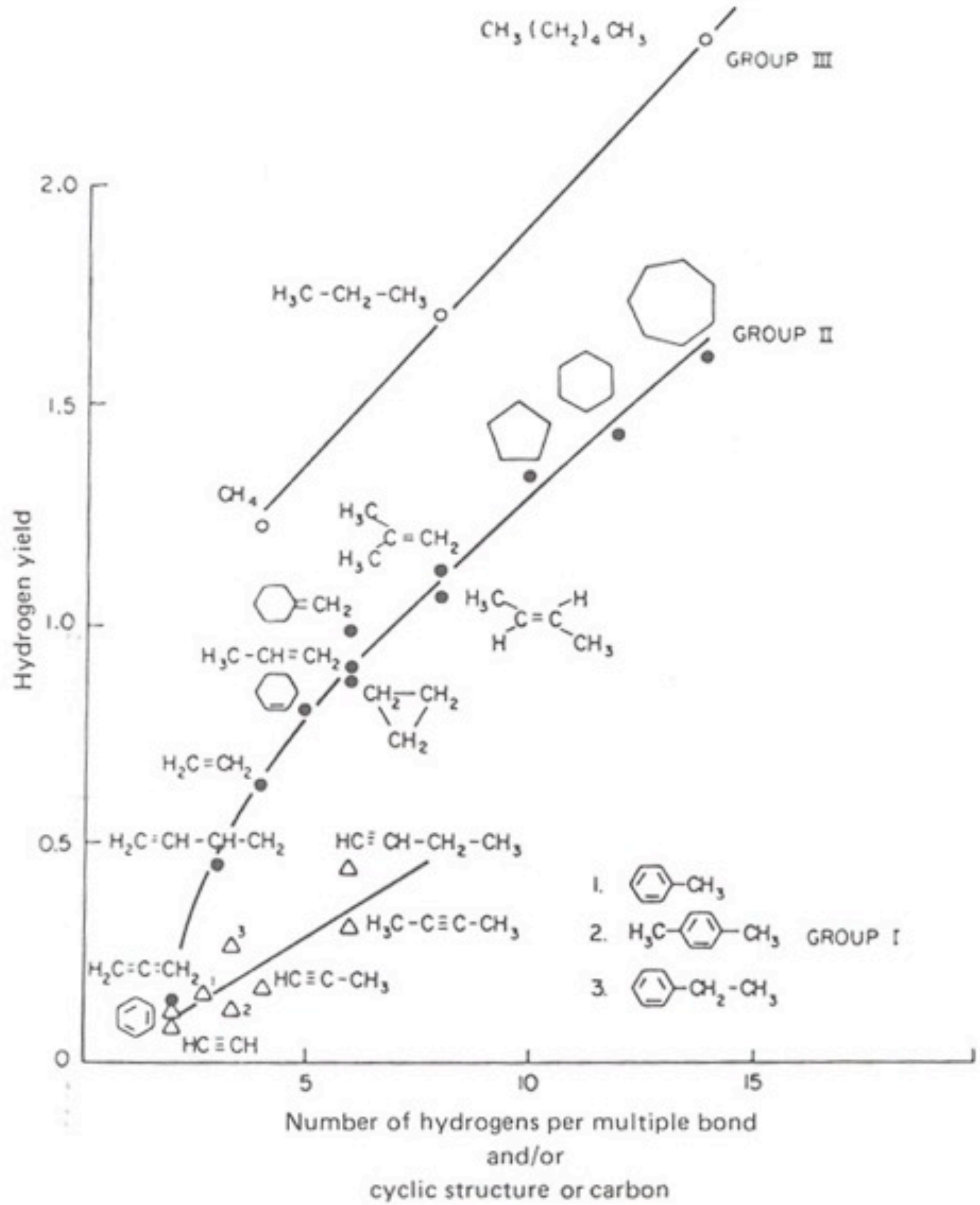


Fig. 6.2 Number of hydrogen molecules evolved per molecule of starting material v hydrocarbons polymerize (hydrogen yield) as a function of chemical structure. Adapted f Yasuda *et al.* (5).

Applications

Application	Substrate	Monomer(s)	Conditions	Comments
adhesion promoter	polyaramid	NH_3		Amination of surface; reaction plateau after 1 minute. Better composites achieved
adhesion promoter	polyaramid (Kevlar)	hexamethyl-disiloxane (HMDSiO)	2.45 GHz, LMP reactor, 0.2–1 torr, 100–700 watts	HMDSiO plasma polymer coating compared to plasma treatment (air, N_2, NH_3, N_2 plasmas) for adhesion. HMDSiO plasma polymer yields best adhesion for fabric/epoxy/fabric laminate.
adhesion promoter	$CaCO_3$	Ar, t-butanol, n-butylamine	microwave, LMP reactor, 0.5–2 torr, 200 watt pulsed	Ar plasma treatment followed by *t*-butanol or *n*-butylamine plasma polymer coating affects acid/base properties of coating thereby improving dispersion of $CaCO_3$ filler in PVC (acid) and polyethylene (base).
adhesion promoter	polyethylene, poly(vinylidene fluoride), poly(tetrafluoroethylene), poly(vinyl chloride)	acetylene	50 Hz, capacitively coupled, 0.1–0.7 torr, 4.7–42 sccm	Acetylene plasma polymer results in better adhesion of all substrates to epoxy because of increased hydrophilicity *and* surface of increased roughness.

Applications

Material transport through plasma polymers.

Barrier and protective films.

Electrical applications.

Abrasion resistant coatings.

Optical applications.