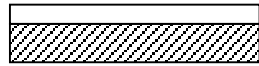


Polymer thin films

A) Introduction

This lecture is concerned with the formation and properties of polymer thin films (SL) and multilayers (ML)

Thin films

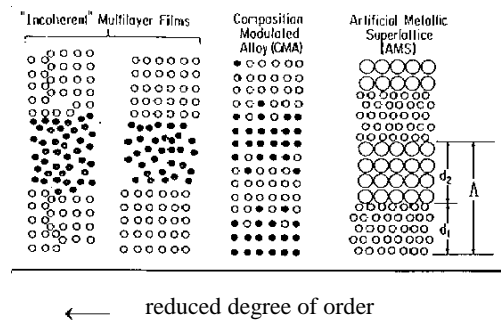
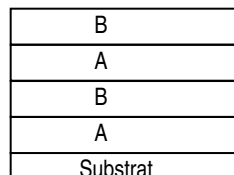


thickness ~ 100-300 nm - some μm ("thin is relative")

Polymers: often weak interaction between polymer and substrate

- Thin polymer films interesting for many reasons, for instance for packaging, coating materials, CD's,
- Enormous **research activities**. Preparation (design) of **new materials**.
- One needs know-how und special techniques.
- Strong correlation to **interface and surface physics**.
- Measuring techniques of surface physics.

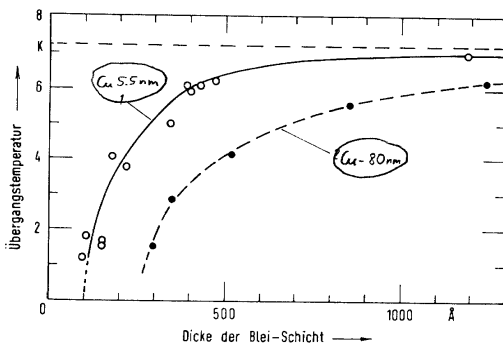
Multilayers



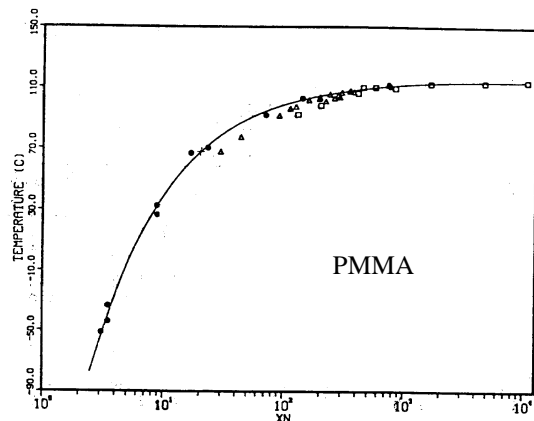
- are artificially typically **in nm-range structured and modulated** layered systems
- problem, degree of **ordering**

Thin film = size reduction of bulk material in one dimension

Reduced dimensionality of multilayers leads to interesting phenomena, when the film thickness or multilayer periods is comparable or smaller than **characteristic length scales**.



for instance in the case of **metals**:
 superconductivity - correlation length $\xi \sim 200$ nm



glass transition vs. chain length

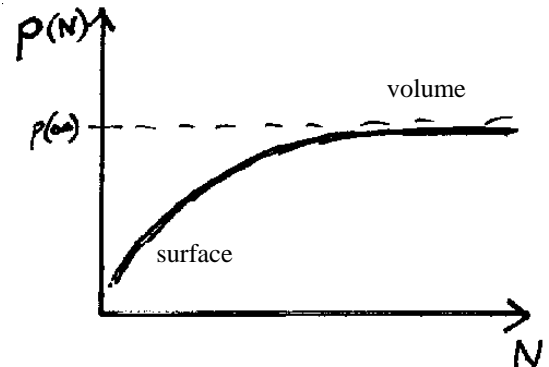
Idea:

Size dependence because of changing influence of volume and surface contributions often describable as

$$p(N) = p(\infty) + \Delta p \cdot N^{-x} \quad 0 < x < 1,$$

$\Delta p = \text{surface effect}$

because of $V = 4/3\pi a_0^3$, $O = 4\pi a_0^2$, $N_O/N = N^{-1/3}$
 $\rightarrow x = 1/3$



Polymer surfaces

air / vacuum



polymer surface

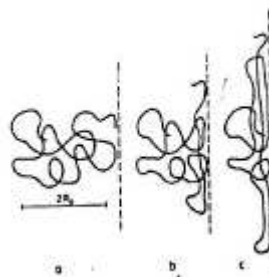
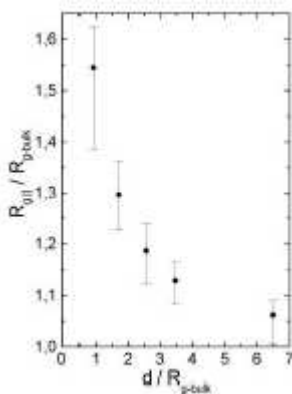
polymer volume (bulk)

microscopical view:

at the surface neighbors are missing (in comparison to bulk)

\rightarrow change of the structure near the surface

a) chain conformation near the surface: Orientation of chain segments parallel to the surface



Radius of gyration

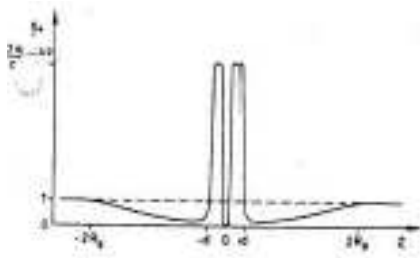
Model system: PS/PS

Gravity point close to the interface and change of conformation

Computersimulation: Influence of the surface over a region of about $2 R_g$
 SANS-measurements: Influence even further

Change of polymer molecule from isotropic Gauß' coil ("Knäuel", spherical) to **elliptical** form.

b) distribution of chain ends: Enrichment of chain ends at the surface due to entropic effects



Density of chain ends at the surface (de Gennes 1992):

$$\rho_e = 0.5 N \Phi_e / \Phi$$

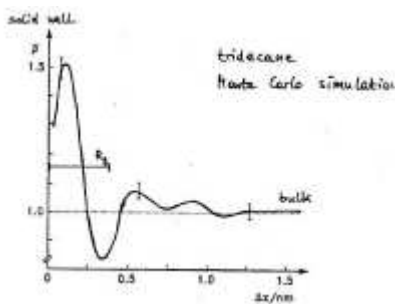
with chain length N , number of chain ends at the surface Φ_e and number of monomers per volume Φ .

→ chain ends from the region $2R_g$ are enriched at the surface of thickness d (typically 1-2 nm) according to

$$\rho_e = 2a/d * N^{1/2}$$

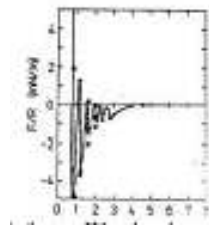
with sector length a .

c) distribution of the segments: strong orientation by breaking the translation invariance



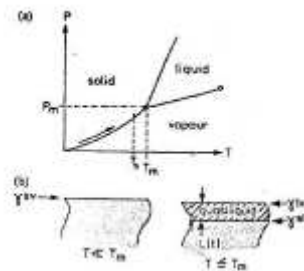
density modulations near the surface and region of lower density

measurement over "force balance"



d) influence on kinetics: mobility at the surface parallel to the surface is strongly increased within a thickness of about 2 nm

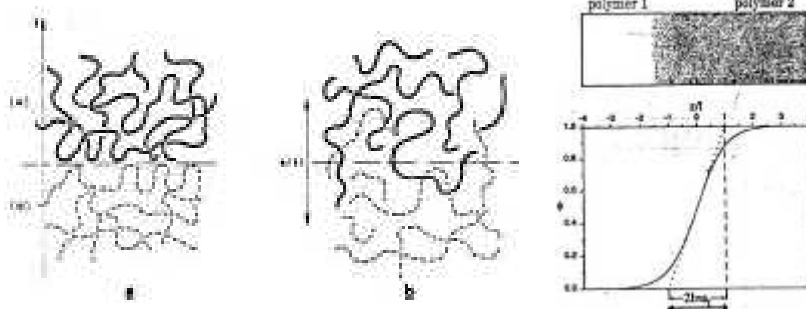
reason: less entanglement ("Verschlaufungen")



Computer simulation:

existence of very mobile, quasi-fluid surface layer well below the melting temperature T_m

Interfaces between polymers



most polymers are immiscible (like for instance PS/PMMA),
 but sometimes interdiffusion of polymers (for instance PMMA/PVC)

B) Formation of polymer films from solution

we go from very simple techniques for thick films to more and more sophisticated techniques for thin films, even to multilayers ("it is an art, design to prepare them") and single monolayers.

1) Solvent casting, painting

- most simple technique
- preparation of relatively thick films $> \mu\text{m}$
- polymer solution is deposited on a substrate – drying – solid film
- for instance: one takes a brush and simply paints the solution on a substrate (wall)
- is of large technical importance: coatings of houses, bridges, (protection against rust, water, ...)
- thickness often inhomogeneous, depending on the viscosity of the fluid, evaporation rate of the solvent
-

Determination of film thickness by optical techniques

widely used. Measurements are nondestructive, relatively inexpensive.

Interferometry relies on the interference of two or more beams of light, e.g. from the air/film surface and the film/substrate interfaces, where the optical path difference is related to film thickness.

conditions for interference:

optical path difference between successive beams is an integral number of wavelengths (with phase δ).

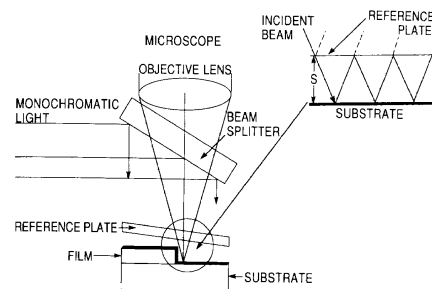
$$2S + 2\delta\lambda/2\pi = j\lambda$$

Phase change δ is assumed to be π at both surfaces. It follows

$$S = (j-1) * \lambda/2$$

The distance between maxima of successive fringes corresponds to

$$\Delta S = \lambda/2$$



2) Thermal spray processing of polymers ("gun")

Thermal spraying of polymers is gaining **increased attention** because the ability to apply coatings of polymers onto a wide variety of materials is seen as an **effective method** to produce protective barrier coatings.

Polymers that have been sprayed to date include PE, PMMA, EMMA, PEEK, PPS, LCP, nylon, phenolic epoxy, Tefzel, and post consumer commingled polymer.

Polymer powder is injected into a heat source (flame or plasma) and transported to a pre-heated substrate. The thickness of the coating is governed by the number of repeated passes of the spray gun across the substrate. A large particle size or molecular weight distribution may facilitate the formation of numerous heterogeneity's within the microstructure of the coating creating voids, trapped gasses, unmelted particles, splats, and pyrolyzed material.

Example: pans or skies

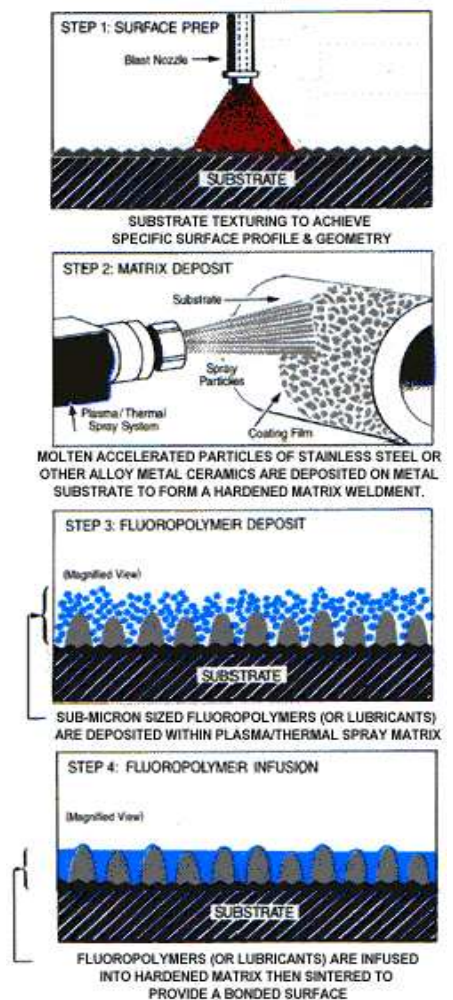
"Thermal Spray Polymer" coatings are multi-step processes which consist of depositing molten or semi-molten particles of stainless steel or other alloys, and ceramics under acceleration to form a matrix on the base metal surface.

The matrix is extremely porous and is sealed with the controlled infusion of high release fluoropolymers or other low-friction, high temperature, lubricating particles.

The newly formed, hardened surface becomes an integral part of the base metal, and is engineered to provide maximum non-stick properties and extreme resistance to wear and abrasion where traditional release surface coatings have limited life.

Endura® provides an entire family of proprietary coatings, each engineered to provide specific performance benefits and proven solutions in today's most demanding applications.

The illustration provides a processing overview.



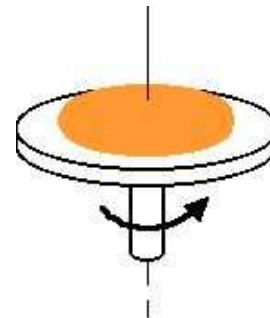
3) Spin coating

Polymer is dissolved in a volatile solvent and the solution is spinned

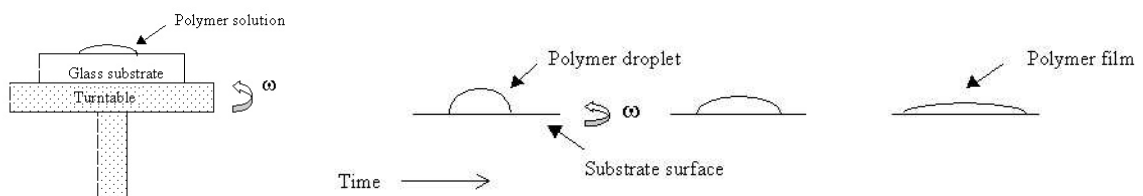
Spin coating is the preferred method for application of **thin, uniform films to flat substrates**. An excess amount of polymer solution is dropped on top of a substrate. The substrate is then rotated at high speed at an angular velocity, ω , in order to spread the fluid by centrifugal force, reducing fluid thickness. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. The solvent is usually volatile, providing for its simultaneous evaporation.

A good reference on spin coating is:

W. Flack, D. Soong, A. Bell, and D. Hess,
 "A mathematical model for spin coating polymer resists," *J. Appl. Phys.*, **56**, 1199 (1984).



applications: photoresists, lithography resists, and protective coatings



In most applications, the evaporation rate varies with the square root of the spin speed: $D \sim \omega^{-1/2}$

$$\text{empirisch (Schubert, 1997)} \\ d = 93.5 \text{ nm} \left(\frac{1950 \text{ min}^{-1}}{\omega} \right)^{1/2} \left(\frac{c}{20 \text{ mg/ml}} \right) \left(\frac{M_w}{100 \text{ kg/mol}} \right)^{1/4}$$

attention: deviations at small layer thicknesses and low atomic weights.
 Spin coating is a complex non-equilibrium process

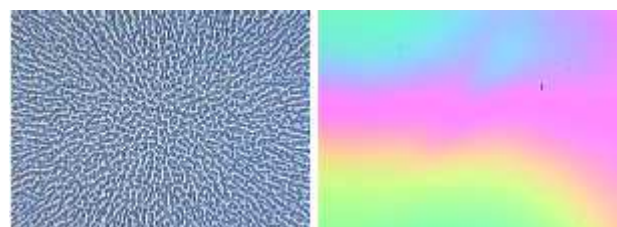
theoretical description in 3 step model (Lawrence 1988):

- 1) starting phase: solvent is put on the substrate, rotation leads to loss of material from substrate, formation of film with homogeneous thickness
- 2) loss of mass and thickness change by convection

$$h(t) = h_0 \left(1 + \frac{4\rho\omega^2 h_0^2}{3\eta_0} t \right)^{-1/2}$$

- 3) evaporation over the film surface (can lead to holes or surface structures)

$$h_f = h_w (1 - \phi_{s,0})$$



a) Special: Free Standing Polymer Films

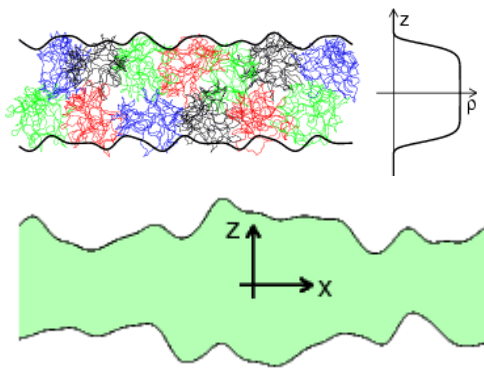
extremely interesting as **model systems to investigate finite size effects** on liquids without any interaction with substrates.

prepared by **spin casting** thin polymer films (here PS) on a glass substrate and **floating** them on a water surface. Then they are picked up by an aluminum disk with a 5mm hole in its center

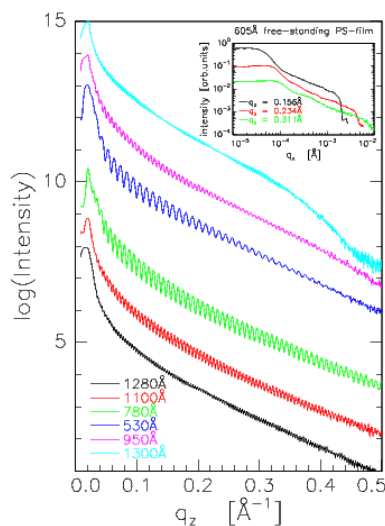


then annealed at 160°C in UHV, well above the glass transition temperature of about 100°C. After quenching the film is completely relaxed and should show liquid like behavior.

properties investigated: density profile perpendicular to the surface, the in-plane correlation function and cross correlations between the surfaces.



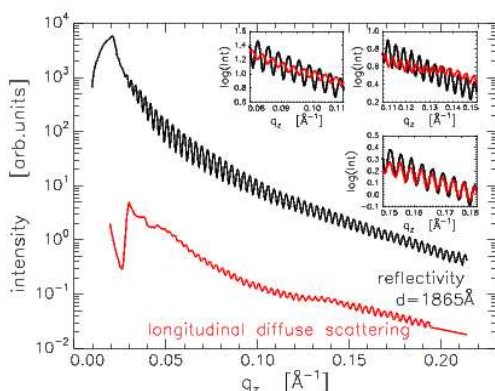
Sketch of a thin free standing polymer with model surfaces roughnesses. Both surfaces are in phase correlated (conformal) for small length scales (see the small bumps) and anti-correlated (anti-conformal) for large length scales (average distance in the center is larger compared to both sides).



The correlation functions $C(x,z)$ of the surfaces determine if the free standing film behaves like a simple bulk liquid. Free bulk liquids exhibit surface correlation functions with infinite correlation lengths. Thus, in the (x,y) -plane all length scales are somehow correlated. However, any perturbation of the system, e.g. by a background potential (substrate), suppresses long range correlations. The length scale at which correlations start to be suppressed is called cut-off.

Reflectivity data of free standing polystyrene PS film (film thicknesses 53-130nm, the radius of gyration ~ 10 nm). The lower reflectivities show the expected behavior: The oscillations due to the film thickness are only slowly damped which means that the rms-roughnesses of both interfaces are pretty much the same.

The inset depicts **diffuse scattering** measurements of free standing films. At least for film thicknesses larger than 5 radius of gyration no finite size effects can be seen in the in-plane correlation lengths.

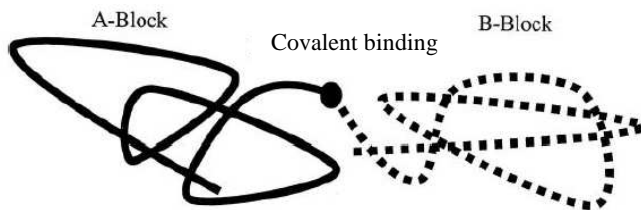


A reflectivity (black) and a longitudinal diffuse measurement (red) of a 186nm PS-film. The diffuse scattering clearly shows oscillation which means that cross correlations between the surfaces are present: Both surfaces are not independent of each other. More surprisingly, the longitudinal diffuse scattering is out of phase for small q_z and in phase for large q_z . This corresponds to a film similar to that one shown above with conformal roughness for small length scales and anti-conformal roughness for large length scales

b) Multilayers: **diblock copolymer thin films** - self organization

Often, a polymer may have a particular, desirable property but processing is difficult or the polymer's surface characteristics are undesirable.

To circumvent such shortcomings there exists the option to mix two polymers with complimentary properties. Unfortunately, most polymers are **immiscible** unless there are specific interactions (e.g. H bonding) between the two components. Consequently, coarse **phase separation** is often observed.



diblock copolymer:
two polymers are bounded
over chemical binding

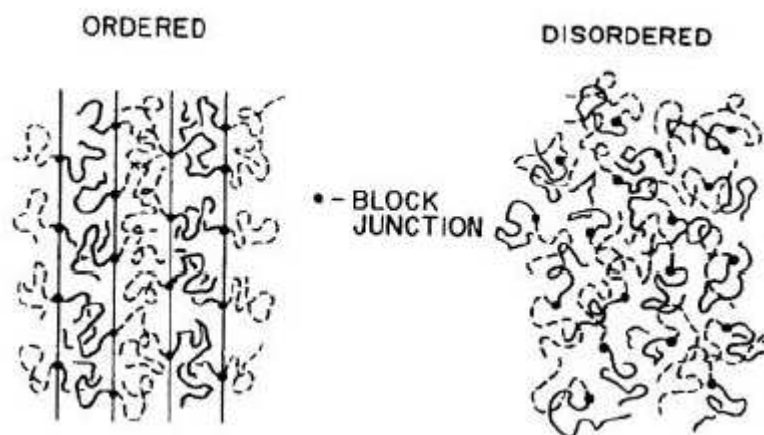
Poly(A-b-B)

But in special cases, two chemically distinct homopolymers can be joined together at one point, forming a **diblock copolymer**. While phase separation may occur, the scale of the domains is restricted to the sizes of the individual homopolymer, which is typically on a scale of tens of nm. An advantage is furthermore that the size of different blocks can be altered by varying the concentration of the different components.

Example: **PS** poly(styrene) – **PMMA** poly(methylmetacrylate)

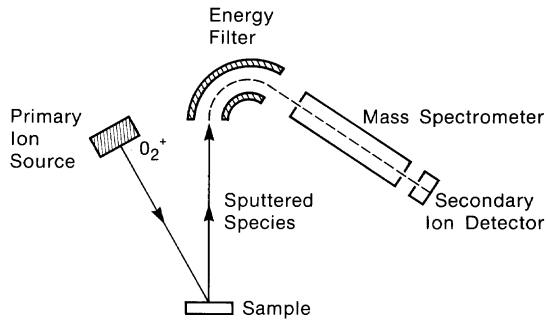
Here is interesting: surface and interfacial behavior of such diblock copolymer thin films.

micro phase separation (here: lamellar)



Experiments (either PS or PMMA is fully deuterated):

preparation: solution of copolymer in toluene spin-casted (2000 rpm) onto Si, dried under vacuum. Then coated with Au marker and a thin PS buffer layer (protects the copolymer surface from unwanted contaminants)



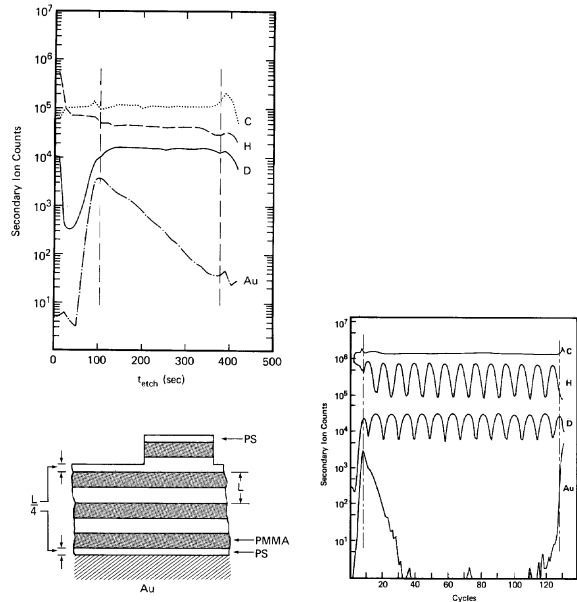
- H and D can be easily resolved
- signals of C, H and D are constant with time
- within the resolution of SIMS (here about 12 nm) no preferential segregation of PS or PMMA to the surface or substrate.
- no information on micro-phase-separation
- Au segregation during sputter etching

After heating: 170°C for 72h:

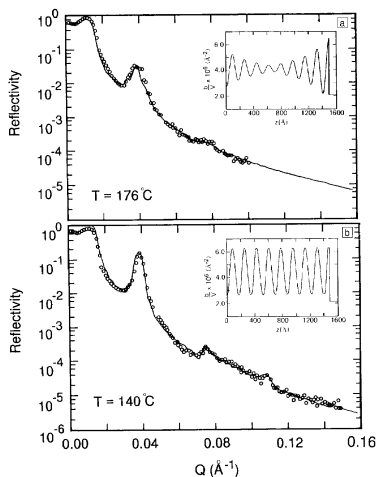
- new SIMS profile with oscillations showing micro-domains on the SIMS-spot of about 80 μm (lamellar microstructure)
- PS (as indicated from the D-signal) is located both at the surface and the substrate (surface tension of PS is 0.1 dyne/cm smaller than that of PMMA)
- microdomains over 500 nm in size !!

SIMS

- ions: a few keV
- sputtered secondary atoms and ions
- sputtered crater
- depth profiling
- mass separation and energy analysis

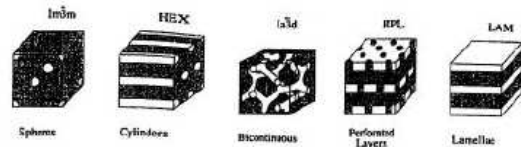


such layered structures can also be observed using SAXS (x-ray reflectivity) or SANS (neutron reflectivity)



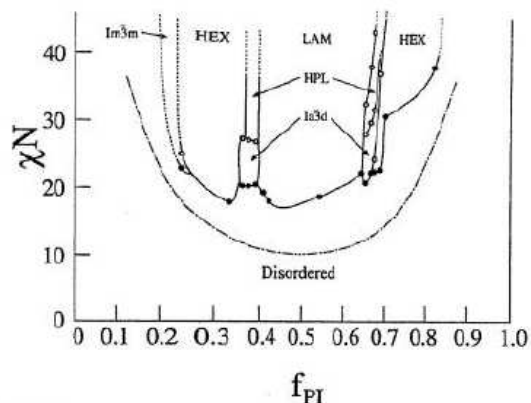
176°C lies above the ordering temperature, 140°C below.

- Fresnel optics: $n = 1 - \delta + i\beta$
- total reflection
- Bragg peak for many periods $n\lambda = 2\Lambda \sin\theta$



Phase separation occurs during the rapid removal of the solvent, leaving a non-equilibrium phase morphology that is likely to result from an interplay between bulk phase separation, surface and substrate interactions, the viscosity and volatility of the solvent.

example: Poly(S-b-I) with different PI-block content f_{PI}



Surface-induced ordering in diblock copolymeres (self-organization)

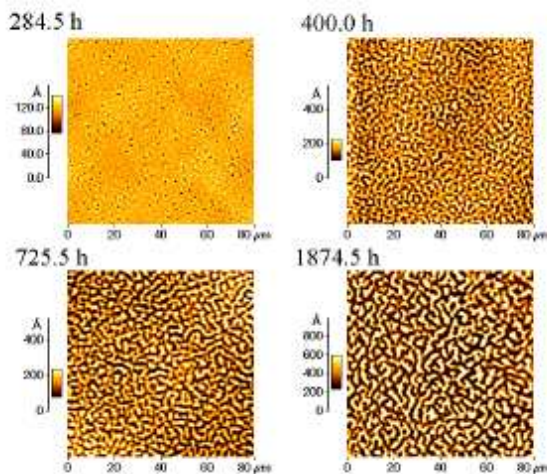
Minimization of the free energy leads to surface induced ordering (Fredrickson, 1987)

$$\phi_A(z) = \bar{\phi}_A + \frac{\phi_{+/-}}{\cos \delta} \exp\left(\frac{-z}{\xi}\right) \cos\left(\frac{2\pi z}{D} + \delta\right)$$

- the component with the higher surface affinity enriches at the surface
- because of the chemical binding the second component is following
- leads to a sin-modulation with periodizity D
- with increasing distance to the surface the amplitude of the modulation decreases
 → correlation length ξ
- δ is the phase shift of the modulation

at the micro-separation temperature: **DMST=3.38 R_g**

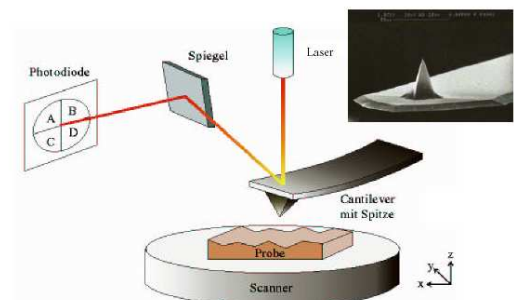
very thin diblock polymer films: → lateral ordering



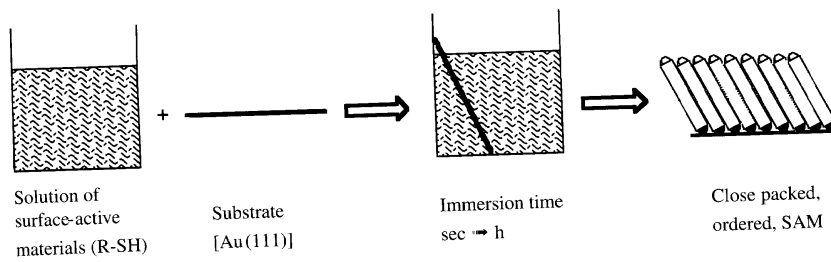
example:

SFM micrographs
 of Poly (S-b-pMS) on Si

AFM = Atomic force microscopy

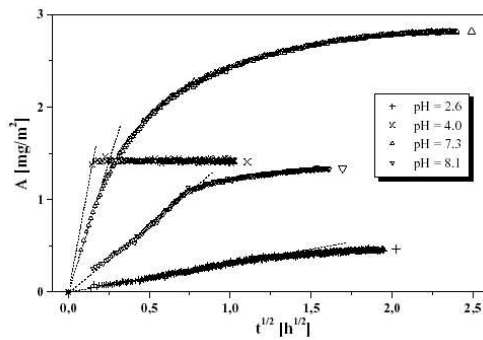


4) Polymers produced by surface absorption of monolayers (SAM)



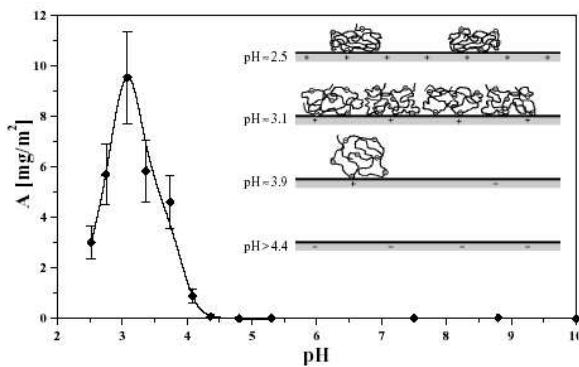
Adsorption from solution

- single molecules or thick films, typical for electrolytes in watery solutions
- it is a slow process because diffusion controlled



kinetics (diffusion controlled)

growing material $\sim t^{1/2}$



dependence on pH-value

SAMs are ordered molecular assemblies formed by the absorption of an active surfactant on a solid surface.

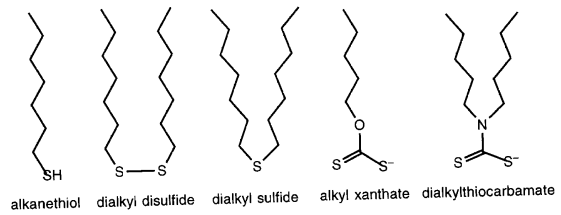
With this technique it is possible to built **monolayers** (or even **superlattices**).

The order in these two-dim. (2D) systems is produced by a *spontaneous* chemical synthesis at the interface as the system approaches equilibrium.

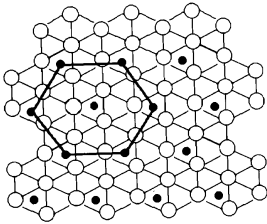
For this, often long-chain hydrocarbons are most frequently used as building blocks of these supermolecular structures.

Example:

Organosulfur adsorbates on metal surface, coordinate very strong (for instance on Au)



sulfur and selenium compounds have a strong affinity to transition-metal surfaces (multiple bonds). The main reason for working with Au surfaces is that Au does not have a stable surface oxide (inert).

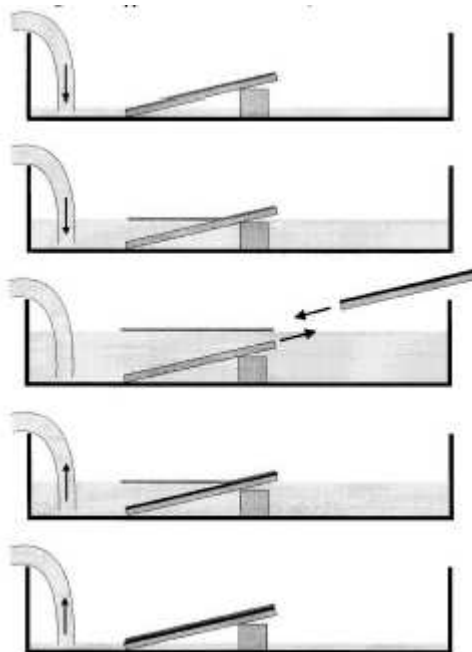


lateral: hexagonal coverage for alkanethiolates on Au(111)
 (open circles are Au atoms)

self-organization

5) Floating technique

for the preparation of single or double films

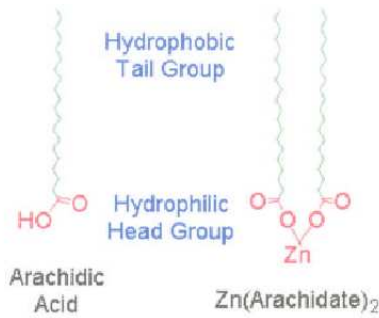


- Film mit Skalpell 2mm von Substratrand entfernt anritzen
 - Substrat in Floatwanne legen (Neigungswinkel zur Abflöten 10-15°)
 - Zugabe von 2-3 Tropfen deionisiertem Wasser pro Sekunde
 - Nach Ablösen des Films leeres Substrat entfernen
 - Zweites Substrat unter steilem Winkel unter Wasseroberfläche bringen
 - Deckfilm an oberer Kante dieses Substrates fixieren
 - Steiges Absenken des Wasserspiegels mit 2-3 Tropfen/sec
 - Trocknung des Doppelfilms (zB 4h bei 50°C)
- Typischer Zeitbedarf je nach M_w und Filmdicke 3-6 h

6) Langmuir-Blodgett films = organic polymers on solid surfaces

applications: sensors, detectors, displays, components for electrical circuits – model systems

amphiphile molecules, for instance carboxylic acids and salts

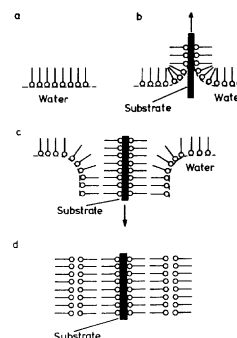
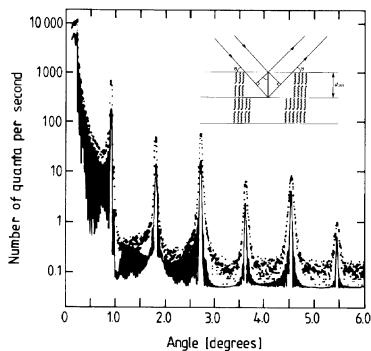
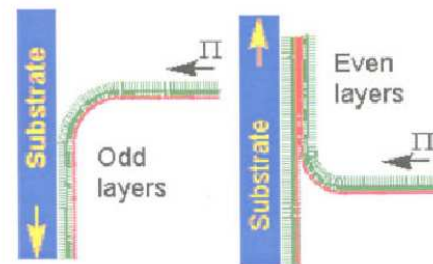
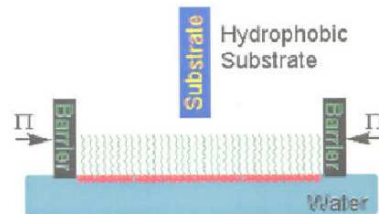
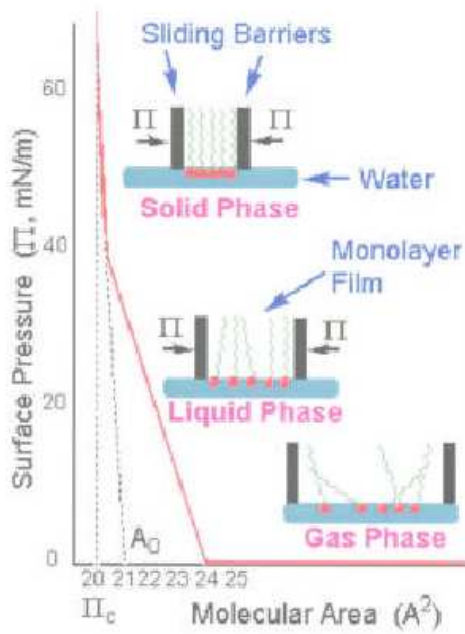


consist of polar head groups and non-polar tail with $(CH_2)_n$ with $n > 12$

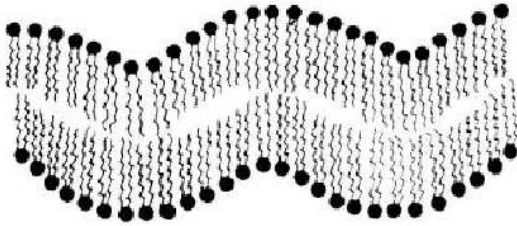
possibility of ordering in a Langmuir pot by moving the walls

in the ordered state possibility to transfer the film to the substrate (= **Langmuir-Blodgett technique**)

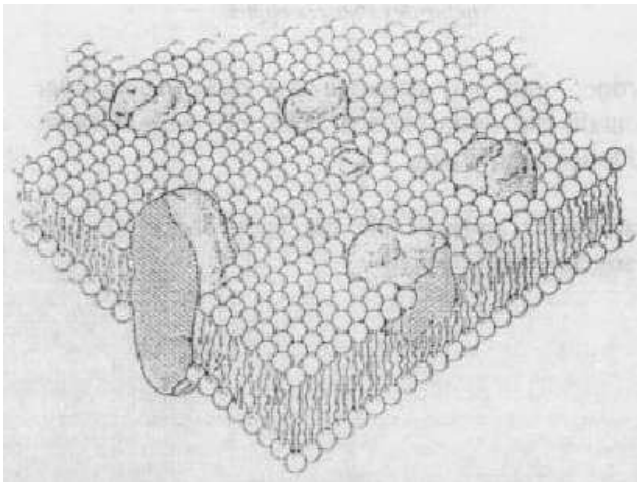
possibility to make **multilayers**



Formation of lipid double-layers:



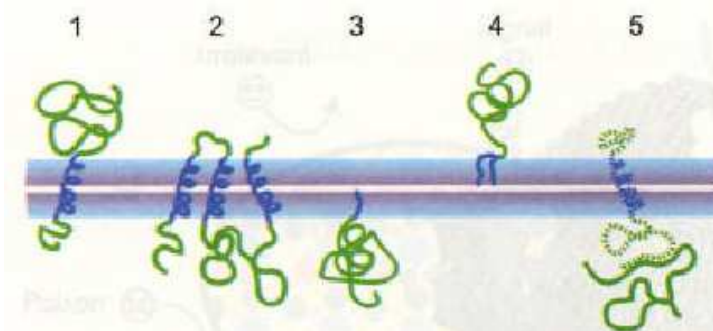
Bio membranes: = building block of bio-material



inclusions of **proteins** in the **double-layer of lipids**

proteins are receptors for hormones, drugs, medicaments, antibodies and regulate the ion-permeability of the membrane

different kinds of fixing proteins in the lipid layers:



1)2) protein with one or more α -helices

3)4) protein anchored by hydrophobic side groups or phospholipide

5) contact to anchored proteins

C) Thin film deposition techniques

Thin film deposition from the vapor phase.

Number of thin film techniques is large. Some of them are also usefull for the preparation of polymer thin films.

<p>Aufdampfen</p> <p>Elektronenstrahlverdampfung Einfachquelle Vielfachquelle reaktives Aufdampfen thermisches Verdampfen Blitzverdampfung Molekularstrahlepitaxie Metallorganische Molekularstrahlepitaxie Strahigestütztes Aufdampfen</p>	<p>Vapour deposition</p> <p>electron beam evaporation single source multiple source reactive vapour deposition thermal evaporation flash evaporation molecular beam epitaxy MBE Metal-organic MBE = MOMBE beam-supported evaporation</p>
<p>Chemische Gasphasenabscheidung</p> <p>Pyrolyse Metallorganische chemische Gasphasenabscheidung thermische Zersetzung Reduktion Oxidation</p>	<p>Chemical vapour deposition CVD</p> <p>pyrolysis</p> <p>metal-organic CVD = MOCVD thermal decomposition reduction oxidation</p>
<p>Aufstäuben</p> <p>Ionenzerstäubung Plasmazerstäubung Vorspannungszerstäubung</p>	<p>Sputter-deposition</p> <p>ion-beam sputtering plasma sputtering bias sputtering</p>
<p>Strahigestützte Schichtabscheidung</p> <p>Ionenmischen Ionenplattieren</p>	<p>Beam-supported film deposition</p> <p>ion mixing ion plating</p>
<p>Verschiedenes</p> <p>Gasphasenepitaxie Flüssigphasenepitaxie Gepulste Laserdeposition</p>	<p>vapour phase epitaxy VPE liquid phase epitaxy LPE pulsed laser deposition PLD</p>

Thin films arise from adsorption of the polymer or parts of it (monomers or smaller fractions) at the substrate or film surface.

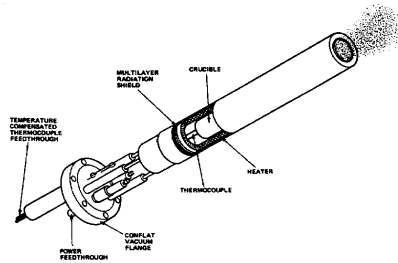
Driving force for the film growth in most cases is the supersaturation of the vapour phase and an undercooling of the film.

Here we discuss:

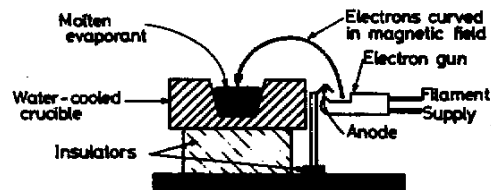
evaporation, sputtering, pulsed laser deposition (PLD), and plasma polymerization

1) Evaporation

During evaporation the material is heated in UHV in a crucible to sufficient high temperatures. The evaporating molecules leave the surface and condense as a thin film on a substrate (and also on the surrounding walls).

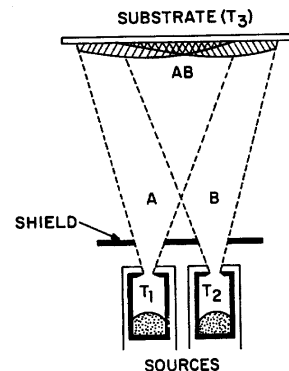
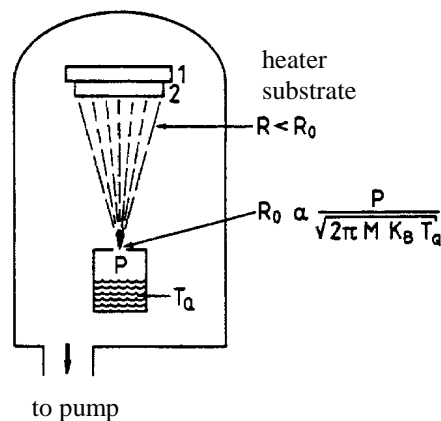


Knudsen cell



electron beam evaporation

- thermally produced atom or molecular beam
- source(s): heated solid states or fluids (for instance in a Knudsen cell)
- atoms possess thermal energies (1200 K corresponds to 0.1 eV)
- preparation of morecomponent systems or multilayers with several sources



Evaporation rate of a Knudsen cell:

In the Knudsen cell an equilibrium vapour pressure p_D of the material exists, which leads to an evaporation of material through the small opening.

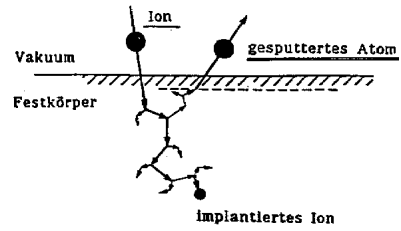
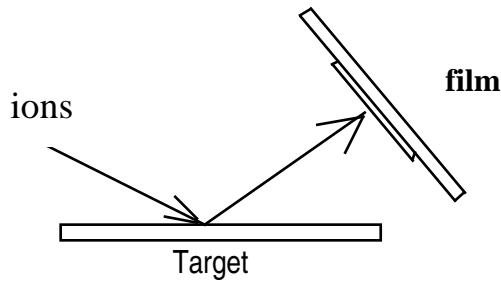
$$R_e = dN_e / (A_e dt) = p_D(T) \cdot \{2\pi m k T\}^{-1/2} \quad \text{(Hertz-Knudsen equation)}$$

$p_D(T)$ is strongly temperature dependent, given by

$$p_D(T) = A e^{-\frac{E_0}{k_B T}}$$

with the **submiation energy** E_0 , defined as evaporation heat of an atom.

2) Sputtering

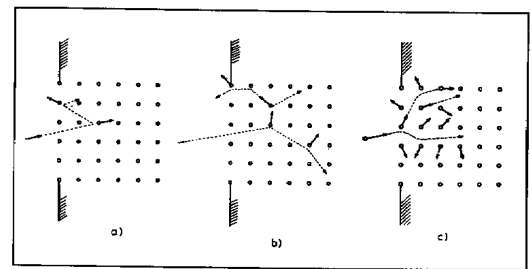


Principle: When ions/atoms hit a target with high enough energy (for instance Ar^+ , $M=40$, kinetic energy $E=1\text{keV}$), transfer of energy and impulse towards the target atoms takes place. Ions are implanted into the material and partially resputtered.

Surface particles leave the surface, as soon as the binding energy of the target material is overcome (sputtering).

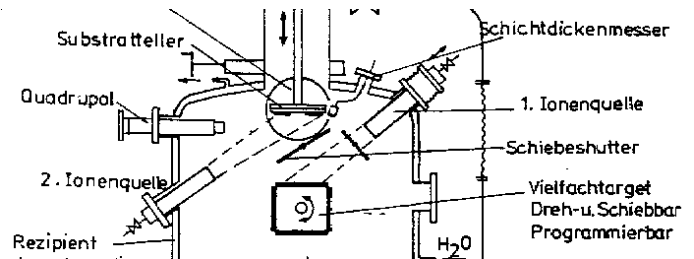
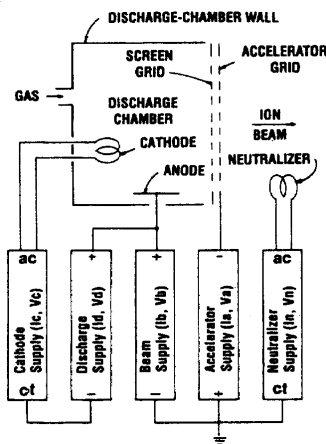
for **metallic targets**

Element	Oberflächen-Bindungsenergie [eV/atom]		
	{111}	{100}	{110}
Al	3.80	3.80	3.53
Cu	4.65	4.62	4.26
Ag	4.08	3.98	3.61
Fe	4.72	5.47	5.48
W	9.75	11.52	11.86



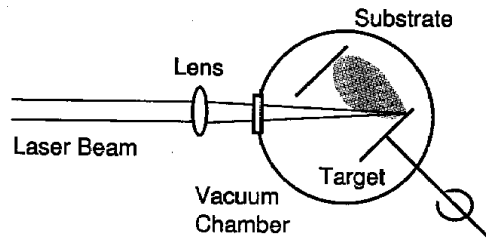
Einzelstoß $E < 50\text{eV}$ **lineare Kaskade** $E > 100\text{eV}$ **Spike**

Kaufmann source



3) Pulsed laser deposition (PLD)

- UV-excimer laser, pulsed: z.B. KrF 248 nm, 30 ns
- UHV oder pressures <1mbar
- energy source is outside the chamber



Properties of the technique:

- stoichiometry transfer
- high deposition rate
- most materials can be prepared (in UHV or in gas environment)

Material		Literaturstelle
Hochtemperatursupral.	YBa ₂ Cu ₃ O _x	Dijkkamp et al. 1987
	BiSrCaCuO	Guarnieri et al. 1988
	TlBaCaCuO	Foster et al. 1990
	YBaCuO/YPrBaCuO	Wu et al. 1990a
	HgBaCaCuO	Higuma et al. 1994
Oxide	SiO ₂	Fogarassy et al. 1990
	SnO ₂	Dai et al. 1990
Karbid	SiC	Balooch et al. 1990
Nitride	TiN	Biunno et al. 1989
	BN	Doll et al. 1991
ferroelektr. Materialien	Ba ₄ Ti ₃ O ₁₂	Ramesh et al. 1990
	Pb(Zr, Ti)O ₃	Kidoh et al. 1991
	LiNbO ₃	Shibata et al. 1992
Heteroepitaxie	YSZ auf Si	Fork et al. 1990
diamantähn. Kohlenstoff	C (kristallin)	Martin et al. 1990
Buckminster Fullerene	C ₆₀	Curl und Smalley 1991
Polymere	Polyethylen, PMMA	Hansen u. Robitaille 1988
Metallische Legierungen	YCo ₅ , YNi ₅	Gavigan et al. 1991
	Ni ₃ Al, NiAl	Singh et al. 1992
	30 Legierungen	Krebs u. Bremert 1993a
Metall. Schichtpakete	Fe/Nb, Fe/Ag	Krebs u. Bremert 1993b

Processes:

- heating of the target by the laser beam
- evaporation (Hertz-Knudsen equation)
- absorption of laser light
- plasma formation and expansion

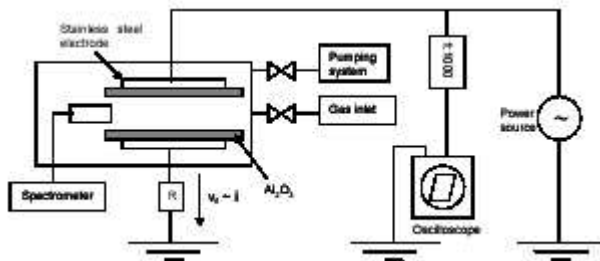
4) Plasma polymerization

When introducing molecular gases into a **plasma**, chemically active species are formed such as molecules in excited states, radicals and ions. These species can react with each other, neutral molecules or with the surface of a substrate. This results in deposition of a thin film.

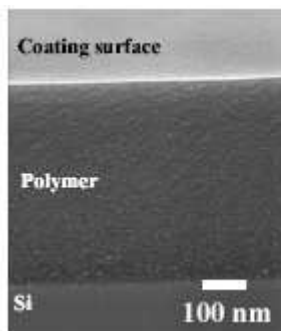
Films resulting from organic precursors are generally known as **plasma polymers**.

The reaction chain leading to a **plasma polymer film is not comparable to common polymerization reactions**. For this reason, the **properties** of plasma polymer films can **significantly differ** from their classic chemical counterparts.

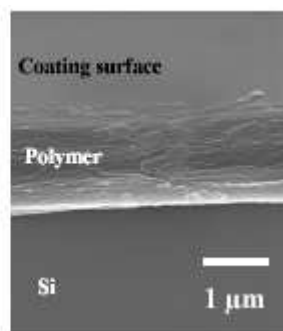
When hydrocarbons are introduced in a DBD at atmospheric pressure, plasma polymerization occurs which results in the deposition of polymer-like material on the surface of the electrodes.



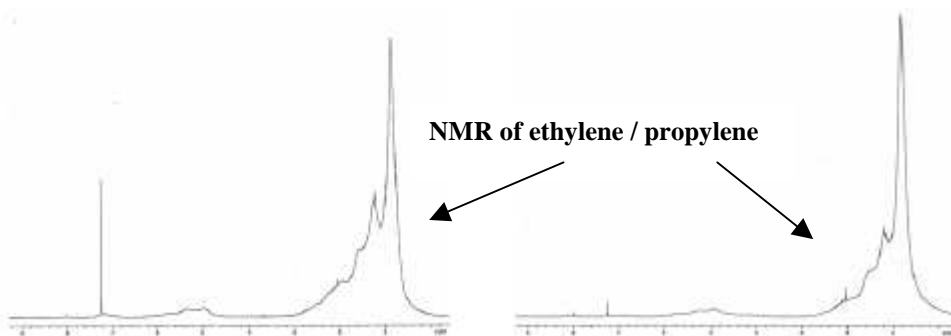
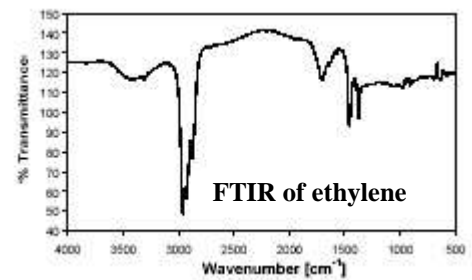
The discharge is obtained between two disk-shaped electrodes. To ensure stable plasma operation, the gap width is typically limited to a few millimeters. The bottom electrode is connected to a variable frequency AC power source (1-30 kHz, 20 kV). The vacuum chamber is first evacuated and subsequently filled with a specific process gas mixture.



ethylene

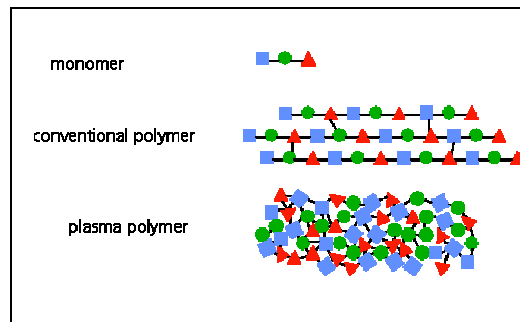


propylene



Film structure:

In most cases plasma polymers are **highly cross-linked** and have a disordered structure. Structural preservation and cross-linking gradients can be controlled through process parameters, such as pressure, working gas-flow and applied electrical output; so one can also construct so-called gradient layers; i.e with increasing degree of cross-linking over thickness.



Special layer characteristics that are qualified for a multitude of applications:

- excellent coating adhesion on almost all substrates
- chemical, mechanical and thermal stability
- high barrier effect

Applications from plasma polymer coatings are as follows:

- scratch resistant coatings (displays or windows)
- corrosion protection
- barrier layers



Water drop on a surface being coated by plasma-polymerization