

Polymers and Cold Plasmas

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Abstract: In the last 15 years the use of plasma for materials processing has received a great amount of interest. The scope of possible applications is expanding rapidly and covers a large range of different fields. Applications may be found in microelectronics, food packaging, decorative and functional coatings; many different materials as metals, semiconductors, ceramics or polymers are involved by the plasma technology as bulk material, surface or interface. Plasma treatment is probably the most versatile surface treatment technique. Different types of gases such as argon, oxygen, nitrogen, fluorine, water etc. can produce the unique surface properties required by various applications. For example, O₂ plasma treatment can increase the surface energy of polymers, whereas fluorine-containing plasma treatment can decrease the surface energy and improve the chemical inertness. Cross-linking at a polymer surface can be introduced by noble gas plasmas. Thin polymer films with unique chemical and physical properties are produced by plasma polymerisation. This technology is still in its infancy, and the plasma chemical process is not fully understood. The present article gives a short and non-exhaustive introduction on plasma polymer interaction and our activities in this field.

Keywords: Cold plasma · Plasma polymerisation · Plasma treatment

1. Introduction

Polymers have been applied successfully in fields such as composites, microelectronic devices, bio-materials adhesion, tribology, protective coatings, and thin-film technology. In these applications the polymers frequently involves interfacial interaction with other polymers and other types of materials (metals, semiconductors, ceramics). Due to their macroscopic nature consisting entangled and cross-linked macromolecules, polymers may be regarded as ‘soft’ materials. The intramolecular forces are responsible not only for their cohesive properties but also for their adhesive properties. The surfaces of polymers are therefore generally characterised by a low surface energy δ and hence bad intrinsic adhesive properties [1]. Examples of technological applications where the adhesive properties of the polymer surfaces are of concern involve

polymer-adhesive, polymer-metal interfaces in electronics, microelectronics, printing, painting or packaging.

2. Definition of the Plasma State

Plasmas are ubiquitous, comprising more than 99% of the known matter in the universe. Taking into consideration the energy of the particles constituting the plasma, plasma is energetically the fourth and highest state of the matter, apart from the solid, liquid and gaseous states. Irving Langmuir and his collaborators at General Electric were the first to study phenomena in plasma in the early 1920’s while working on the development of vacuum tubes for high currents. It was Langmuir [2] who in 1929 used the term ‘plasma’ for the first time to describe ionised gases.

In our everyday life encounters with plasmas are limited to a few examples: the aurora borealis at the polar regions, the flash of a lightning bolt, the conducting gas inside a fluorescent neon tube, and the slight amount of ionisation in the flame of a welding torch. The reason why plasmas are so rare in our everyday life can be seen from the Saha equation, which describes the amount of ionisation to be expected in a gas in thermal equilibrium:

$$\frac{n_i}{n_n} \approx 2.4 \cdot 10^{15} \frac{T^{3/2}}{n_i} e^{-\frac{U_i}{kT}} \quad \text{Saha equation}$$

Here n_i and n_n are, respectively, the density of ions and neutral atoms, T the temperature, k the Boltzmann constant, and U_i the ionisation energy of the gas. For dry air at room temperature the fractional ionisation $n_i/n_n \approx 10^{-122}$, predicted by the Saha equation is negligible low. As the temperature increases and U_i is only a few times kT the degree of ionisation rises abruptly, and the gas goes into the plasma state.

The plasma contains a multitude of different neutral and charged particles, as well as UV and VUV radiation. It is broadly characterised by the following basic parameters:

- The gas pressure (p) or the density of the neutral particles, n_n
- The ion- and electron-density, n_i and n_e , which are equal in the quasineutral state of the plasma. ($n_i = n_e = n$, n is the plasma density)
- The energy distributions of the neutral particles, $f_n(E)$, the ions, $f_i(E)$, and the electrons, $f_e(E)$.

The essential mechanisms in the plasma are excitation and relaxation, dissociation, ionisation and recombination. To maintain a steady state in the plasma den-

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sity, the recombination must be balanced by an ionisation process, *i.e.* an external energy source is required. Usually an electric field is used as energy source, acting directly on the charged particles only. The energy transfer W from the electric field \vec{E} to a simple charged particle with mass m is given by:

$$W = e\vec{E} \cdot \vec{r} = \frac{(eEt)^2}{2m}$$

where r is the distance travelled in time t .

The expression for the energy transfer W from the electric field \vec{E} to a charged particle shows clearly that the field primarily gives energy to the electrons since the mass of the ions m_i is much larger than those of the electrons m_e ($m_i \gg m_e$). From the electrons the energy is transferred to atoms and ions by collisions. Therefore, at low pressures, the electron temperature T_e is much higher than those of the ions T_i and neutrals (gas) T_g , respectively. The three temperatures converge to similar values at a pressure around 100 mbar and the plasma becomes arc-like. Atmospheric pressure plasmas have temperatures of a few thousand Kelvin. Such plasmas, where local thermodynamic equilibrium ($T_e = T_i = T_g$) is achieved, in volumes of the order of the mean free path length for collision, are called local thermodynamic equilibrium (LTE) plasma or thermal plasma. In low-pressure plasmas, where the collision rate and therefore the energy transfer from electrons to neutrals is reduced, the electron temperature is much higher than the temperature of the ions and the gas ($T_e \gg T_i \approx T_g$). In such plasmas the LTE conditions are not achieved and therefore called non-LTE plasmas or cold plasmas. Cold plasma because the ion and gas temperatures are at about room temperature ($T_i = T_g \approx RT$), whereas the electron can reach temperatures of 10^4 – 10^5 K (1–10 eV).

In cold plasmas the electrons and the heavy particles are not in thermodynamic equilibrium, even at local scale in the order of the Debye length λ_D . The formula for the Debye length λ_D can be deduced from the Poisson equation and is:

$$\lambda_D = \left(\frac{\epsilon_0 k T_e}{n_e e^2} \right)^{1/2}$$

Cold plasmas can be excited and sustained by direct current (DC), radio frequency (RF), or microwave (MW) electric fields applied to the gas. From the

electric field the energy is transferred to the available free electrons by accelerating them, as mentioned before. Concomitantly the electrons lose energy in collisions with the gas. As long as the energy of the electrons is too low to excite or ionise the gas, the collisions will necessarily be elastic, and therefore heating the gas. Since the energy transfer from the electron to the gas is extremely small in the elastic collision the electron gains energy from the electric field until it is sufficiently high to cause ionisation or excitation through inelastic collisions. The electrons produced in the ionisation process are in turn accelerated by the electric field and produce further ionisation up to the plasma state.

In thermodynamic equilibrium the velocity distribution and consequently the energy distribution of the particles in the gas is Maxwellian. In cold plasma the electrons are in a non-equilibrium state ($T_e \gg T_g \approx RT$). The slower electrons make elastic collisions only, whereas electrons with higher energies are liable to lose a much larger fraction of their energy by inelastic collisions. Therefore the energy distribution of the electrons in cold plasmas is shifted to higher energy compared to the Maxwell-Boltzmann distribution. Instead of using the Maxwell-Boltzmann distribution $f_{MB}(E)$ it is better to approximate the electron energy distribution in cold plasma by the Druvestyn distribution $f_D(E)$.

$$f_D(E) = 1.04 \cdot \langle E \rangle^{-3/2} \cdot E^2 \cdot \exp\left(\frac{-0.55E^2}{\langle E \rangle^2}\right)$$

The Druvestyn distribution considers the motion of electrons in a weak electric field, such as existing in cold plasmas. Characteristic for both energy distribution functions is the high-energy tail. For reactions in the plasma requiring relevant electrons energies between 3 and 10 eV the Druvestyn distribution predicts a higher reaction rate as the Maxwell-Boltzmann distribution.

3. Plasma Treatment of Polymers

Owing to the low intrinsic adhesive properties of polymers, many applications of these materials require a surface pretreatment. Therefore, surface pretreatments of polymers in order to enhance their adhesive properties are of great technological importance. Plasma treatment of polymers is one of the more recent methods to achieve improved adhesion in systems such as polymer-adhesive

[3][4] or polymer-metal interfaces [5]. The merits of plasma surface treatment to improve the macroscopic adhesion strengths are generally accepted. Different effects of the plasma treatment on polymers are known. They include cleaning by ablation of low-molecular-weight material, activation of the surface, dehydrogenation, change in surface polarity and wetting characteristics, crosslinking and chain-scission and structural modification. These effects depend very much on the considered polymer and plasma used.

3.1. Chemical Modifications

Plasma treatment is a very efficient process to increase the surface energy γ , *i.e.* wettability of polymers dramatically. After plasma treatment polymer surfaces can easily show water contact angles ϑ smaller than 15° , as illustrated in Fig. 1. The increase of the surface energy γ of polymers by plasma treatment is related to the surface cleaning and the formation of polar bonds at the surface. For example, O_2 plasma is very effective to increase the surface energy of polyolefines as polypropylene (PP) or polyethylene (PE) by forming oxygen functionalities (Fig. 2a). The oxidation of PP ($-\text{CHCH}_3 - \text{CH}_2-$) in the O_2 plasma occurs *via* dissociation of the methyl group ($-\text{CH}_3-$) [5][6], as indicated by the relative intensity decrease of the associated peak in the valenceband spectrum (Fig. 2b).

The susceptibility of a polymer on structural changes induced by plasma treatment depends strongly on its chemical structure. For example polymethylmethacrylate (PMMA) is very susceptible for structural changes during plasma treatment especially in plasma with high ionisation degree [7]. Positive ions from the plasma react and neutralise at the partially negatively charged carbonyl oxygen (Fig. 3). After that, the created electron hole in the carbonyl group becomes filled by an electron transfer from the neighbouring non-polar C–C bond, cleaving side chains from the polymer backbone. In noble gas plasmas, where no incorporation of chemical active species is possible, all side chains within a thickness of 10 nm are removed after few seconds of plasma treatment. The ion-induced degradation process is in competition to the aspired formation of polar bonds and must be suppressed.

The C1s XPS spectra in Fig. 3 illustrate the effect of the ion flux during O_2 ECR plasma treatment on the chemical composition of the PMMA surface. The ion flux was varied, by changing the po-

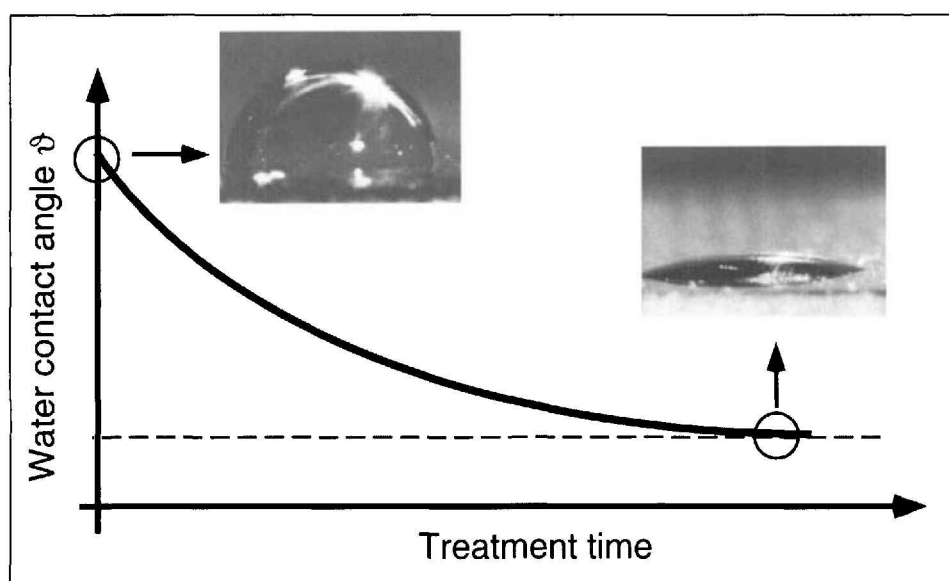


Fig. 1. Schematic illustration of the surface energy γ of a plasma-treated polymer surface as a function of the plasma exposure time.

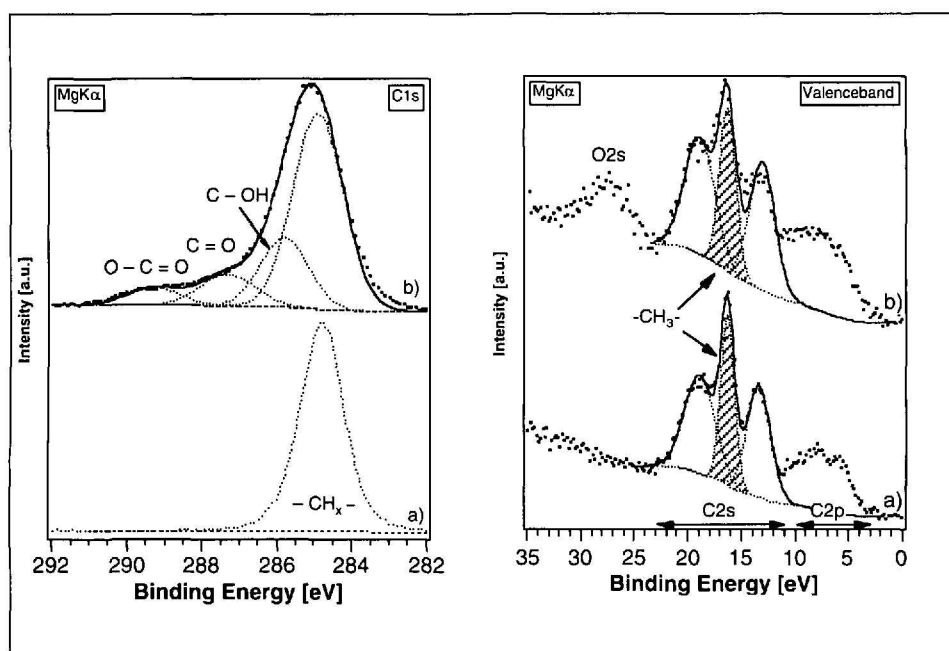


Fig. 2. Top; a) C1s XPS core level spectra and b) valenceband XPS spectra of polypropylene (PP). Bottom; a) untreated, b) O₂ plasma treated ($t = 5$ s, $p = 1 \times 10^{-2}$ mbar) [7].

sition of the sample, relative to the plasma zone. In this way the influence of the UV/VUV radiation is the same for both treatments and differences in surface modifications are correlated to the ion flux. Polymers with delocalised electrons (phenyl ring) in their chemical structure are generally less susceptible to ion-induced damage [8–10]. This, because electron transfer from the delocalised electrons system to electron hole, created by the ion neutralisation, can occur without breaking a bond.

The stability of a polymer in the plasma is primarily determined by the response of the polymer on the plasma induced damage and less on the primary damage itself. Generally, surface modifications of polymers by plasma are ac-

companied with degradation reactions of the polymer in the near surface layer. The thickness of the modified surface layer is typically 10 nm. This plasma modified surface layer is initially in a highly excited state and likes to relax. In the presence of a reactive metal film (adhesive layer, e.g. Cr) the functional groups introduced by the plasma tend to segregate to the metal, forming a covalent bond [7]. This process becomes equal to a phase separation process between the plasma-modified surface layer and the bulk polymer, resulting in the formation of a weak boundary of a few nanometers underneath the surface. Plasma pre-treated metallised polymer foils show therefore usually cohesive fractures in peel strength measurements.

To avoid phase separation processes between the plasma modified polymers and the bulk polymers degradation reactions must be minimised in the plasma treatment. Radicals in the plasma remove hydrogen atoms on the polymer surface to form carbon radicals. Successively, these radicals combine with other radicals in the plasma to form new functional groups. On the other hand electrons and ions bombard the polymer surface making chain scission to form carbon radicals at the end of the polymer fragments. This may result in degradation reactions of the polymer chain to yield degradation products with low molecular weight. These low molecular weight polymer chains are then subjected to reorientation at the polymer/metal interface, which may result in

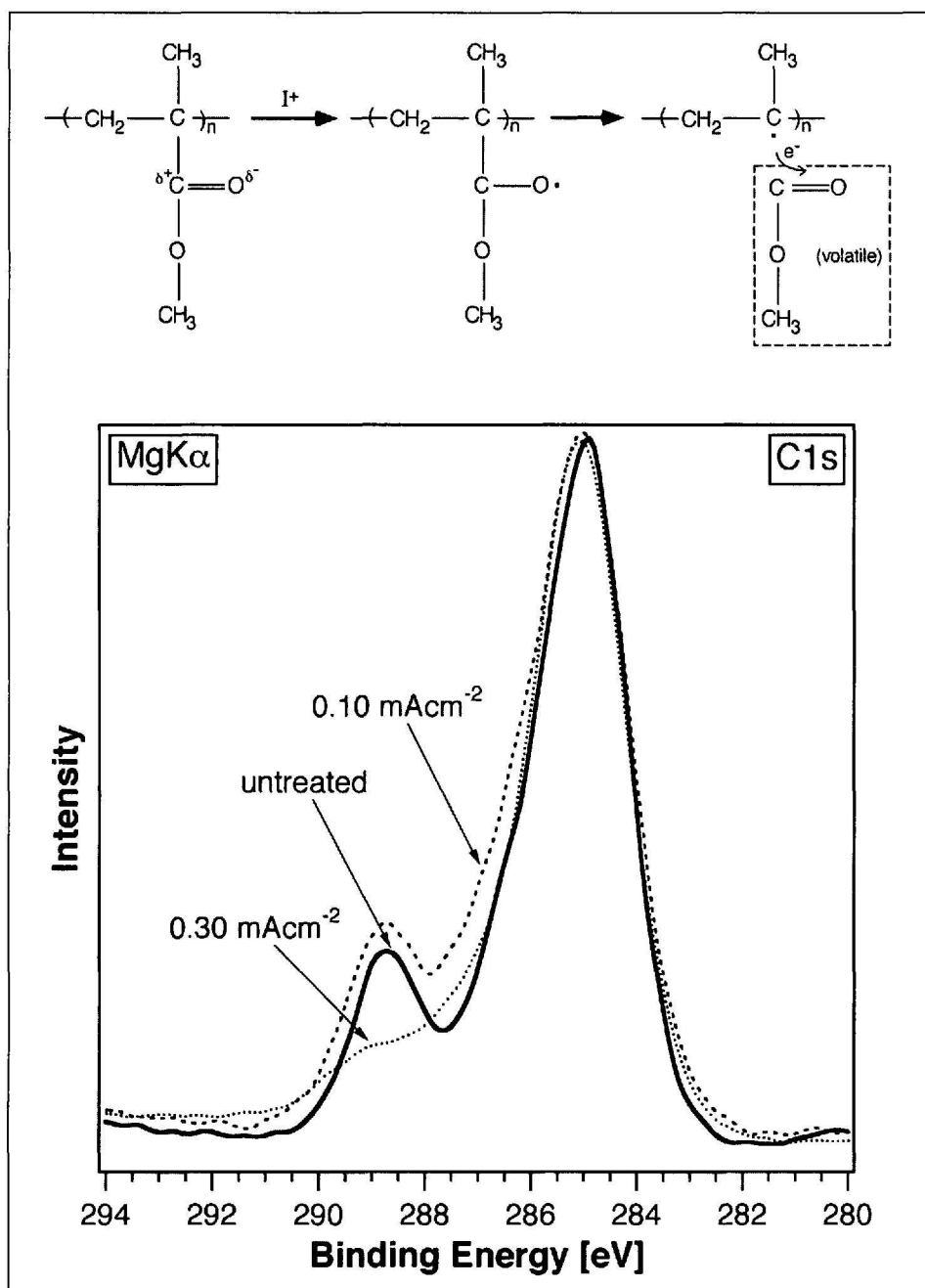


Fig. 3. Top; illustration of the side-chain scission in PMMA due to low energy ions. Bottom; C1s XPS spectra of PMMA, untreated and after O₂ plasma treated with two different ion fluxes [11].

the formation of a weak boundary layer. To escape from these degradation effects the plasma parameters must be tuned in the direction that the charged particle concentration in the treatment zone is minimal so that radicals alone are predominantly used as active species for the surface modification. This is possible

because the lifetime of radicals in the plasma is generally much longer than those of the electrons and ions (Table 1). In addition electron-ion recombination takes place generally via radical formation. As a result, radicals will outlive ions and electrons by far outside the plasma excitation zone or when the plasma is

Table 1. Reaction constants of the dominant recombination processes in an O₂ plasma [12].

Reaction	Rate constant k
$e + O_2^+ \rightarrow O^+ + O$	$< 10^{-7}$ [cm ³ / s]
$e + O^+ \rightarrow O$	$< 10^{-7}$ [cm ³ / s]
$2O + O_2 \rightarrow 2O_2$	$2.33 \cdot 10^{-33}$ [cm ⁶ / s]

switched off. This opens now the possibility of reducing the electron and ion reaction during the plasma treatment by operating the plasma either in the remote mode (separation in space) or as pulsed plasma (separation in time).

3.2. Topographical Modifications

Besides chemical modifications, physical and topographic modifications can also be made on polymer surfaces by plasma treatments. The ability to change the topography of polymers by plasma is for example very interesting for the fabrication of soft contact lenses. The eye tolerability and the wearing comfort of such contact lenses are determined considerably by its surface topography and wettability. Both properties can be optimised by plasma treatment. The surface topography of polymers has also influence on the adhesion of metallised films. Several publications report on investigations on the topography of treated polymer surfaces with atomic force microscopy (AFM) or scanning electron microscopy (SEM) analysis. The applied treatments were ion bombardment [13], excimer laser treatment [14], or various plasma treatments such as corona discharge [15][16], RF or DC plasmas [17–20].

Our AFM investigations on PP [21] and PMMA have shown that completely different surface topographies can be created by plasma treatment depending on the gas used. Plasma treatments with reactive gases (O₂, N₂, NH₃) induce weak morphology changes. Moreover, the modifications of the surface roughness are very sensitive to the plasma conditions, so that polymer surfaces treated in reactive gas plasmas can be either smoother or rougher than the untreated polymer. For the untreated PP (Fig. 4a) we measured for a 6 μm x 6 μm area a RMS roughness of 45 nm. After N₂ plasma treatment the RMS roughness is between 5 nm and 100 nm, depending on the treatment conditions. The situation is totally different by using noble gas plasmas. Noble gas plasmas (He, Ar, Ne, Xe) are able to create complete new morphologies at polymer surfaces. The AFM images in Fig. 4 show the morphology changes on PP induced by Ar and He plasma. The He-treated PP surface is covered by a dense network of macroscopic chains, while the Ar-plasma-treated surface presents a smaller granular structure. In fact the granular structure of the Ar-plasma-treated surface is only a first stage in the process of chain formation as observed on the He-treated surface. Actually, all noble gas plasmas

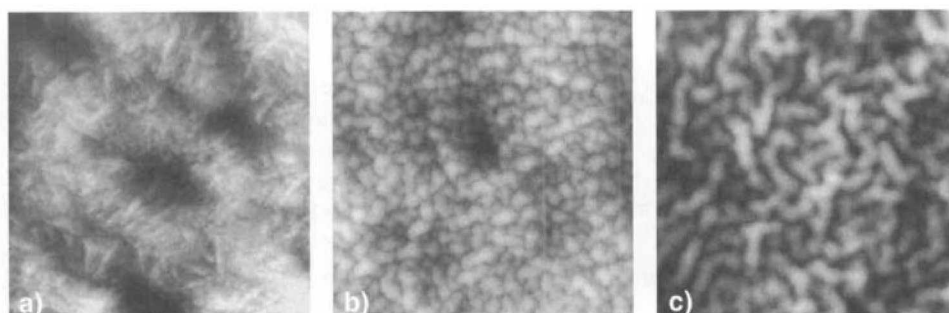


Fig. 4. AFM images ($1\mu\text{m} \times 1\mu\text{m}$) of PP, a) untreated, b) Ar ECR plasma, and c) He ECR plasma treated for 120 s and with -120 V RF-bias [21].

form first the granular and afterwards the chain structure at the PP surface, depending on the treatment time. The formation of chain like structures finds application in the manufacturing of soft contact lenses (www.solvias.com).

Overney *et al.* [15] found that corona treated PP (energy dose 112.5 J/cm^2) presents droplet-like protrusions of about 450 nm in diameter. The protrusion size increases (up to 700 nm) with increasing energy dose. They attribute the protrusion formation to local surface melting. Similar morphologies as on the noble gas plasma treated PP and PMMA surfaces have been found on polyethersulphone (PES) and polyarylsulphone (PAS) after XeCl or KeF excimer laser ablation in air and under vacuum [22]. A minimal energy deposition of 0.5 to 1.0 J/cm^2 is needed to obtain the characteristic chain structure with diameter ranging from $0.7\text{ }\mu\text{m}$ to $1.3\text{ }\mu\text{m}$. They attribute this phenomenon to photo-induced thermal processes of high mobility and solidification at the etched polymer surface during and after ablation. These results indicate that the difference between noble gas and reactive gas plasma treatments on the surface morphology is associated to a much higher mobility of noble gas plasma modified polymer chains. The main difference between reactive gas plasmas and noble gas plasmas is the lack of chemical active species in the latter. In reactive gas plasmas the radicals formed on the polymer can be saturated by chemical active species from the plasma forming new chemical groups or cross-links. Due to the lack of chemical active species this is not possible in noble gas plasmas. Therefore radicals formed at the polymer surface are forced to saturate themselves on the polymer. In the particular case of polyolefins, containing only carbon and hydrogen, noble gas plasma treatments induce hydrogen desorption resulting in the formation of carbon double bonds, clearly evidenced by XPS measurements [23]. The formation of carbon double bonds in polyolefines by noble gas plasma treat-

ments leads to a dramatic decrease in the electrical resistance [23]. Actually, a resistance drop of up to ten orders of magnitude was measured on He-plasma-treated PP. Table 2 shows the resistance of PP after plasma treatments with several gases. The resistance values are steady-state values obtained by the individual plasma treatment. The results in Table 2 show that the decrease in resistance by noble gas plasma treatments becomes smaller with increasing mass of the gas atoms, and reactive gas plasma treatments do not affect the resistance. The change in resistance by noble gas plasma treatments can be traced to ions in the plasma. The saturation of the resistance decrease occurs at ion doses between 10^{17} and 10^{18} ions/cm^2 and the higher the ion energy (RF-bias: 0 – 230 V), the lower the resistance. Taking into account the penetration depth of low energetic ions in polymers which is between 1 and 10 nm , the resistivity of the He plasma modified surface layer can be estimated to be around $0.1\text{ }\Omega\text{cm}$.

4. Plasma Polymerisation

The development of plasma polymerisation processes began in the 1950's [24][25] and since the 60's plasma polymerisation processes have been studied intensively [26][27]. Plasma polymerisa-

tion is essentially a plasma enhanced chemical vapour deposition (PECVD) process. It refers the deposition of polymer films through reactions of the plasma with an organic monomer gas. Plasma polymerisation is a specific type of plasma chemistry and involves homogeneous and heterogeneous reactions, the former are reactions between plasma species and the latter between plasma and surface species and the surface species itself. The two types of reactions are often called 'plasma-state polymerisation' and 'plasma-induced polymerisation'. Several kinetic models of plasma polymerisation have been proposed. The most popular are the models of Yasuda [28], Poll *et al.* [29] (Fig. 5), and Lam *et al.* [30]. These models involve ablation and polymerisation mechanism in a competitive process.

The expression 'plasma polymerisation' is strictly speaking not correct because the process results in the preparation of a new type of material and is not a kind of polymerisation in the classical sense. In contrast to conventional polymerisation, based on molecular processing, the plasma polymerisation is an atomic process with rearrangements of the atoms within the monomer. Consequently the materials formed by plasma polymerisation are very different from conventional polymers. Its structures are more like highly cross-linked oligomers. This special structure makes plasma polymers generally chemically and physically different from conventional polymers. Plasma polymers are generally:

- 1) chemically inert
- 2) good adherents to a variety of substrates including, polymer, glass, and metal surfaces
- 3) pinhole-free and
- 4) can be easily formed with thicknesses from microns down to nanometers, and as multilayer films, or films with grading of chemical or/and physical properties.

Table 2. Resistance of PP after ECR plasma treatments with several gases [23].

Treatment	Resistance [Ω]	RF-bias [V]	Treatment time [s]
As-received	$> 10^{16}$	-	-
N_2	$> 10^{16}$	-200	600
O_2	$> 10^{16}$	-200	600
H_2	$> 10^{16}$	-200	600
He	2×10^7	-230	30
Ne	1×10^{10}	-220	120
Ar	1×10^{10}	-150	120

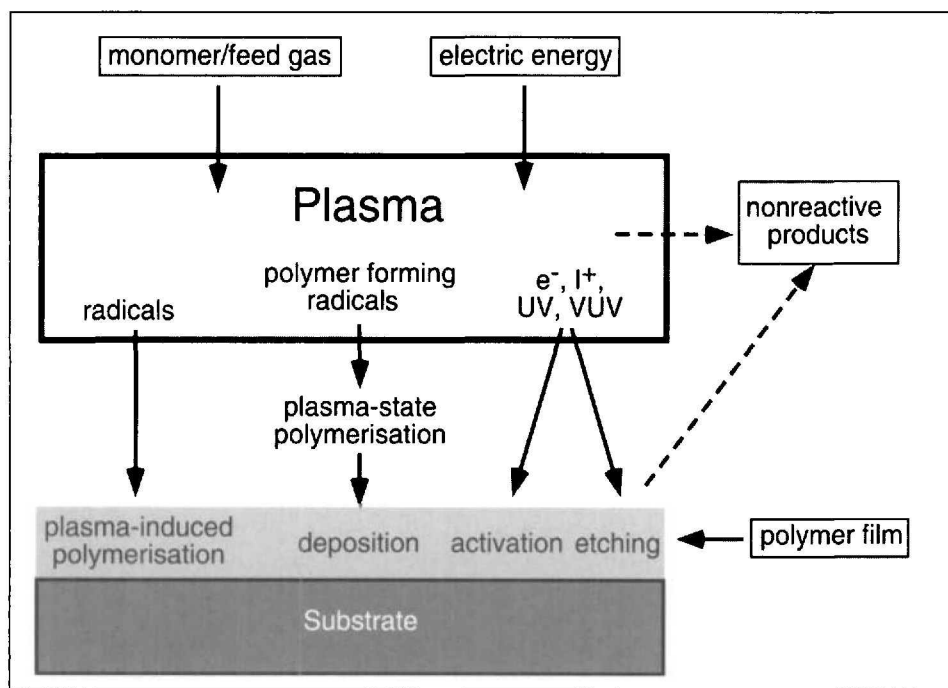


Fig. 5. Reaction diagram of the plasma polymerisation process accordingly to Poll *et al.* [29].

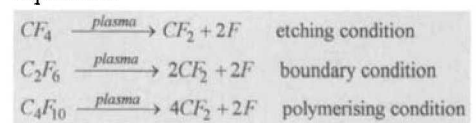
Plasma polymers find applications as adhesion promoter for all kind of substrates, membrane for gas separation or vapour barrier, UV protection coating, anti-reflection coating, photo-resist, anti-adhesive film, *etc.* Plasma polymerisation involves deposition and ablation mechanisms in a competitive process. This behaviour can be observed particularly well in fluorocarbon sustained discharges. Pioneer work on fluorocarbon sustained discharges has been done by Coburn and Winters [31] in the late 70's.

They found that fluorocarbon sustained discharges can be operated in

overall polymerisation or etching conditions depending on the F/C ratio of the precursor (Fig. 6). Typically, a high F/C ratio of the precursor, *e.g.* CF₄, leads to efficient etching, whereas a low F/C ratio, *e.g.* C₂F₄, favours easy polymerisation.

The ability to tune the fluorocarbon sustained discharge for polymerisation or etching demands the presence of three competitive active species in the discharge. Namely CF_x radicals as reactive fragments for the polymer deposits, the F atoms to trigger the etching by forming volatile fluorides and charged particles.

The excess of one of these species defines the polymerising or etching behaviour of the discharge. If we consider the CF₂ radicals as the main polymerising species then the characteristic of the fluorocarbon discharge can be simply determined by the corresponding chemical equation:



Therefore, a better criterion for characterising the plasma behaviour is the ratio of the active species [F]/[CF_x] rather than the F/C ratio of the precursor. The active species in excess defines etching or polymerising behaviour of the plasma. The relative ratio of the active species can be varied by changing precursor gas or by varying the type and the amounts of additive gases. Oxygen as additive gas increases the etching behaviour of the fluorocarbon discharge, while the addition of hydrogen increases the polymerisation behaviour. In fact, hydrogen reacts with F atoms leading to non-reactive HF resulting in a reduced etching activity. Obviously similar behaviour can be obtained with a precursor containing hydrogen, such as CHF₃. On the other hand, active carbon sites can be saturated by O atoms and converted to inactive CO, CO₂ and COF₂. F atoms are no longer recombined and their content therefore increases resulting in a higher etching activity. Positively charged particles are the third active species influencing the characteristic of fluorocarbon discharges. These particles are accelerated to the substrate and affect etching and heterogeneous polymerisation processes. With increasing particle energy (substrate bias) the etching process is enhanced, as indicated by the bias dependence of the polymerisation/etching boundary in Fig. 6.

We take advantage of the behaviour illustrated in Fig. 6 to develop a 'self-thickness-limited' plasma polymerisation process to create an ultra-thin anti-adhesive film [32]. With this process we were able to produce films with an extremely low surface energy of 4 mJ/m² and 5 nm thickness, auto-controlled by the plasma. The developed deposition process takes place in two steps, a growth and a treatment step. With the CF₄/H₂ gas mixture used, we tuned the plasma conditions such that the polymerisation starts close at the polymerisation/etching boundary (Fig. 7, point I). Due to the mobile electrons in the plasma the growing insulating polymer film becomes negatively charged until it reaches the poly-

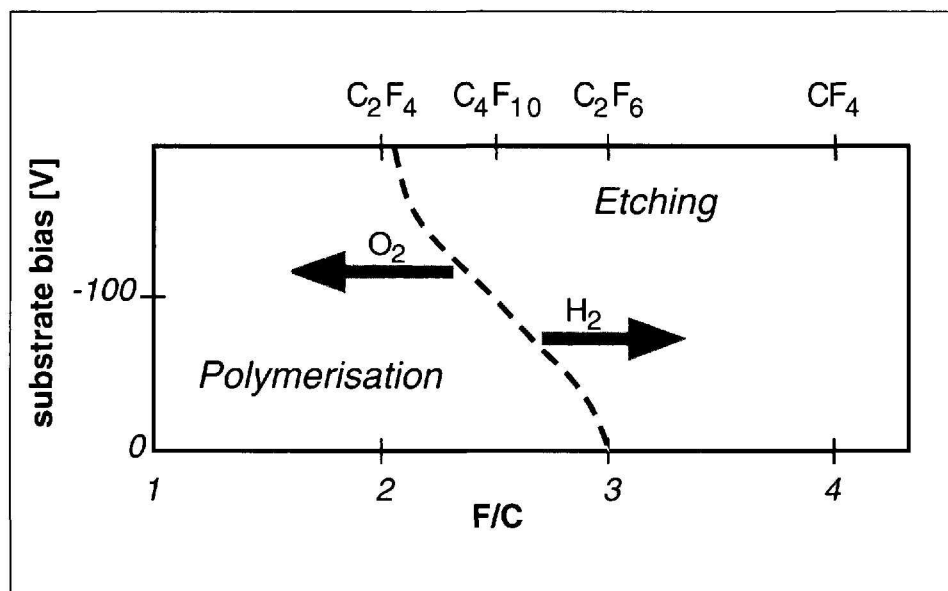


Fig. 6. Boundary between polymerisation and etching conditions as a function of the fluorine to carbon (F/C) ratio and the negative substrate bias. Additional oxygen displaces the boundary to lower F/C ratio, hydrogen to higher F/C ratio (according to Coburn and Winters [31]).

merisation/etching boundary (Fig. 7, point E). At this point, the etching process balances the polymerisation process and the deposition changes from the growth to the treatment step. At the end of the deposition process the plasma polymer film contains 85% CF_2 groups and shows the extremely low surface energy of 4 mJ/m^2 , which is four times lower than that of Teflon®.

The excellent hydrophobic behaviour of this film is demonstrated in Fig. 8 by a water droplet on a Swiss coin covered with such a plasma polymer film. The film was tested as an anti-adhesive coating for the replication of micro-optical structures, using a Ni-shim with a very fine surface relief grating (400 nm periodicity) to hot emboss ($T = 180 \text{ }^\circ\text{C}$) polycarbonate (PC). The tests demonstrate the excellent anti-adhesive property of the film against the PC and reveal a good adhesion of film with the Ni-shim [33].

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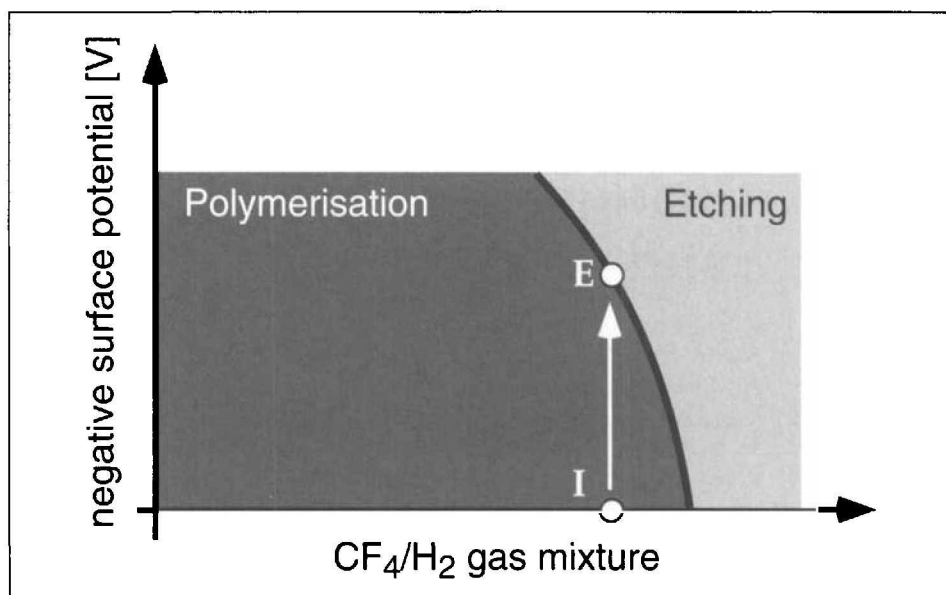


Fig. 7. Schematic illustration of the 'self-thickness-limited' plasma polymerisation process [32].

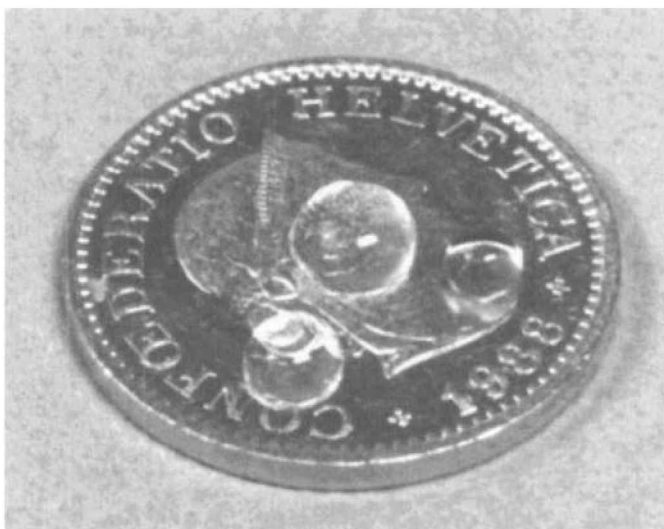


Fig. 8. Water droplet on a Swiss coin covered with a 5 nm thick anti-adhesive plasma polymer film [33].

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