University of Technology Delft
Julianalaan 136, 2628 BL, Delft, The Netherlands

University of Technology Delft
Department of Polymer Science and Technology
Delft – The Netherlands

Supervisor: Prof. Dr. Ir. J. van Turnhout

Influence of the discharge current on the deposition of $HMDSO/O_2$ – plasma at polypropylene membranes

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Remco Gulickx

Université Paul Sabatier
Laboratoire de Génie Electrique
Toulouse III – la France

Supervisors: dr. P. Raynaud
dr. Y. Ségui

Laboratoire de Génie Electrique de Toulouse-associee au C.N.R.S.
118, Route de Narbonne – 31062 Toulouse Cedex, la France

Resumé

Ce rapport présente l'influence du courant de décharge sur des dépots plasma de HMDSO/O_2 sur des films de polypropylene (PP). Les expériences se font dans un réacteur de verre cylindrique fonctionnant à basse fréquence (3.8 kHz). Le mélange gazeur dans le réacteur se compose de 90% d'0_2 et de 10% d'HMDSO pour une pression totale de 40 mTorr. L'echantillon de PP est placé sur l'electrode inférieure qui est réliée au générateur, l'épaisseur de la couche déposée est fixée à 1000 Å.

Plusieurs méthodes de diagnostic ont été utilisées pour étudier l'influence du courant sur la perméabilité des films traites: mesure de perméabilité bien sûr, mesure d'epaisseur, mesure de densité et spectrométrie d'absorption IR.

Quand le courant de décharge augmente, c' est à dire que la puissance amenée à la décharge croit, l'autopolarisation (V_{DC}) augmente (en valeur absolue) pour des courants supérieurs à 1 mA ainsi que la vitesse de dépot (V_{dep}). Le rapport R traduisant le caractère inorganique des films déposés reste faible avec ses conditions de manipulation, beaucoup de liasons organiques (Si-CH_3, Si-$(CH_3)_2$, C=0, ...) restent présentes dans le dépot. Lorsque la puissance augmente, on peut aussi constaté que le flux d'0_2 à travers le film diminuait alors que la densité, la vitesse de dépot et le rapport R augmente.

Il semble difficile d'obtenir une couche homogène à cause de la formation de plis durant le dépot, due au bombardement ionique. L'epaisseur fixée de 1000 Å est elle aussi difficile à respecter, à cause du temps très court (à partir de 30 secondes) de manipulation durant lequel on doit maintenir le courant à la valeur déterminée et mesurer le différentes grandeurs électriques. Les vitesses de dépot calculées varient aussi quelque fois avec l'expérience, notamment avec les faibles variations du mélange gazeur.

Le meilleur résultat en ce qui concerne la perméabilité à l'0_2, est obtenu pour les plus fortes courants, ici 8 mA; le flux d'0_2 par rapport à un film vierge est alors de 17% in the film.

Abstract

In this report the influence of the discharge current on the deposition of HMDSO/O_2 onto polypropylene (PP) membranes is discussed. The experiments took place at a low frequency (3.8 kHz) in a cylindrical glass reactor. The gas mixture in the reactor consisted of 90% O_2 and 10% HMDSO reacted at a low pressure of 40 mTorr. The polypropylene substrate was positioned on the lower electrode, and was covered with a layer of 100 nm of plasma deposited film.

Several different diagnostic techniques were used to study the influence of the discharge current I_d on the permeability of the treated PP membranes such as thickness and density measurements, FTIR absorption spectrometry and of course permeability measurements.

When the discharge current increases, that is to say the discharge power P_d increases, the autopolarisation voltage V_{DC} increases (in absolute value) for currents larger than 1 mA as does the deposition rate, v_{dep}. The inorganic part of the film R remained very low under the process circumstances used, which points to a large quantity of organic bonds (Si-$(CH_3)_3$, Si$(CH_3)_2$, C=O....) in the film. With increasing plasma power, the flux of oxygen through the membrane decreases while the density, the deposition rate and the R-factor increase. The quality of the plasma deposited membrane improves.

It is difficult to create a homogeneous layer, because of the formation of pleats during deposition, due to ionic bombardments. The goal of creating a uniform thickness of 100 nm on the PP substrate is difficult to reach, because of the very short manipulation time (of 30 seconds) available. During this time the desired current has to be set and several electrical quantities must be measured. The uniformity of measurements is also affected by variations in gas mixture, furthermore a difference in calculated deposition rate occurs.

The plasma polymer film with the best results, regarding O_2 permeability, is reached at the highest currents (here 8 mA); the maximum reduction in flow, when compared to non-deposited membranes, is 17 %.

Contents

I. Introduction

One can obtain very thin, uniform and pinhole-free films (a few nm's) with a high gas selectivity because of their high density by using a plasma polymerization process. Applications can be found in the field of membranes, barrier coatings for gases in packaging and various other areas.

As a precursor HexaMethylDiSiloxane (HMDSO) has been chosen because of previous measurements <1>. These have shown good durability properties due to the siloxane functionality, which would be beneficial in coupling the silicate network to the polymeric substrate. The substrate, a polypropylene (PP) 18 □m film from the Mobil company, has a good chemical resistance, good thermal insulation characteristics and PP-fibers are the lightest of all commercial textile fibers <2>.

In this study the influence of the discharge current I_d (during plasma deposition) on the oxygen permeability of PP was measured. A bell-jar, low frequency (3.8 kHz) glow discharge reactor was used. The plasma conditions were as follows: 90% O_2 and 10% HMDSO mixture and a pressure of 40 mTorr. The deposited substrates were compared to PP substrates without deposition. Several diagnostics on the films obtained such as thickness measurements, density measurements and FTIR absorption spectrometry were applied.

This traineeship took place at the Laboratoire de Génie Electrique in Toulouse (LGET) in the group "deposition and treatment of surfaces by plasmas", under the supervision of Dr. Y. Ségui and Dr. P. Raynaud.

II. General plasma theory

Plasma is considered as being the fourth state of materials. A plasma is at a much higher energy level compared to the solid, liquid, and the gas state. To reach the plasma state of atoms and molecules, energy for ionization must be supplied by an external energy source. In general the plasma state is obtained at low pressure of $1\text{-}10^{-3}$ Torr, accept for the atmospheric pressure glow discharge (APG) discussed in <3>. In general, the distance between the electrodes in the normal glow discharge plasma corresponds to characteristic dark spaces and luminous regions. These zones depend on the nature of the gas, the distance of the electrodes, the pressure and the potential between the electrodes, as shown in figure 1.

II.A Plasma reactions

Plasma polymerization is a process of acquiring polymer films by utilizing high-energy electrons, ions, atoms, radicals, excited molecules, and various other active species provided by an electric discharge. To make a plasma state, electron separation from atoms or molecules in the gas state (ionization) is required. Generally, molecules are dissociated into atoms before ionization, and, then, the dissociated atoms are ionized. The energy for dissociation is fairly low compared with that for ionization.

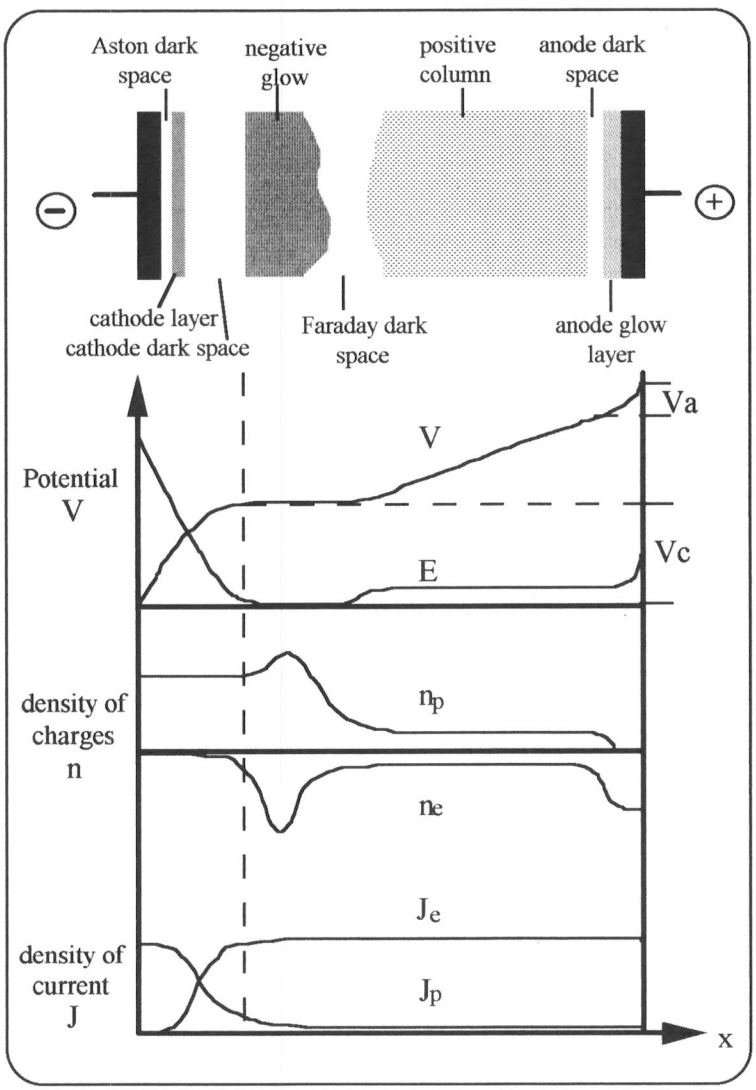

Figure 1. Structure and properties of a luminescent normal glow discharge <4>

Upon increasing the voltage in a diode structure an abrupt increase in the current appears. This marks the so-called electrical breakdown voltage, V_B. A self sustaining discharge (when $V>V_B$) is created which depends on the product of pressure and distance of electrodes (d) The relationship between these parameters is given in figure 2 by Paschen's law, $V_B = f(pd)$,. Processes

that generate charged particles must be in balance with losses to the walls (which usually predominate) and volume recombination. This law provides guidance for a design of a stable glow discharge apparatus and for shielding.

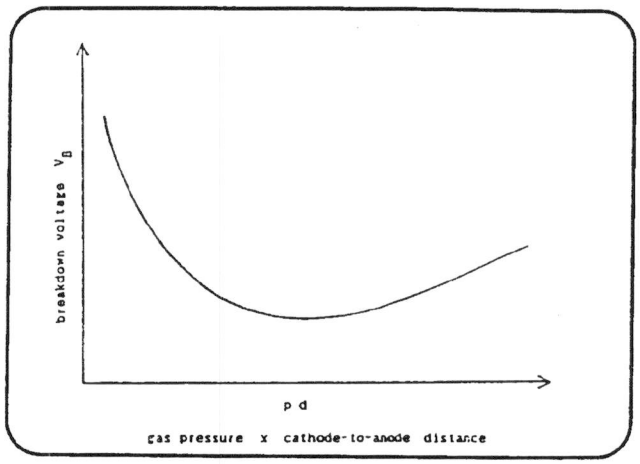

Figure 2. Illustration of Paschen`s law for gas breakdown

Further, the behavior of the charged particles depends on the frequency, f, and on the applied signal. At low frequencies (<100 kHz), the electrons and also the ions follow the variations of the electrical field, as given by

$$\mathbf{f} < \mathbf{f_{pi}} = \frac{1}{2\cdot\pi}\cdot\sqrt{\left(\frac{n_i\cdot e^2}{\varepsilon_o\cdot m_i}\right)} < \mathbf{f_{pe}} = \frac{1}{2\cdot\pi}\cdot\sqrt{\left(\frac{n_e\cdot e^2}{\varepsilon_o\cdot m_e}\right)} \qquad (1)$$

f_{pi} = ionic plasma frequency (s^{-1})
n_i = ion density (cm^{-3})
e = electron charge = 1.6 10^{-19} (C)
ε_o = permittivity of vacuum = 8.854 10^{-12} (Fm^{-1})
m_i = ion mass (kg)
f_{pe} = electron plasma frequency (s^{-1})
n_e = electron density (cm^{-3})
m_e = electron mass (kg)

Cold low-pressure plasma (in this report a normal glow discharge) has typically 1 charge carrier per 10^4 neutral species (atoms, molecules etc.). The negative particles are mostly electrons. However, in the presence of an electronegative gas (e.g. oxygen) a considerable number of negative ions are formed. The overall electrical charge of the thermodynamic system is zero, so a plasma is electrically neutral. Cold plasmas are not in thermodynamic equilibrium. It is to say the average temperatures (energies) of the particles present in the plasma are different. The ion temperature, T_i, is a fair amount lower than the electron

temperature, T_e, because ions loose a greater part of their kinetic energy in collisions with other ions and neutral atoms or molecules. The ion temperature is very low and nearly equal to that of the neutral atom, $T_i = T_n$.

II.B Plasma interactions

From a phenomenological point of view, plasma is distinguished into two categories, the non-polymer-forming plasma and the polymer-forming plasma, table 1.

Table 1. Phenomenological distinction

Kind of plasma	**Kind of gas**	**interactions**
non polymer forming gas	inorganic gas	etching reactions implantation of atoms radical generation
polymer forming gas	organic gas	polymer deposition

Considering a polymer substrate the chemical meaning of such reactions is that the etching reaction is a degradation reaction of polymer materials occurring at the surface of the polymers. The implantation is a recombination reaction between the radicals generated at the polymer surface and the radical activated from gas molecules. The radical generation is a hydrogen abstraction reaction from the polymer chains or chain scission of the polymer chains. The polymer deposition is a polymerization reaction of organic molecules introduced into the plasma. The durability of composite membranes prepared by plasma polymerization has been shown to be excellent. The monomer molecules are exposed to all the energetic particles in the plasma (mainly electrons). The competitive ablation and polymerization (CAP), shown in figure 3, takes place when the monomer gas or vapor passes through the plasma zone <5>. It becomes a complex mixture of the original monomer, ionized and excited species, or fragments from the monomer, and gaseous products that do not participate in plasma polymerization.

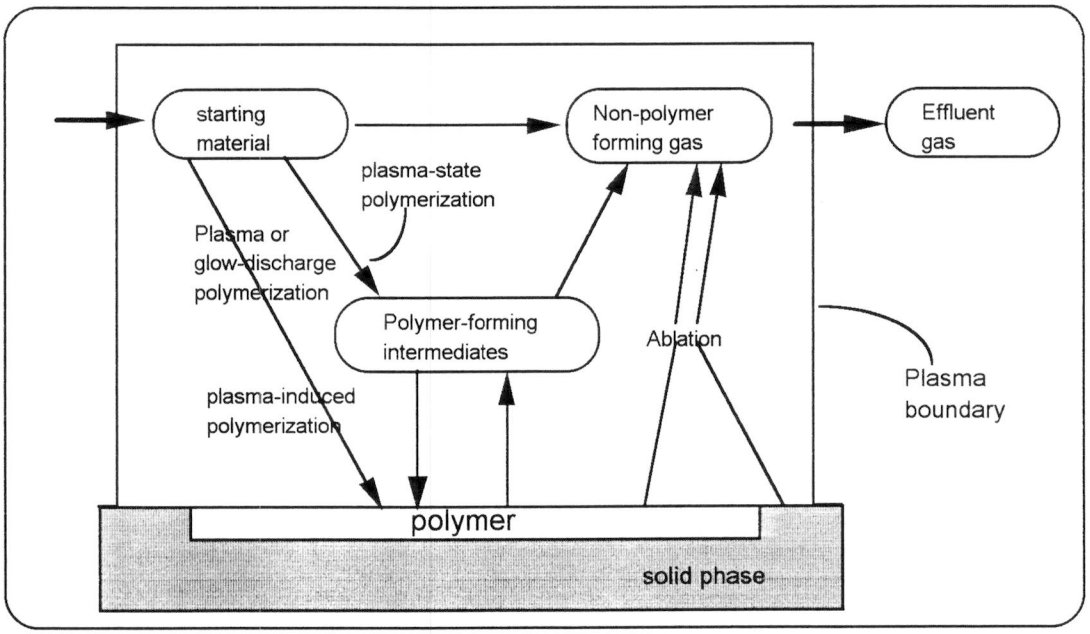

Figure 3. Competitive Ablation Process (CAP) of plasma polymerization, Yasuda

II.C Electrical properties

The electrical excitation used in this study is an alternative voltage,

$$V(t)=V_m \cdot \sin(\omega t) \qquad (2)$$

V_m = maximum amplitude of the applied voltage (V)

ω= radial frequency of the voltage (s^{-1})

t = time (s)

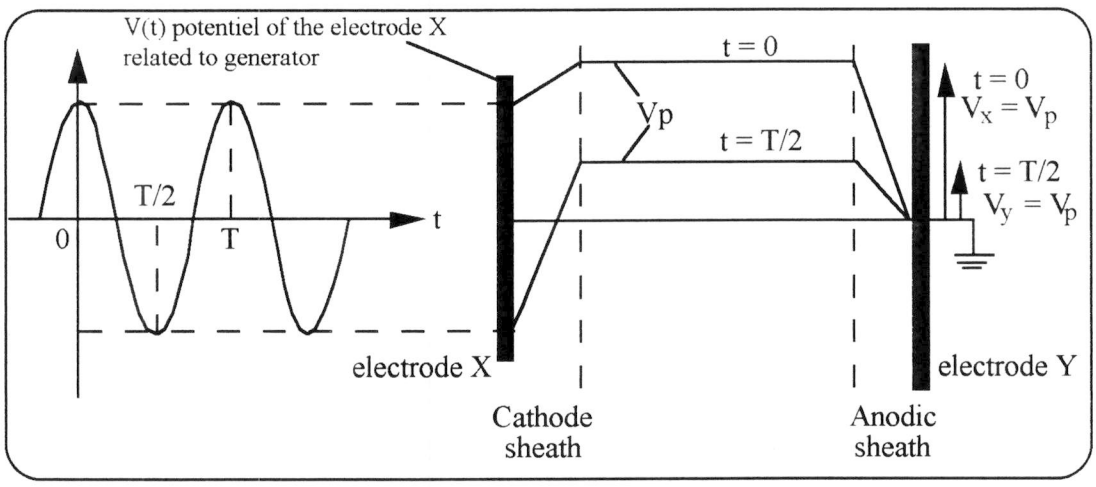

Figure 4. Voltage between two electrodes in a capacitively coupled system

Insulating materials are used as substrate and this doesn't allow the use of a continuous voltage with a direct coupling system. Here a blocking capacitor (capacitively coupled system) is used. Due to the difference in the mobility of

ions and electrons a continuous voltage at the cathode (generator electrode), V_{DC} , is created which can be quite negative, as shown in figure 4. V_{DC} is related to the characteristic plasma potential, V_P, and depends of the geometry of the electrodes, see figure 5 <6>. This gives at a low frequency the equation

$$\overline{V}_P = \frac{1}{\pi}\left(V_m^2 - V_{DC}^2\right)^{1/2} + \frac{V_{DC}}{\pi}\cdot\cos^{-1}\left(\frac{-V_{DC}}{V_m}\right) \qquad (3)$$

When both electrodes areas are equal, average plasma potential is given as,

$$\overline{V}_p = \frac{V_m}{\pi} \qquad (4)$$

which is a constant, always positive and higher than the potential V(t) of the two electrodes. With the value of V_P you can measure the energy of the ions that bombard the walls and the surface of the substrate. Another value of the potential is of theoretical importance, the floating potential, V_f. This is the potential of an electrically isolated surface, and is related to V_P as follows

$$V_p - V_f = \frac{k\cdot T_e}{2\cdot e}\ln\left(\frac{m_i}{2.25\cdot m_e}\right) \qquad (5)$$

k = the Boltzman constant = 1.38 10^{-23} $J.K^{-1}$
T_e = the electron temperature (K)
e = electron charge = $1.6\cdot10^{-19}$ (C)
m_i = ion mass (kg)
m_e = electron mass (kg)

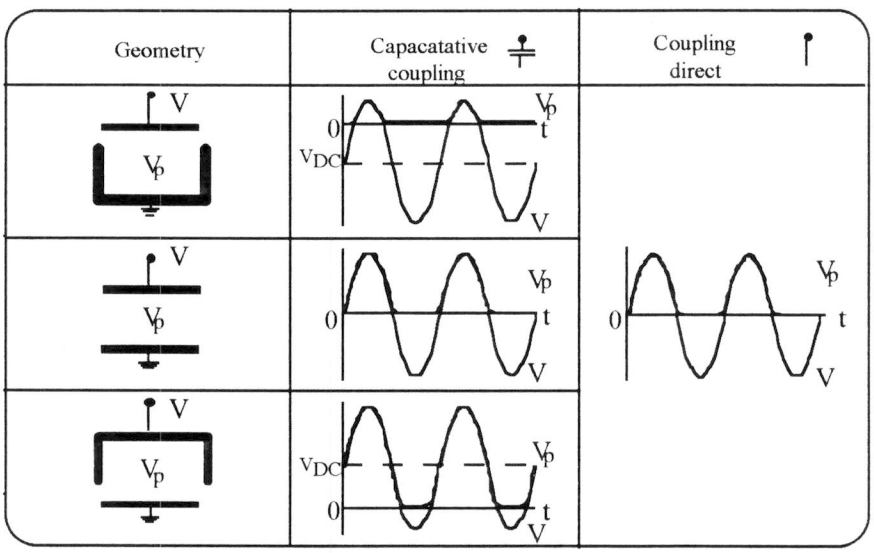

Figure 5. Influence of geometry and coupling at excitation signal in a low frequency reactor.

III. Permeability theory

The fundamental properties of membranes required for gas separation are a high permeability and a high permselectivity. For barrier coatings a very low permeability is important.

Membrane separation processes require ultrathin films in order to give a reasonable flux to make the process practical. So, polymer thin films produced by plasma polymerization have found potential applications as separation membranes and barrier packaging materials. If such a film exhibits an extraordinarily low permeability, it can be applied to the surface of the bulk material to improve its barrier quality. Frequently, silicone compounds and fluorine compounds are used as monomers for plasma polymerization. Silicon-containing polymers have good gas permeability, but poor gas separating ability. On the other hand, fluorine containing polymers have good gas separating ability, but poor gas permeability.

III.A Permeation

The permeability characteristics of plasma polymers deposited on porous substrates are different from those of conventional polymer films. The characteristics are closely related to the deposition mechanism of plasma polymers on porous substrates and the polymerization mechanism of plasma polymers, as presented in figure 3. Also the quality of deposition is important, see figure 6, to form a uniform film without pleats.

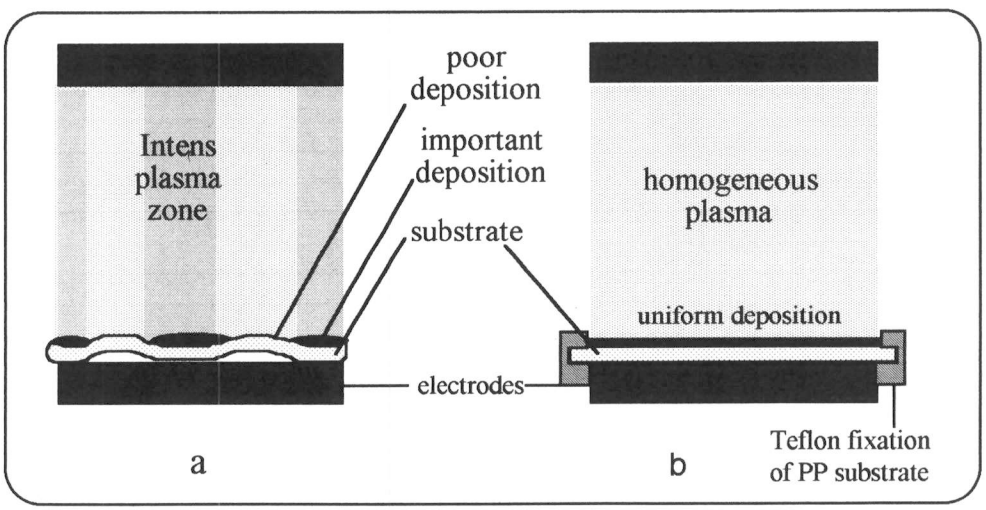

Figure 6. Influence of pleats on the quality of deposition

The permeability coefficient for conventional polymer films (solid membranes) is an intrinsic value and is constant even when the thickness of the films

increases. The permeability coefficient of plasma polymers deposited on porous substrates (composite membranes) shows a strong dependence on the film thickness and the monomer composition <7>. So, the permeability coefficient of plasma polymers is not only intrinsic in nature, but also extrinsic. In comparing the permeability coefficient of plasma polymers, the plasma polymerization conditions, the porous substrates used for plasma deposition, and the thickness of the deposited films should be taken into consideration.

When polymer barrier properties are considered, the permeation process is of practical importance. Molecules of gases and liquids move from one side of the polymer film to the other side of the film.

This process involves three elemental steps:

1. adsorption of molecules at the surface of the film and solution of the adsorbed molecules near the upper layer of the film (the combination of these two steps is called the sorption step)
2. diffusion of the dissolved molecules to the other side of the film as a result of concentration differences, and
3. desorption of the molecules reached at the surface of the film.

The permeation is controlled by the sorption and the diffusion step. The activation energy of the desorption step is negligible compared with that of the sorption and the diffusion step.

The permeability of gases and vapors in a flawless polymer matrix is well established by the solution-diffusion principle. Due to a significantly lower level of solubility, the permeation through the plasma polymer occurs not according to a true solution-diffusion principle. Many plasma polymers show characteristics in between solution-diffusion type polymers and molecular sieves. We do not take this in consideration and describe the solution-diffusion principle in a simple way.

III.B The principle of the Solution-Diffusion

Let us consider the simplest case the gas sorption following Henry's law and the diffusion following Fick's law. The solubility is described by several different kinds of isotherms, Henry's, Langmuir, Flory-Huggins, Brunauer-Emmet-Teller (BET) etc. <8>. When the transport of gas molecules through a film is in the steady state, the flux (J) of the molecules across the film (figure 7) is given by Fick's law

$$J = -D \cdot \frac{\partial C}{\partial x} \qquad (6)$$

D = diffusion coefficient of the penetrating molecules (cm^2/s)
δC = concentration difference across the membrane (cm^{-3})
δx = path of the molecules through the film (cm)

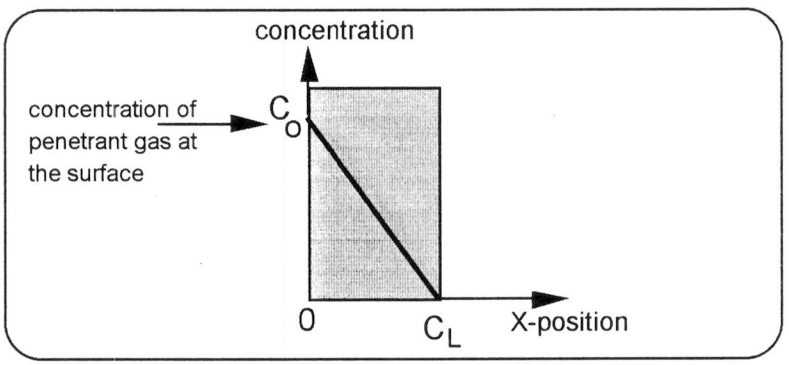

Figure 7. The concentration gradient across a membrane

The diffusion follows an activation process identical to the sorption. It depends on the energy required to create a passage through the polymer permitting the penetrants to migrate from site to site. This explanation is associated with the free-volume theory which leads to the expression of the diffusion coefficient according to the Cohen-Turnbull and Fujita theory

$$D = A \cdot R \cdot T \cdot \exp \cdot \left(-\frac{B}{V_f}\right) \qquad (7)$$

A and B are characteristic constants for a given gas
V_f = free-volume fraction inside the material (cm^3)
R = gas constant = 8.31 J/mol.K
T = temperature (K)

The diffusion of liquids in polymers is in general slower than the diffusion of gases. The major difference is that the equilibrium solubility can be much larger than that of gases, and the liquid can change the diffusion constant, or even the physical state of the polymer.

The $\delta C/\delta x$ in Fick's law is the concentration gradient of the molecules. If the concentration gradient is linear (the concentration of the molecules at a side of the film is C_1 and the molecule concentration at the other side of the film is C_2 ($C_1 > C_2$)), $\delta C/\delta x$, can be written as

$$\frac{\partial C}{\partial x} = \frac{C_2 - C_1}{L} \quad (8)$$

L = film thickness (cm)

The transfer of a gas at a pressure P_1 on one side of a polymer film of thickness L, to a pressure P_2 on the other side is defined in two possible ways. If the film is initially free of the gas then there will be a transient period while the gas concentration reaches its steady state distribution in the film. After this period the gas concentrations will be constant, C_1 and C_2 respectively at the two surfaces of the polymer.

The flux of the molecules, J (in $cm \cdot s^{-1}$), with combining equations (6), (8), and Henry's law is then given by

$$J = D \cdot S \cdot \frac{P_1 - P_2}{L} \quad (9)$$

P_1 = partial pressure on one side of the membrane (atm)
P_2 = partial pressure on the other side of the membrane (atm)
S = solubility (cm^3(STP)/cm^3(polymer).atm)

The permeability, P (in cm^3(STP).cm/cm^2.s.atm), is given as follows

$$P = D \cdot S = \frac{J \cdot L}{P_1 - P_2} = \frac{\Delta Q}{\Delta t} \frac{L}{A \cdot (P_1 - P_2)} \quad (10)$$

ΔQ = total effluent from a film area (cm^3)
A = film area (cm^2)
Δt = period of time (s)

The permeability coefficient, P, is the total effluent in a unit of transport time from a unit of membrane area, at a unit of pressure difference and at a unit of film thickness and has the dimensions cm^3(STP)/$cm^3 \cdot s \cdot$atm. The solubility of the gas depends on the nature of the polymer, it is affected by the strength of the intermolecular forces between a pair of gas molecules. The strength of the Van der Waals bond can be characterized by the depth of the potential energy. The diffusion coefficient depends on the flexibility of the polymer chains. Therefore, the magnitude of P could be altered by either changes in the chemical composition of the polymers or in the crosslinking of the polymer chains

IV Experimental characteristics

IV.A Reactants

IV.A.1 HexaMethylDiSiloxane (HMDSO) precursor

The chemical structure of the monomer HexaMethylDiSiloxane $O[Si(CH_3)_3]_2$ is shown in figure 8.

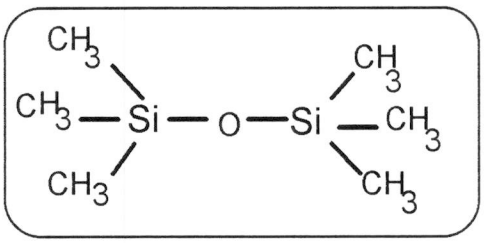

Figure 8. The chemical structure of HMDSO

SiO_x thin films give good results as oxygen barrier, thermal and chemical stability, electrical properties, and durability. Hence, organosilicon precursors were used for this purpose in plasma polymerization. But to obtain an ablation of the organic part during the deposition process O_2 is mixed with HMDSO. The hardness increases with the degree of polymerization. HMDSO is at atmospheric pressure a liquid, but it is introduced in the vapor phase in the plasma reactor. Due to the low vapor-pressure, HMDSO vapor is easily created by heating with a thermostatic bath. The pipe supplying HMDSO is heated in order to prevent sublimation of HMDSO. In table 2 the binding energies in a HMDSO molecule are given. The Si-O binding is strong and thermally very stable.

Table 2. Binding energies of a HMDSO molecule

Binding	**Binding energy (kJ/mol)**
C - H	337
Si - C	435
Si - O	799

HMDSO is a product of Merck company (Darmstadt), M=162.38 g/mol and 1 l = 0.76 kg. The density of the conventional polysiloxanes is typically 0.97 g/cm^3. Plasma siloxanes obtained from HMDSO, without the addition of oxygen in the gas phase, have a slightly higher density (1-2 g/cm^3). The density of plasma films increases and the growth rate of the plasma film decreases by increasing the oxygen content. Although the thickness of the coating decreases its barrier efficiency increases with the oxygen contents <7>. It's necessary to make

plasma polymer coatings as thin as possible to avoid the development of micro cracks <9>. The minimum thickness of plasma polymerized film needed to plug all pores and show permselectivity is about five times the pore radius of the porous substrate. The maximum oxygen permeation rate of permselective membranes is approximately proportional to the effective area for the gas permeation and inversely proportional to the pore size and the thickness of the plasma polymer films <10>.

IV.A.2 Substrate polypropylene (pp)

The structure of polypropylene is given in figure 9. The polypropylene (PP) substrate with an average thickness of 18 μm was delivered from MOBIL company (2-96), with one side corona discharge treated. In a former study PP substrates of another company COURTAULDS were used, which lead to enormous fluctuations in permeability measurements <11>. One of the problems is also described in figure 6.

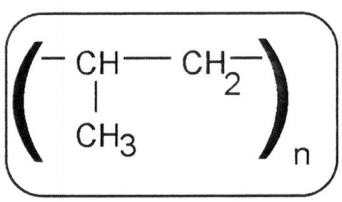

Figure 9. The chemical structure of polypropylene

IV.B Reactor

IV.B.1 Overall properties

The reactor used for these experiments consists of 2 parallel-electrodes at a distance of 3.7 cm, with an area of $S=\pi/4 \cdot D^2$ (D_{lower} = 7.1 cm, A = 39.59 cm^2), in a cylindrical bell-jar (figure 10). The cathode (lower electrode), is covered with the PP substrate and is attached with an inert teflon cover. Specimens of quartz and silicium are positioned on PP, in such a way that there is no difference in deposition between substrate and specimens. The cathode is coupled via a capacitor to a 3.8 kHz/3V RMS high voltage amplifier (function generator DF1614A), and is called capacitively coupling system. A primary vacuum is created with a Leybold type D166 vacuum pump and measured with a Pirani gauge, type PKG 100. A liquid nitrogen trap between reactor and pump prevents pollution. The mixture of gases is introduced in the reactor as given in figure 10, by using stop valves and needle valves, creating a total operating pressure which was measured with a Baratron gauge, type 122B.

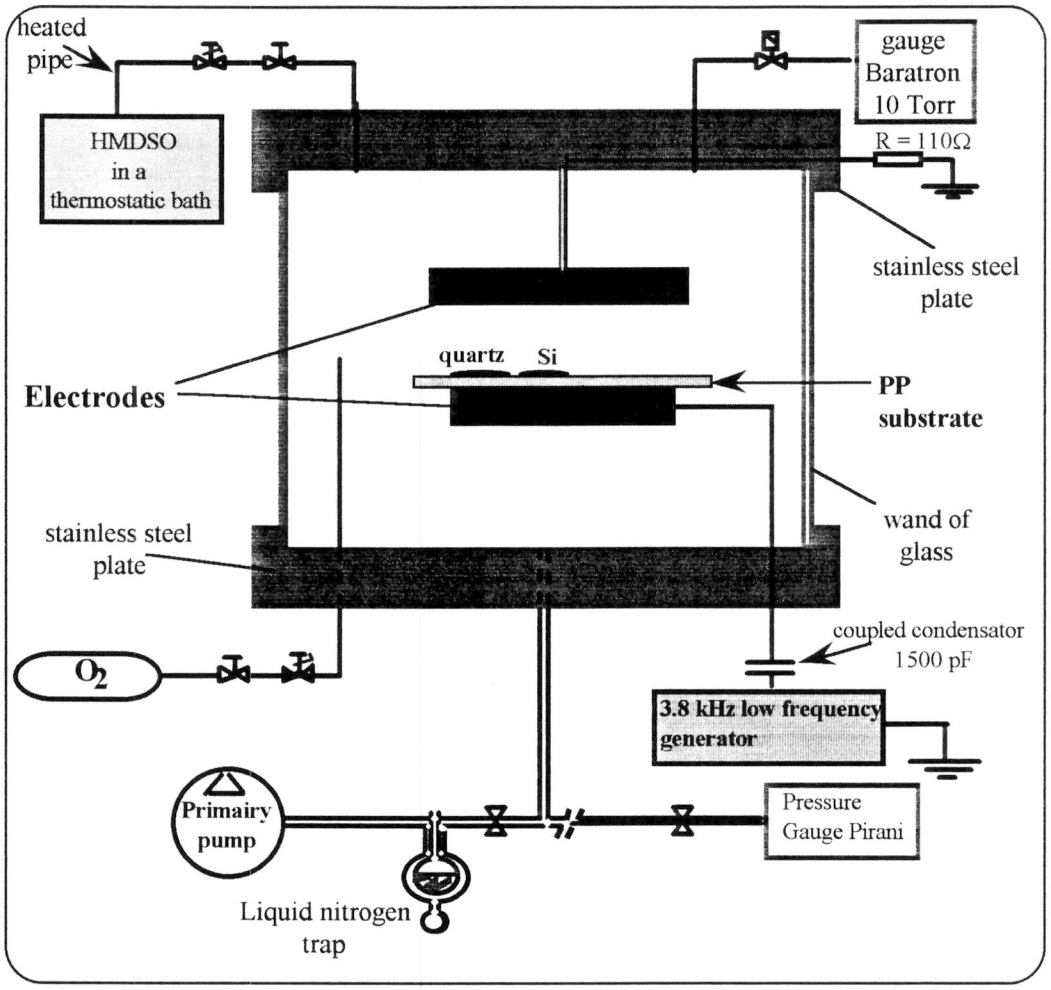

Figure 10. Low frequency (3.8 kHz) bell-jar reactor

IV.B.2 Electrical plasma properties

To calculate the power of discharge, P_d, which is a characteristic value for comparing specimens, we can use the following equation

$$P_d = V_d \cdot I_d \cos \varphi \quad (11)$$

V_d = voltage of input (V)
I_d = discharge current (A)
$\cos\varphi$ = cos of phase angle

An oscilloscope (Beckman 9020) can be used to measure the difference in phase between the current and voltage, due to the use of isolated substrates and space between the electrodes. The phase angle can be easily calculated with

$$\varphi = \frac{360° \cdot \phi}{T} \quad (12)$$

T = period of time of one wave (s), here 262 μs (3.8 kHz)
ϕ = time difference between I and V (s)

In this research the discharge current I_d is set, and measured by a Keithley 179 TRMS multimeter as a potential V_{Id} over a 110 Ω resistance, as shown in figure 11.

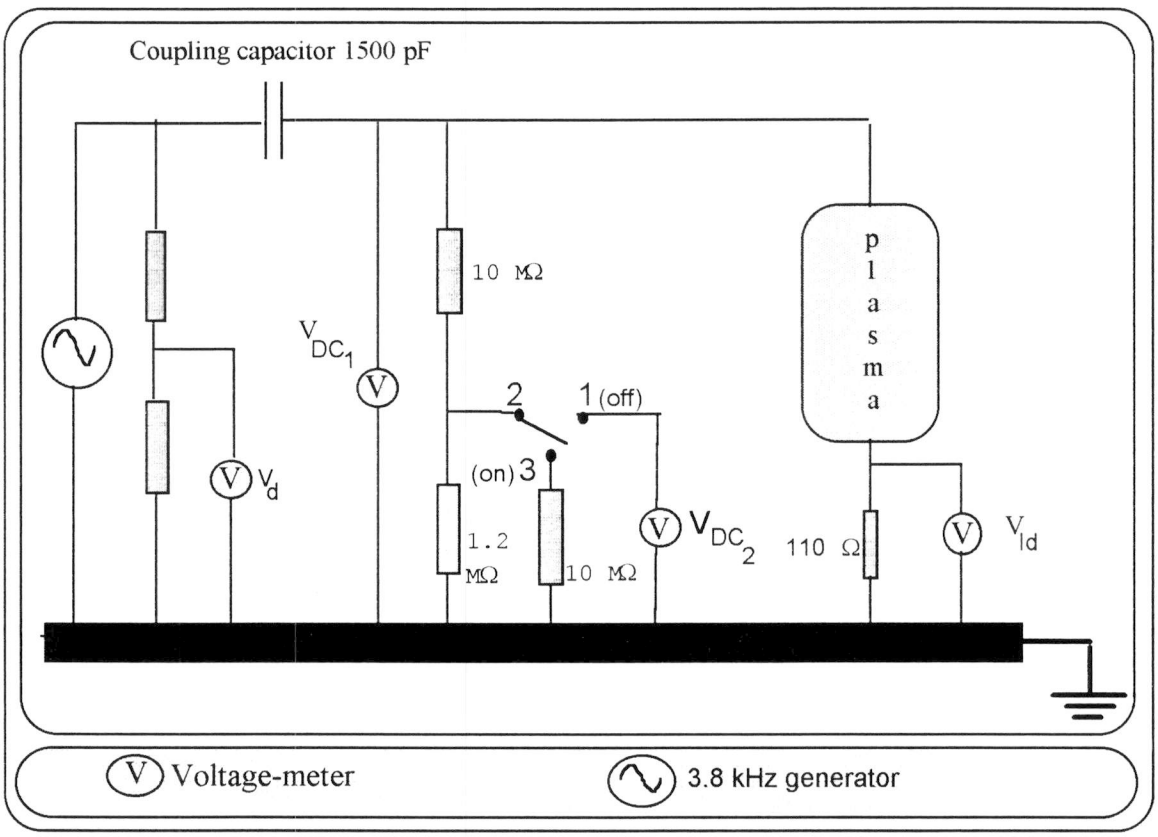

Figure 11. Electrical scheme for measuring during plasma deposition

The voltage of the input, V_d, is measured with another multimeter (Keithley 175). The output of the amplifier is 1/500 of the effective voltage, due to the voltage divider system. The oscilloscope is also used to measure the peak to peak values, V_{pp}, which deliver the same value when they are divided by $2\sqrt{2}$.

The autopolarisation V_{DC} can be measured by another voltage divider, 1/10, which measures V_{DC1} and V_{DC2} by using multimeters (with an internal resistance of 10 MΩ).

V Plasma treatment procedure

In order to create a good reproducibility in plasma deposition the experimental menu presented in figure 12 is accurately reproduced each measurement. Before starting the deposition, the reactor was thoroughly cleaned (both

electrodes, gaskets, and teflon covers). The discharge current, I_d, was set and all other parameters were kept as constant as possible, see table 3.

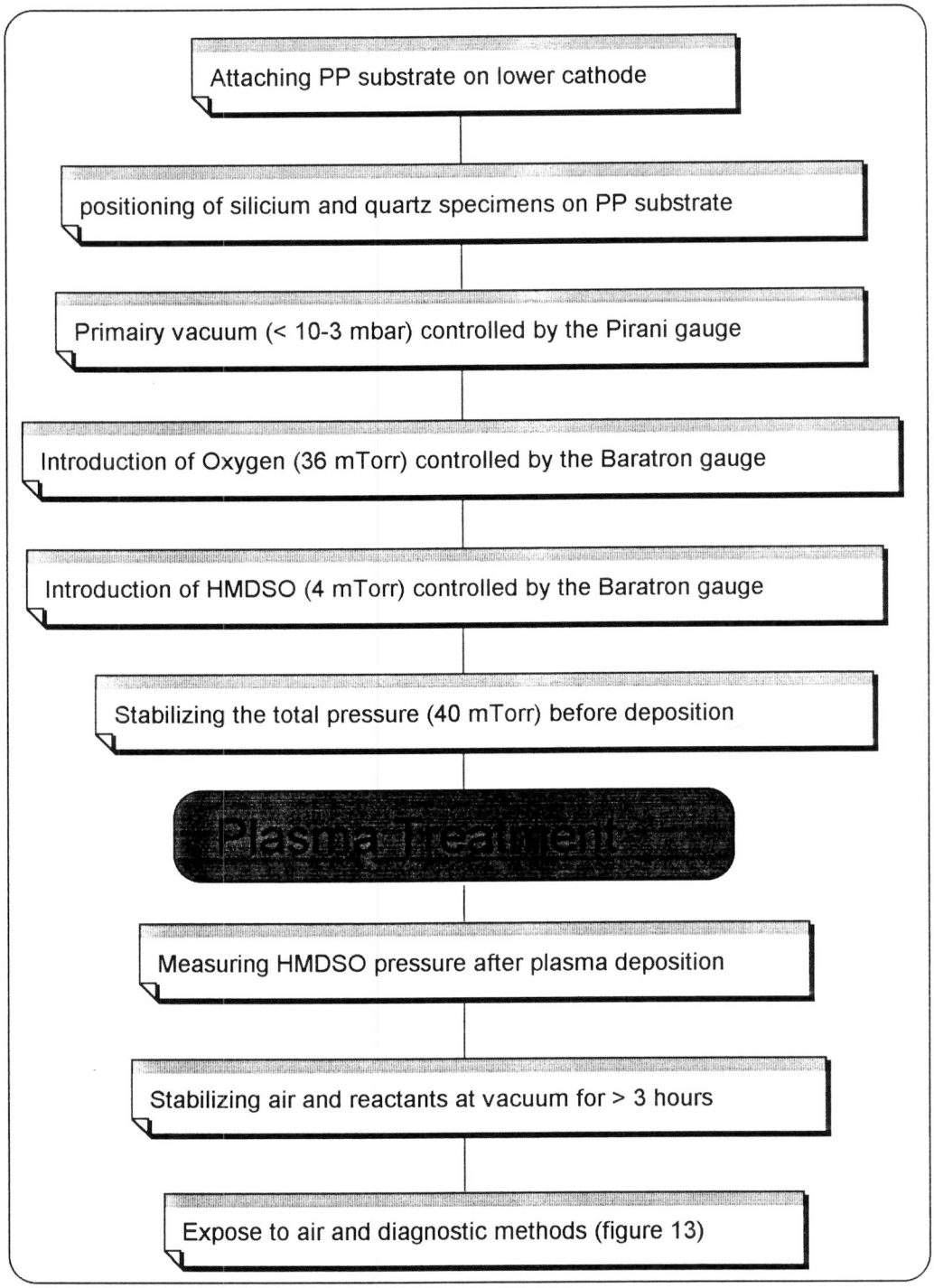

Figure 12. Scheme for plasma manipulations

On the lower electrode the PP substrate is correctly fixed. During all depositions the silicon and quartz specimens (with a known frequency of vibration), were positioned on the PP substrate, in such a way that the same deposit occurs on the specimens as on the polypropylene substrate. This last

assumption has been checked for a given film thickness in a former research <6>.

Table 3. Classification of different plasma parameters

Gas related parameters	Plasma related parameters	Substrate related parameters
Monomer gas mixture	**Frequency**	**Nature**
Gas vector - position of the entrance gas - system of entrance gas	$f>f_{pi}$ or $f<f_{pi}$ -mobility - diffusion	- insulator - conductor
		Relative position
Pressure	**Electrodes**	**Temperature**
Flow rate	--extern/intern	
- position of the entrance of the pump	-coupling/direct - nature of electrodes	
	Injected Power - discharge current - effective voltage - phase angle	
	Reactor type bell jar/Tubular	

After filling the nitrogen trap, a primary vacuum of about 5.5 10^{-4} mbar is created, during at least 2 hours. This is measured with a Pirani gauge. Then O_2 is regulated with a microvalve, and measured accurately with a Baratron gauge, leading to 36 mTorr. After stabilizing the O_2 pressure, HMDSO vapor (32-35 °C) is added, with a microvalve. The Baratron gauge was finally stabilized at 40 mTorr, leading to a stable gas mixture of 90% O_2 and 10% HMDSO. The thickness of the deposited layer is kept constant 1000 Å, in an earlier study a good relation between the thickness of the film, the discharge current and the rate of deposition was found as given in table 4.

Now for a certain I_d the time of deposition can be calculated. During the time of plasma the Pirani gauge was isolated to prevent damaging. During deposition time a violet color occurred, with intensity increasing with I_d. Pleats are introduced due to the high energy of bombardments of radicals, ions and other specimens. The pleats can be easily distinguished during deposition because less luminous zones occur, as depicted in figure 6.

Table 4. Relation between deposition rate and current during a 10 minutes deposition time in a BF 3.8 kHz reactor (collaboration between Elf company and Laboratoire de Genie Electrique in Toulouse)

Layer thickness	Current (mA)	Vd (Angstrom/sec
150	0.7	2.5
200	1.0	3.3
400	2.0	6.6
520	3.0	8.7
520	3.0	8.7
460	3.0	7.7
550	4.0	9.2
530	4.0	8.8
680	5.0	11.3
720	6.0	12

After the plasma polymerization the HMDSO and O_2 pressure are measured again to check for any difference. For at least 3 hours the reactor is kept in vacuum, to be sure that all radicals have reacted and cannot recombine with extern particles (oxygen, water vapor, dust ...). Then the diagnostic methods as discussed in the next chapter can be applied.

VI Diagnostic tools

To measure the influence of the change of current I_d in plasma-reactor on deposition layer several diagnostic methods can be used, as described in figure 13.

VI.A Permeability

The permeability of oxygen was measured at room temperature using a laboratory test, consisting of a cell separated in two parts by the PP membrane under experiment and a gas chromatograph (Intersmat IGC 120 ml), see figures 14, 15 and 16.

During a few minutes both parts of the cell were purged by a gas flow in order to remove all exterior contaminants. Oxygen was introduced into the upper part and helium (carrier gas) in the lower part. To prevent introduction of stress in the membrane, this is done at exactly the same time leading to the same pressure of 1 bar. The gas supply was cut off and the cell was isolated from the rest.

To give the peaks that occur during measuring the O_2-permeability a useful sense, a calibration is necessary. Therefore 100 µl of air is introduced in the chromatograph, this shows up as a peak with a certain area. Knowing the contents of O_2 in air (20 %) and the area of the peak, the flux of pure O_2 through the membrane can be calculated.

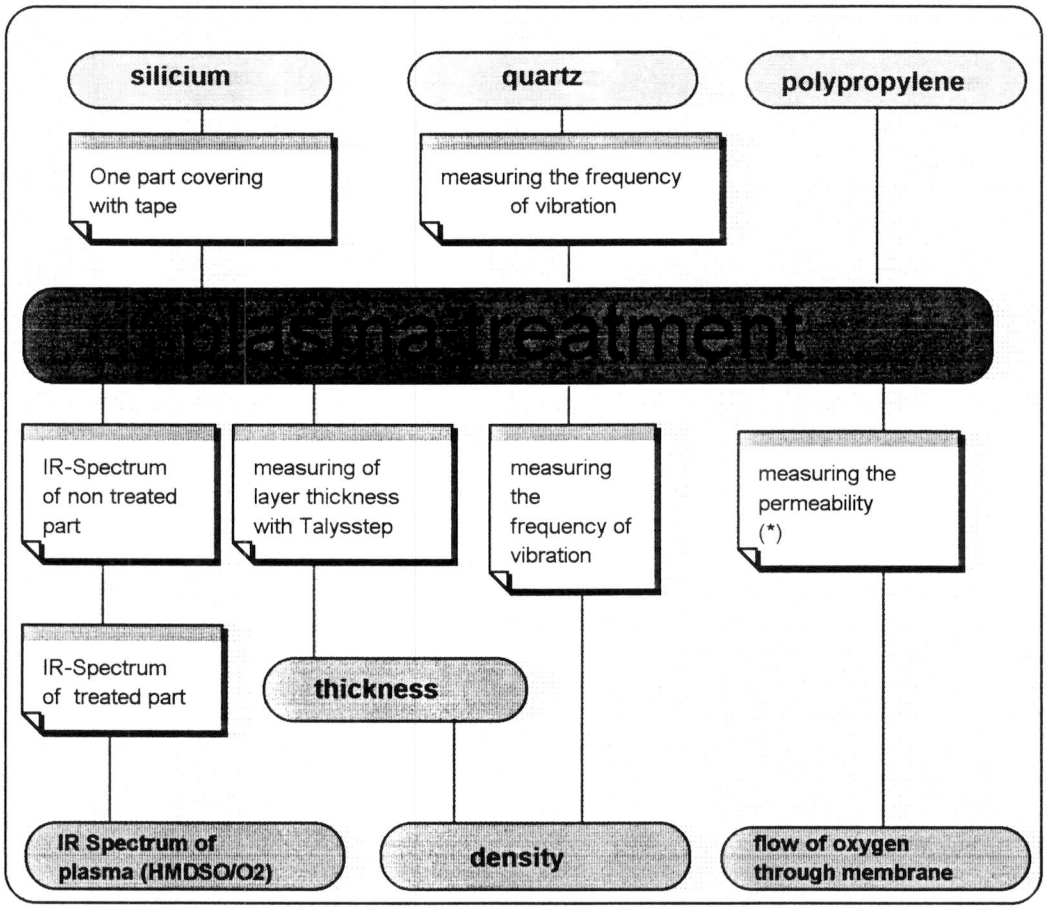

Figure 13. Diagnostic scheme

(*) Before and after permeability measurements blank substrates (without deposition) were measured, in order to have a good reference value

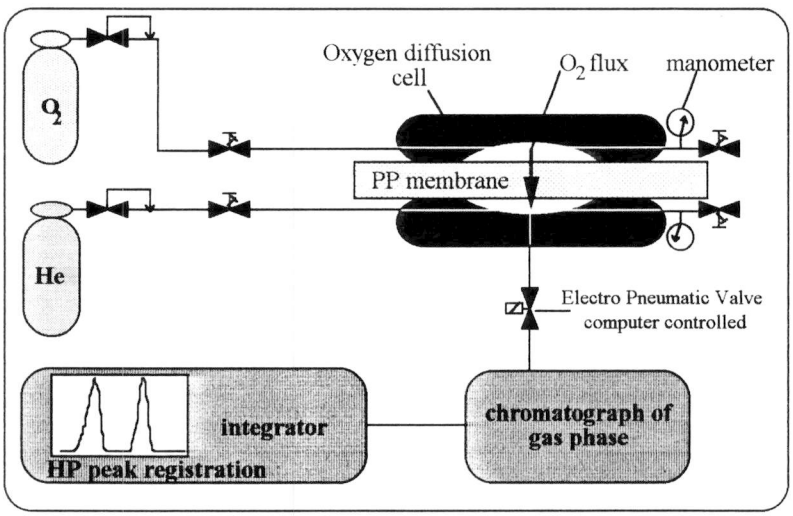

Figure 14. Overview of permeability measurements

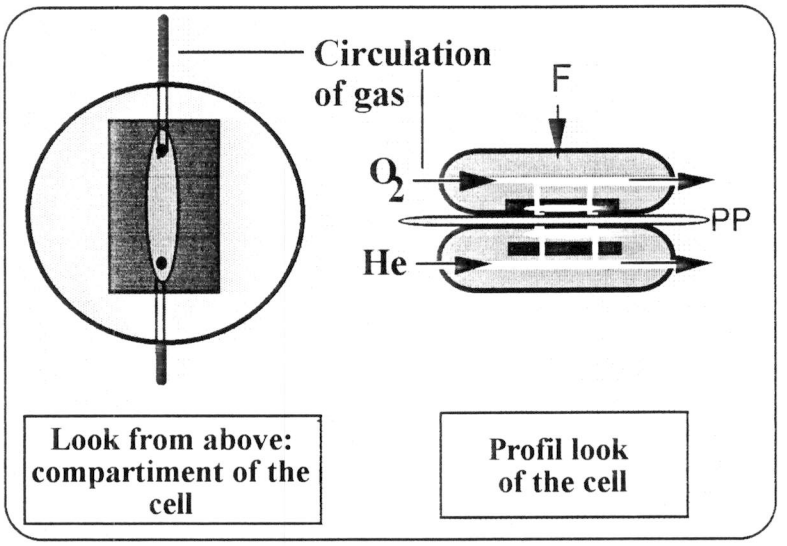

Figure 15.Detail view of the membrane compartment

Due to the driving force, resulting from the oxygen-concentration difference across the membrane, diffusion of oxygen takes place. During 18 hours, for 5 minutes every hour, the gas contained in the lower part of the cell was analyzed using the gas chromatograph. The oxygen diffused through the membrane appears as peaks on the recorder (Hewlet Packard 3396 series II integrator). After the experiment a new calibration is done, leading to an average calibration. Now the oxygen flow (in $cm^3/m^2.day$) can be calculated.

First a few untreated PP membranes are measured. Then all the treated PP substrates with a plasma film are measured. Afterwards the blank membranes were measured again, which lead to an average blank reference value of 1815 $cm^3/m^2.day$.

VI.B Thickness measurements

Thickness measurements were carried out with a Talystep (Taylor Hobson, Cranck Organization), as described in the manual <12>. And by using a computer controlled Tencor P2 long scan profiler. Both use the same system of measuring, a very sensitive needle. A part of the silicon substrate is covered with a polyimide (PI) tape during deposition. When taking off the PI tape, a way to measure the thickness of the deposit is provided, by passing the created step twice in both directions, see figure 17.

However, a relatively large error remains possible especially for small thicknesses due to the lack of accuracy in the thickness measurements. As mentioned before a film with a thickness of only 1000Å is deposited.

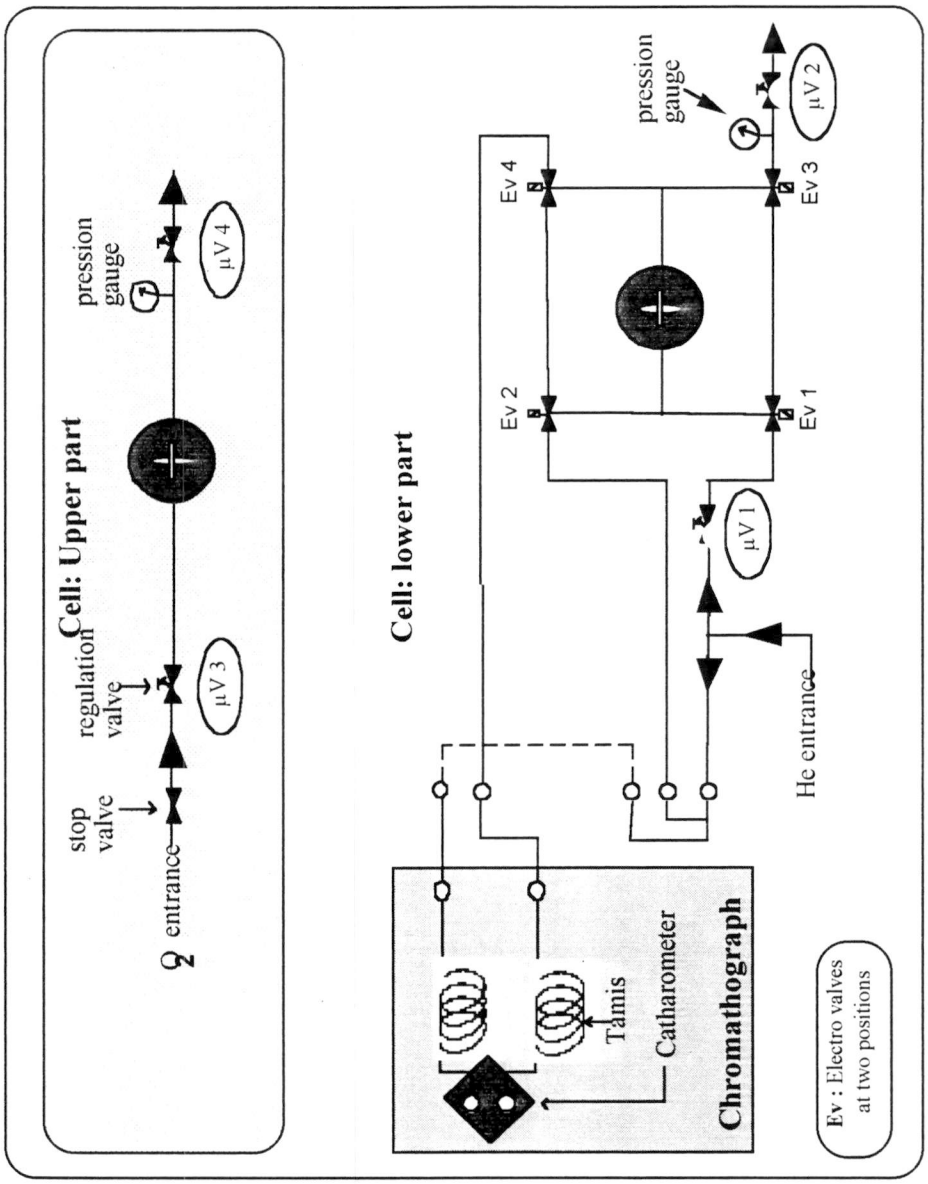

Figure 16. Schematic view of permeability

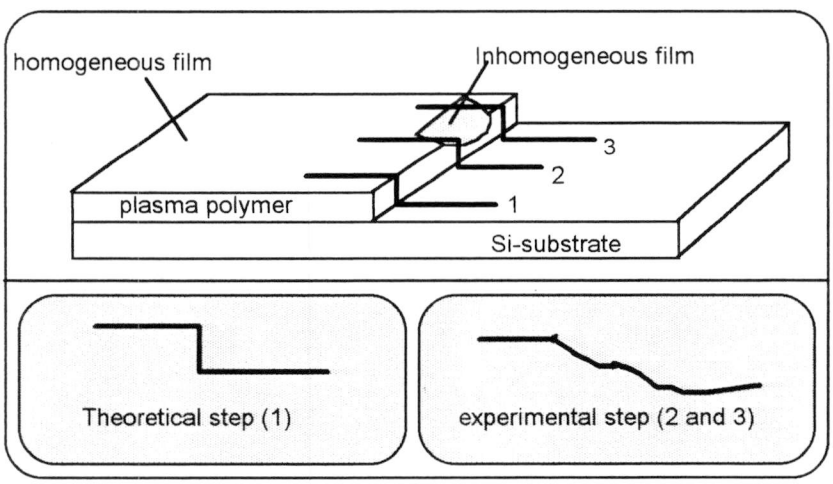

Figure 17. Thickness measurements with Thalystep and Tencor long scan profiler

VI.C Film densities

Film densities were determined using a quartz balance, Plassys IL 150 <13>. Usually, this system is used to control the thickness of a deposit assuming a known mass density. In these experiments, the oscillation frequency is measured before deposition. Then, the quartz sensor (with a mask D = 6 mm) is placed in the reactor on the PP substrate. After the deposition the new oscillation frequency is measured. From this oscillation frequency shift, the thickness of the deposited film and several quartz constants, it is possible to estimate the density with,

$$d_f = \frac{N_d \cdot d_q}{T_f \cdot f_q^2} \cdot (f_q - f_c) \qquad (13)$$

d_f = density of the deposited film (g/cm^3)
T_f = thickness of the deposited film (cm)
d_q = density of the quartz (6.648 g/cm^3)
$N_q = f_q \cdot l_q$: constant dependent on the slice of quartz (here $1.668 \cdot 10^5$ Hz·cm)
l_q = thickness of quartz (cm)
f_q = frequency of quartz resonance before deposition (s^{-1})
f_c = frequency of quartz after deposition (s^{-1})

VI.D Fourier Transform Infra-Red Spectroscopy (FTIR)

IR can be used for the identification of functional groups in plasma polymer films. Plasma-deposited siloxanes can be shifted from organic to inorganic by controlling the plasma parameters. In general, the higher the input energy per single molecule, the more inorganic the nature of the film becomes. The effect of an O_2 plasma on organic siloxanes is to remove the organic pendant groups and to create an inorganic-like phase, greatly increasing the number of O to Si bonds <14>.

A Biorad FTS 60 A IR spectrometer is used for FTIR measurements on silicon substrates. Table 5 gives the band assignments of Infra-Red spectra of HMDSO-plasma-deposited films. These can also be seen in figure 18, for the pure HMDSO spectrum.

A typical value, R, is created which gives the ratio of inorganic part to the organic part,

$$R = \frac{Area[inorganic]}{Area[organic]} = \frac{Area(Si-O-Si)Stretching}{Area(Si-(CH_3)_3 + Si-(CH_3)_2)} \qquad (14)$$

Table 5. Assignment of vibration characteristics of a HMDSO film with IR spectrometry

Wavenumber(cm^{-1})	binding	vibration
2960	C-H in CH_3	asymmetric stretching
2880	C-H in CH_2	asymmetric stretching
2150	Si-H	stretching
1400	C-H in Si-CH_3	asymmetric bending
1360	C-H in Si-CH_2-Si	asymmetric bending
1250	C-H in Si-CH_3	asymmetric bending
1150 – 1000	Si-O-Si	asymmetric stretching
840	Si-$(CH_3)_3$	rocking
800	Si-$(CH_3)_2$	rocking

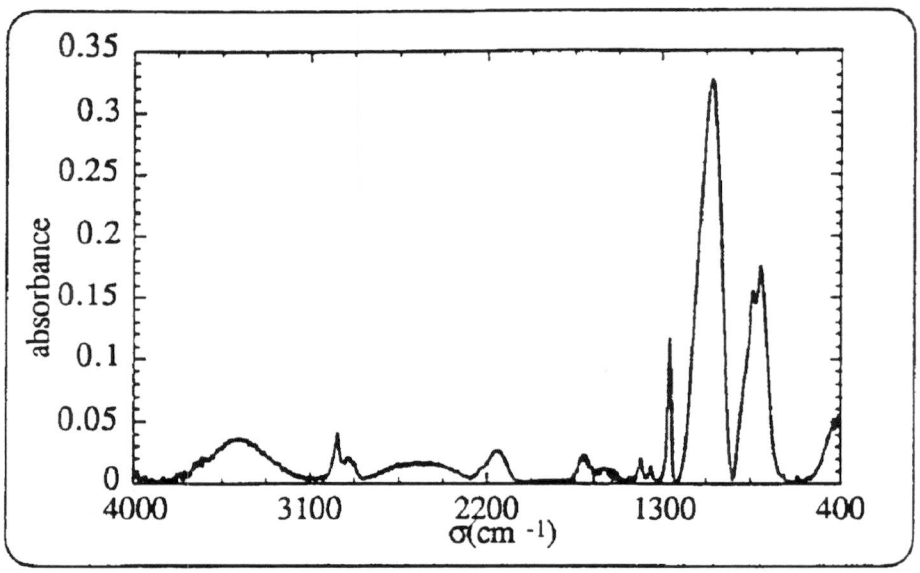

Figure 18. Infrared spectrum of pure HMDSO for a plasma deposited film

VII Results and discussion

The influence of changing the discharge current I_d during plasma deposition, on the permeability of the deposited film was measured. Several parameters were used:

- discharge power P_d
- autopolarisation voltage V_{DC}
- deposition rate v_{dep}
- density of the film ρ
- ratio R

VII.A Electrical properties

Formula 3 gives a relation between the autopolarisation voltage V_{DC} and the electrical excitation. The discharge power P_d can be calculated by using formulas 11 and 12, and is directly related to I_d. Dividing P_d through the surface of the power electrode (Diameter = 7.1, Area = 39.59 cm^2), gives the density of the discharge power, see table 6 and figures 19 and 20. Before the constant I_d was put at the desired value, a few moments of uncontrolled plasma took place, due to the delay of the measuring equipment. This causes an inaccuracy in the measurement and an inhomogenity of the plasma film. During the deposition time the thickness of the plasma polymer film increases. The thickness of the insulating film increases although the discharge voltage, V_d, decreases due to a higher inter-electrode resistance. Continuous control of the value of V_d maintains a constant discharge current. The higher the desired discharge current, the shorter the time to measure the electrical properties and the larger the chance of measuring errors. In an earlier internal research <11> it was shown that with increasing I_d, P_d increases while the negative V_{DC} decreases.

Table 6. Power P_d and autopolarisation V_{DC} as function of the discharge current I_d.

I_d (mA)	P_d (mW/cm^2)	V_{DC} (V)	I_d (mA)	P_d (mW/cm^2)	V_{DC} (V)
0.7	3.8	-0.03	4.0	40.0	-220
1.0	6.2	-0.02	5.0	68.6	-330
2.0	15.0	-0.3	6.0	75.0	
2.0	15.3	-1.5	6.0	90.0	-500
2.0	15.3	-0.6	7.0	97.2	-350
3.0	27.0	-130	7.0	135.2	-680
4.0	37.7	-210	8.0	127.2	-600

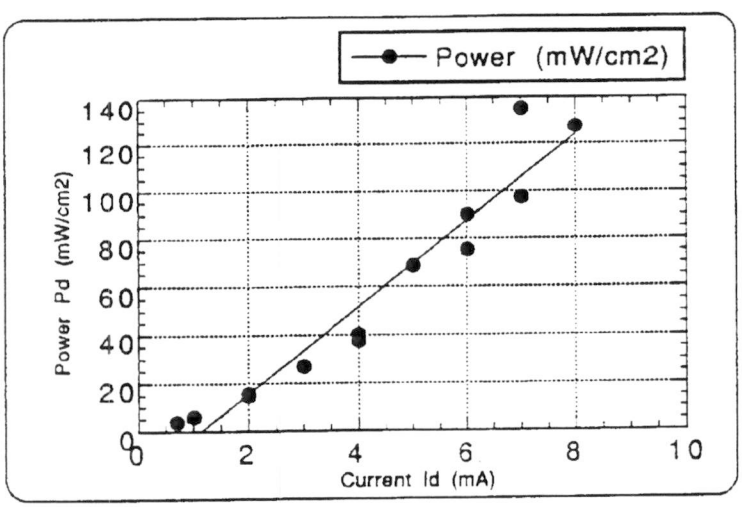

Figure 19. Discharge current versus the plasma power.

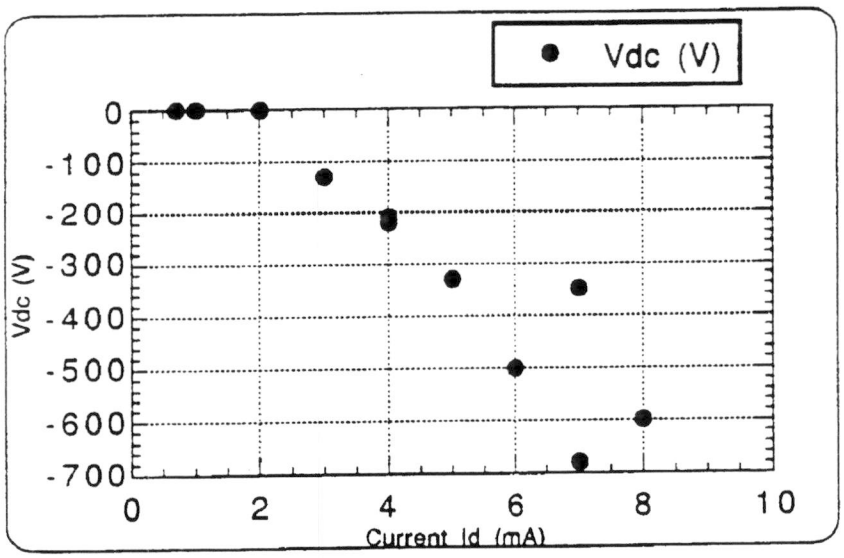

Figure 20. Discharge current versus the Autopolarisation Voltage

With increasing applied discharge current (power), either the mean electron density or the electron mean energy rises (or both rise). Therefore the number of electrons that accumulate at the electrode increases. The coupling system prevents that the charges fade away in the circuit, though the negative V_{DC} decreases with increasing I_d.

VII.B Thickness and deposition rate

As mentioned before in chapter V the goal was to create a uniform film with a thickness of 1000 Å, the results are given in table 7 and figures 21, 22 and 23. As can be expected the polymer thickness is seen to depend on the duration of plasma treatment.

Table 7. Film thicknesses measured with Thalystep (T_S), Tencor (T_C) in nm, the calculated deposition rates respectively $v_{dep,s}$ and $v_{dep,c}$ in Å/s, as function of current I_d in mA.

I_d mA	T_S nm	T_C nm	$v_{dep,s}$	$v_{dep,c}$	I_d mA	T_S nm	T_C nm	$v_{dep,s}$	$v_{dep,c}$
0.7	120	159	3.0	3.9	4.0	130	150	19.5	22.5
1.0	190	177	5.7	5.3	5.0	150	159	17.0	18.0
2.0	140	190	8.2	11.2	6.0	200	214	40.0	42.8
2.0	110	136	5.8	7.2	6.0	130	120	28.9	26.6
2.0	110	110	8.8	8.8	7.0	210	269	26.2	33.6
3.0	150	210	12.7	17.5	7.0	150	164	37.5	41.0
4.0	180	261	15.0	21.8	8.0	135	115	33.7	28.7

When the thickness increases the risk of forming micro cracks also increases. In order to solve the problem of the formation of micro cracks, it is necessary to make the film as thin as possible <9>. In a previous research <15> it was shown that with an increase of the oxygen concentration in the plasma mixture, the deposition rate and the density of the film are higher. A constant thickness of 1000 Å is not achieved as is shown in table 7. The thickness varies a lot, between 900 Å and 2690 Å. The thickness of the HMDSO polymer layer obtained in a plasma did not really affect the FTIR spectra as mentioned in chapter VII.D.

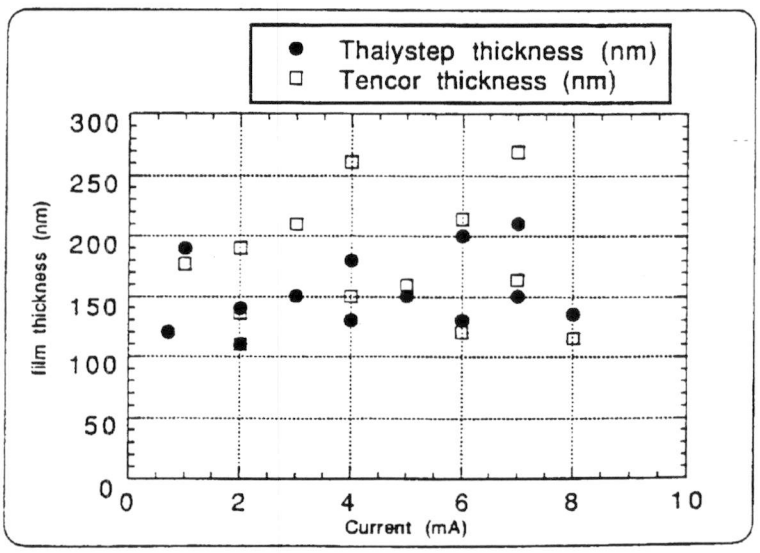

Figure 21. Plasma film thickness versus the discharge current

Even between the two methods of measuring the film thickness, Thalystep en Tencor, there is a big difference in results. The Tencor is probably more accurate due to a larger scan profile and it is computer controlled. Inaccuracy is introduced in calculating the deposition time before deposition by using table 4. In these measurements a constant deposition time of 10 minutes is used, which seems to give other rates for deposition. In our experiments after the first deposition the original deposition rate is readjusted. This leads to a better approach of the 1000 Å thickness. It can be seen that with a reproduction of the same current, for instance 6 mA, the film thickness decreases from 200 nm to 130 nm. Inaccuracy is also introduced because the two methods of measuring the thicknesses are both very local. At one silicon substrate a color difference can be distinguished, which is related to a difference in thickness, as given in table 8 <16>.

Table 8. Relation of film thickness and the colour of SiO_2 on Si substrates

colour	gray	havana	brown	blue	violet	clear blue	green	yellow	orange	red
thickness (A)	100	300	500	800	1000	1500	1800	2100	2200	2500

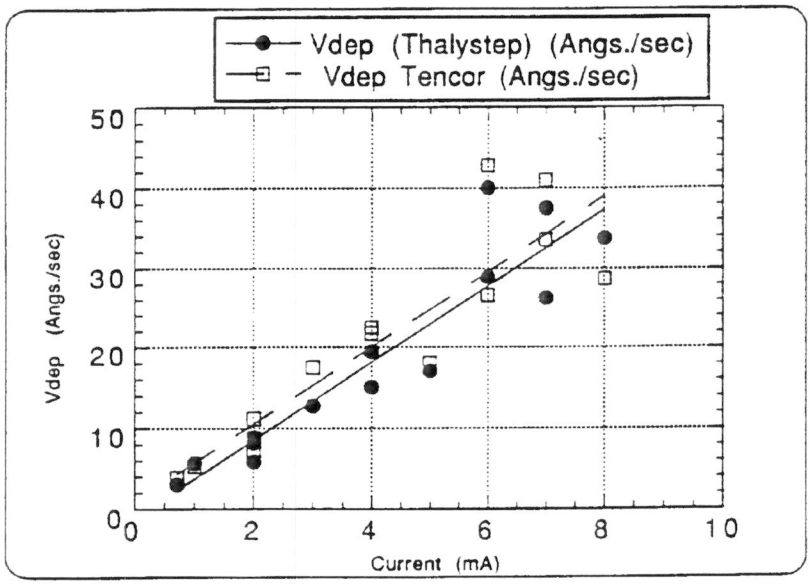

Figure 22. Deposition rate versus the discharge current

As also mentioned in <17>, for very low (< 20 cm^3/min) and very high monomer flow rates, above a certain maximum the deposition rate rises by increasing the power. In this case a very low rate is obtained due to a low entrance pressure of the O_2 flux, 0.2 Bar. The deposition rate increases linearly with the power, figure 23 illustrates that the polymerization reaction is energy limited. For these very low flow rates the increase in rate of deposition with the increase of discharge current I_d (see also figure 22) and also with the input power, can be explained by an increase in electron temperature and the density since both enhance the rate of production of ions and radicals, hence the rate of polymerization.

At very high flow rates, the residence time of the monomer is so reduced that only a few effective free radicals are formed and therefore, the deposition rate is also reduced considerably. A decrease in deposition rate with an increase of the discharge current I_d (or power) can occur, due to degradation <17>. But at very high deposition rates, an inhomogeneous film is deposited which will contain cracks. Yasuda <21> stated that the deposition rates of monomers are dependent on the plasma-energy input per unit mass of monomers.

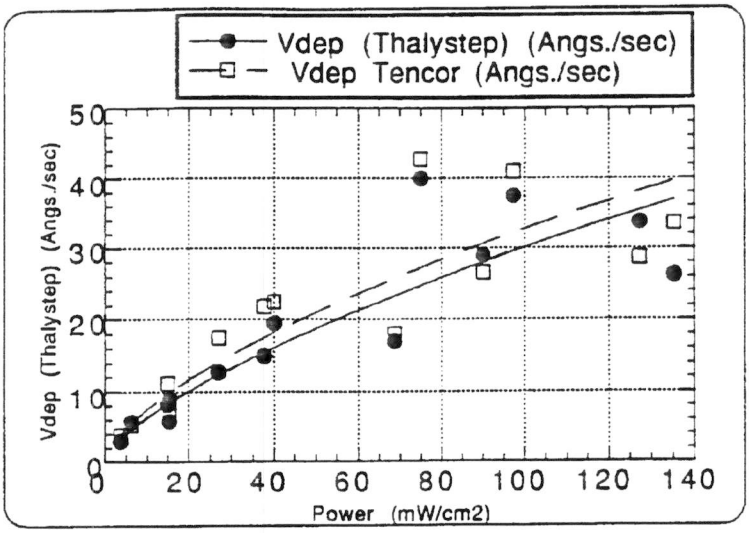

Figure 23. The influence of the power on the deposition rate

VII.C Density measurements

With the use of formula 13, given in chapter VI.C, it is possible to calculate the density of the deposited film in g/cm^3 (as shown in table 9 and figure 24). The thicknesses of the deposited films are given in table 7. Film densities lower than 1.4 g/cm^3 are accompanied by defects <18>.

In a former research <6> the place of the quartz substrate has been verified, an inaccuracy in measuring is possible because of the use of a mask. This mask is necessary because the area of measurement needs to be exactly 6 mm in diameter and to maintain the quartz on the substrate during plasma deposition. But due to a lack of a good connection to the quartz and an imprecise diameter of the mask, inaccuracy is easily introduced.

Table 9. The density as a function of the discharge current I_d.
ρ_{ts}= density with thickness measured with the Thalystep
ρ_{tc} = density with thickness measured with the Tencor long scan profiler

Id (mA)	ρts (g/cm^3)	ρtc (g/cm^3)	Id (mA)	ρts (g/cm^3)	ρtc (g/cm^3)
0.7	2.600	1.964	4.0	2.654	2.300
1.0	1.980	2.125	5.0	3.795	3.580
2.0	1.220	1.295	6.0	2.333	2.180
2.0	3.300	3.950	6.0	2.468	2.674
2.0	2.610	2.610	7.0	3.240	2.966
3.0	2.784	1.988	7.0	2.698	2.106
4.0	3.828	2.640	8.0	2.863	3.361

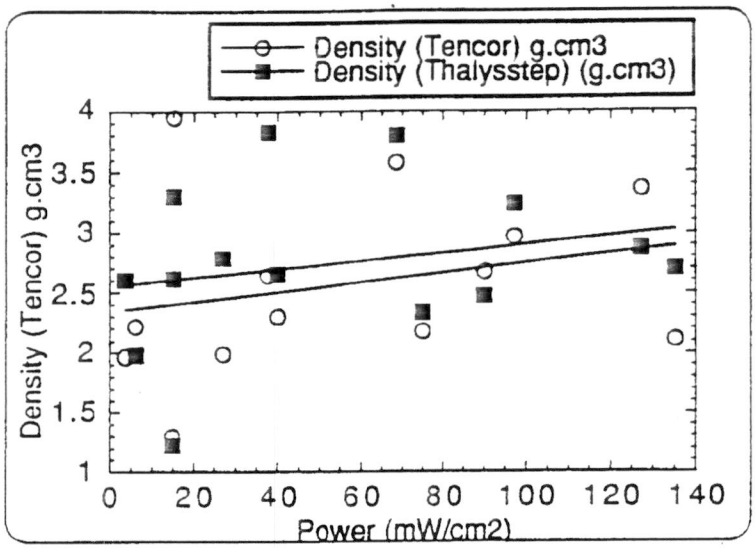

Figure 24. The density of the plasma film versus the current

It can be concluded from the table 9 and from figure 24, that there is a large dispersity in density values. When the inaccuracy of measurements is not taken in consideration, it can be concluded that with increasing current a small increase in density occurs. Inagaki et al. <19> suggested that the chemical structure of plasma polymers strongly depends on the fragmentation of the polymer in the plasma. With increasing power the number of reactive particles grows due to breaking, of bonds of the polymer and the increasing charged particles. The plasma reactions of polymeric fractions result through thermal decomposition of highly crosslinked polymers. Highly crosslinked polymers can introduce cracks in the film <9>. The crack formation depends on the thickness of the films; the number of cracks increases with the thickness, and the permeability decreases.

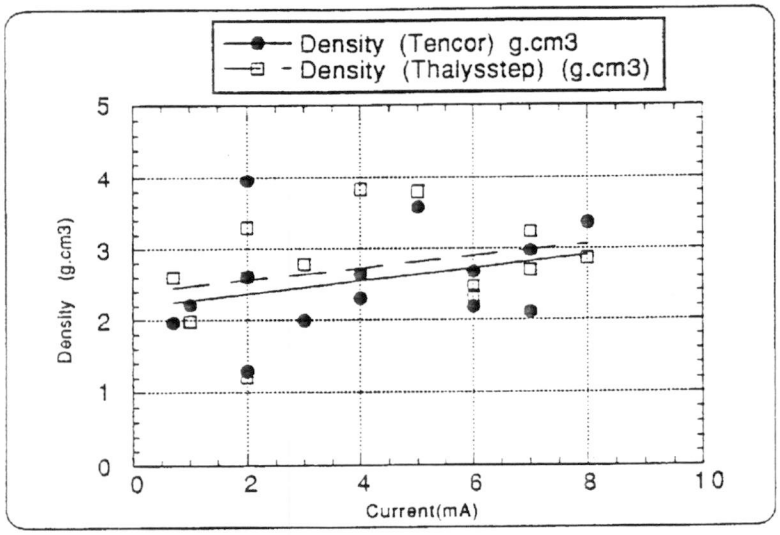

Figure 25 The density of the plasma film versus the power

The small increase in density, as shown in figure 24 and 25, may also be due to the increasing temperature of the substrate, as was proven in <20>. The temperature of the substrate rises with the bombardment from reactive particles of the substrate and with the current.

VII.D FTIR measurements

The interesting part of plasma deposition of siloxane is that the nature of the deposited film can be shifted from organic to inorganic, and can be controlled by the "external" plasma parameters. Organo-silicon compounds can be used to achieve Si-O-Si based crosslinked structures, which change the surface properties of the material to an inorganic structure. In general, the higher the input energy per single molecule, the more inorganic the nature of the film <6>. The interesting effect of O_2 on organic siloxanes is that organic groups are removed and inorganic-like phases are created, increasing the average number of O to Si bonds. The production of inorganic Si/O polymers directly from plasma treatment usually leads to defective or highly stressed films. In table 10 and figures 26 and 27 the R-factors are given as function of the current and the power.

Table 10. The R-ratios as function of the discharge current and power.

I_d (mA)	P_d mW/cm^2	R-factor	I_d (mA)	P_d mW/cm^2	R-factor
0.7	3.8	2.879	4	40.0	
1	6.7	3.76	5	68.6	3.148
2	15.0	2.498	6	75.0	
2	15.3	3.811	6	90.0	
2	15.3	2.934	7	97.2	
3	27	4.601	7	135.2	3.58
4	37.7	3.183	8	127.2	

The removal of methyl groups is a function of the power, with more groups being knocked off at higher power levels <6>. Higher electron energy levels cause a major increase in the $Si(CH_3)_3$ end group splitting only, the rest of the fragments undergo non-significant compositional changes. It is also noteworthy that higher energy levels do not create new fragments, only their relative ratio is modified <20>.

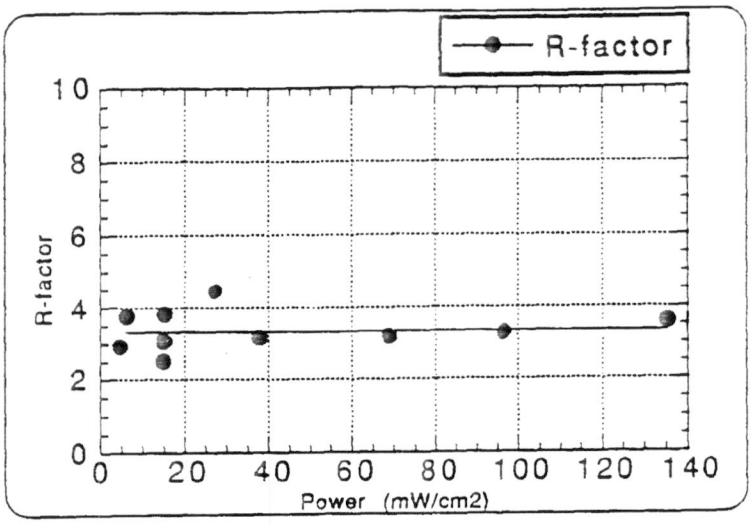

Figure 26. The influence of the discharge power on the R-factor

As mentioned in <6> a high percentage of oxygen in the plasma can lead to R-factors with a value of more than 15. As can be seen in figure 26 the inorganic part of the film, R, maintains very low (R = 3.3) under the used process circumstances (also high oxygen contents). This points to a large quantity of organic bonds (Si-$(CH_3)_3$, Si$(CH_3)_2$, C=O....). The expected relation between the power and the R-factor was not found, instead an almost constant R-factor occurs, upon increasing the power. It seems that for a certain plasma mixture, certain threshold reaction energy (time and power) is necessary to achieve the removal of the organic part. In figure 27 <6> for a plasma mixture of 50% HMDSO and 50% O_2 the threshold current, was ≈3 mA. In the experiments reported in this rapport, the energy threshold value was not achieved.

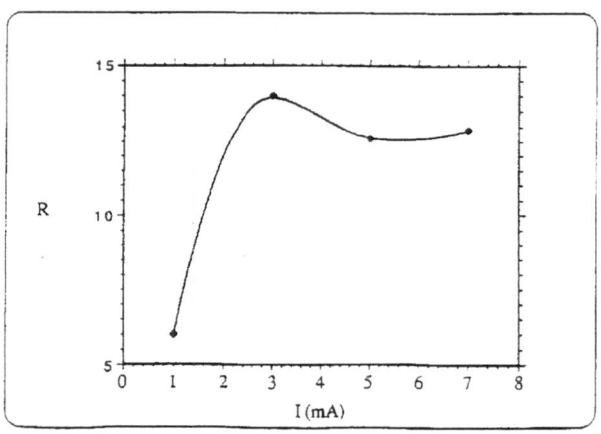

Figure 27 Influence of the discharge current on the R-factor for a plasma mixture of 50% HMDSO/50% O_2 plasma (at 0.1 mbar pressure) <6>.

Although there is a large difference in results in figure 28 an increase in density can be seen when the R-factor increases. Upon increasing the power of the discharge an increasing fragmentation of the HMDSO molecules takes place. An effect consistent with the growing electron mean energy or mean electron density (or both). This leads to a higher inorganic factor, R. Si-O-Si has a more compact structure with a higher binding energy, than the larger organic parts. If the power is increased, the increase in crosslinking (density) also causes an increase in background absorption.

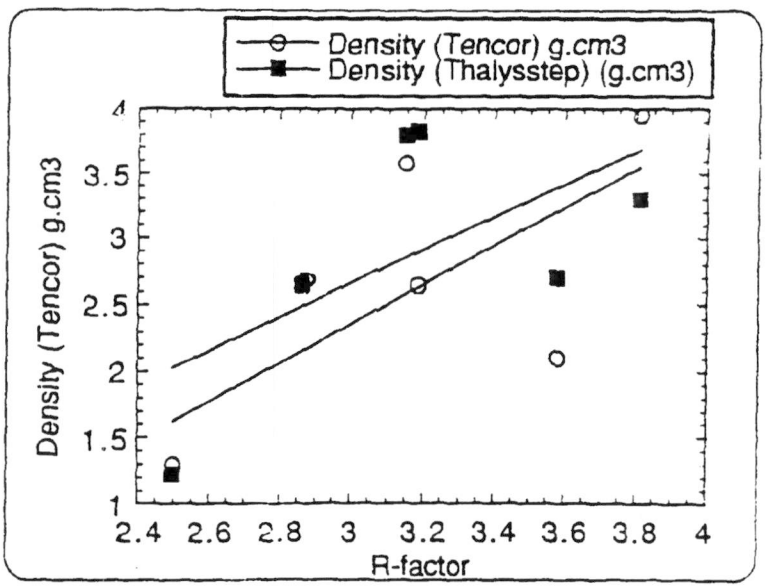

Figure 28. The influence of the R-factor on the density

Longer treatment times result in a marked decrease in the intensities of absorption bands corresponding to CH_2 and CH_3 vibrational bands and an amplification of Si-C and Si-O-Si vibrations. If the plasma reaction continues for long periods of time, then probably only (Si-O-Si) inorganic type structures will be left. These phenomena can be explained by <20>:

- an increase of the thickness of the Si-C and Si-O based polymeric layers
- the simultaneous development of plasma induced demethylation, dehydrogenation and cross-linking mechanisms.

VII.E Permeability

Before and after measuring deposited substrates, blank substrates without deposition were measured in order to get a reference value for the flux. During 18 hours of measuring, the permeability of these membranes is not constant. In figure 29 (only four blank substrates before the test are given), it can be seen that a large difference in flux occurred. For one blank polypropylene substrate, the permeability measurements as function of time are not very accurate. Leading after eight blank substrates (also four measuring after the test) to a reference value of 1815 $cm^3/m^2 \cdot day$. In table 11 the power P_d in mW/cm^2 and the flux ϕ in % of the reference value is calculated as function of the discharge current I_d.

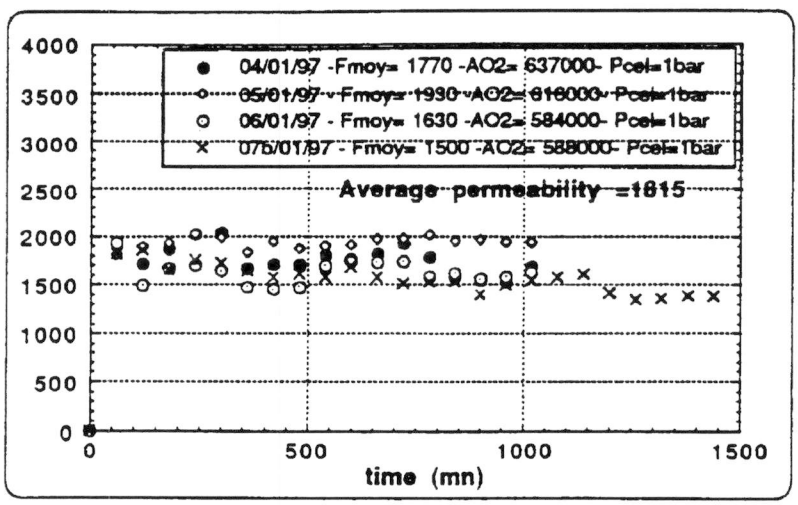

Figure 29. The flux values of blank PP membranes as function of the time (min)

Table 11. The influence of the discharge current I_d and the power P_d in mW/cm^2 on the flux ϕ in % of the reference value

Id (mA)	Pd (mW/cm^2)	flux ϕ (%)	Id (mA)	Pd (mW/cm^2)	flux ϕ (%)
0.7	3.8	118.5	4.0	40.0	44.6
1.0	6.2	114.9	5.0	68.6	24.2
2.0	15.0	131.1	6.0	75.0	75.5
2.0	15.3	116.8	6.0	90.0	40.5
2.0	15.3	97.5	7.0	97.2	29.3
3.0	27.0	66.4	7.0	135.2	17.1
4.0	37.7	52.3	8.0	127.2	18.7

Looking at the table it is remarkable that for low currents, 0.7, 1.0 and 2.0 mA the flux of oxygen is larger than the blank PP membrane. This effect is may be caused by O_2 plasma etching of the polymeric substrate. The organic carbon-containing portion is etched away, as is observed in the case of siloxane

polymers (i.e. nonplasma-deposited) <14>. At higher energies a larger amount of polymer molecules is fragmented. The number of reactive polymer particles therefore increases and lead to extensive reactions with oxygen, forming a plasma film.

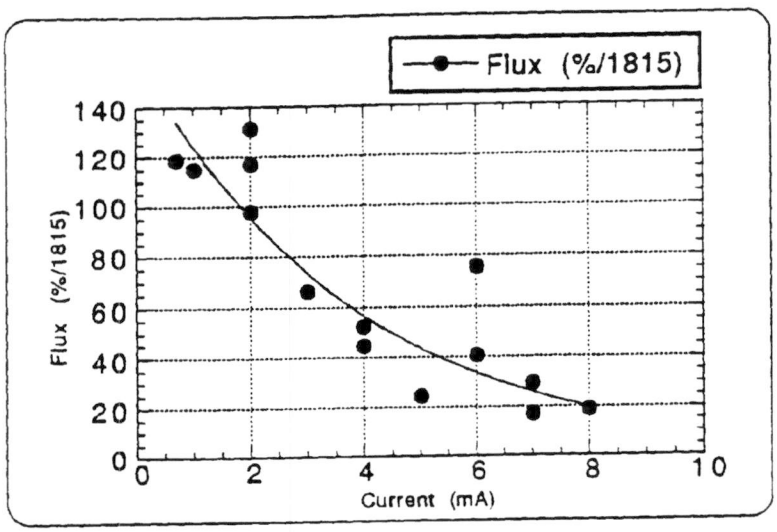

Figure 30. The discharge current as function of the flux (%)

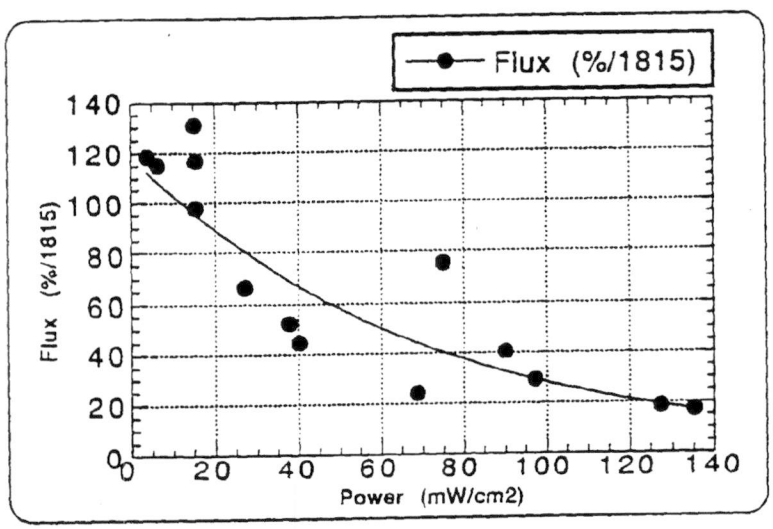

Figure 31 The influence of the discharge power on the permeability

As figures 30 and 31 show, the flux decreases (and the quality of the membrane improves) upon increasing the current and the discharge power. The decrease of flux through the membrane means that the diffusion of oxygen is decreased due to the forming of a more O_2 resistant layer on the PP membrane. The earlier mentioned influence of the increasing density, due to crosslinking, plays probably a major role in this phenomena.

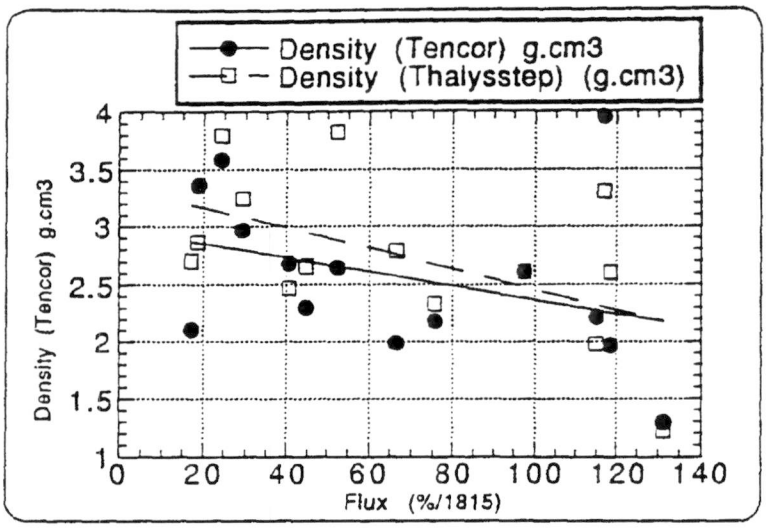

Figure 32 The influence of the density on the flux

As the density increases due to the tighter crosslinking, the free volume (pores) of the polymer decreases. As a consequence the gas flow through the membrane decreases, as depicted in figure 32. In figure 33 the influence of the deposition rate on the flux is given. The higher the deposition rate the lower the flux quantity through the membrane becomes.

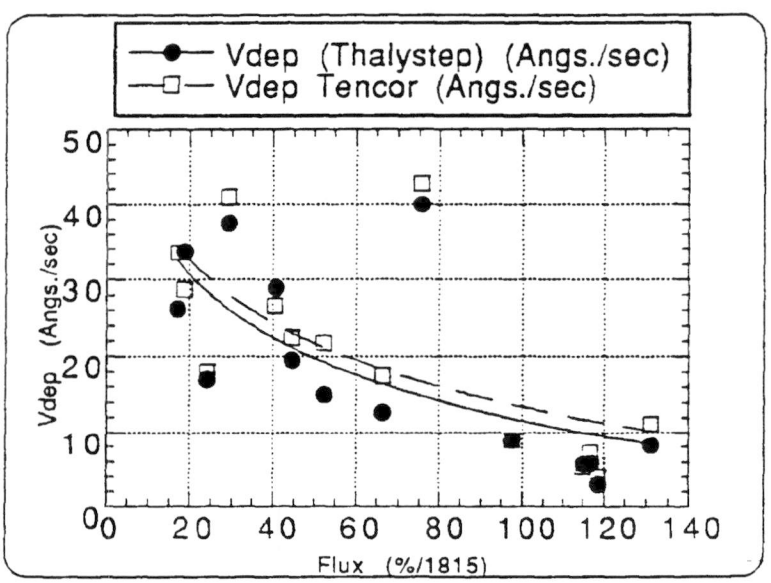

Figure 33 The influence of the deposition rate on the flux

VIII Conclusions

In order to investigate the influence of the discharge current I_d during plasma deposition, several parameters were measured. We found that when the discharge current increases:

- the discharge power P_d increases
- the autopolarisation voltage V_{DC} decreases for currents larger than 1 mA
- the deposition rate, v_{dep}, increases
- the density of the film r increases a little
- the inorganic part of the film R remains very low under the process circumstances used, which indicates a large quantity of organic bonds in the film.

The influence of these parameters on the flux through the membrane were examined intensively. The flux decreases, and therefore the quality of the plasma deposited membrane increases if:

- the current of discharge increases
- the power of discharge increases
- the density increases
- the deposition rate increases

The goal of creating a uniform thickness of 100 nm on the PP substrate seems to be difficult to reach, because of the variation in deposition rate, complex manipulation of the electrical equipment (measuring and maintaining) and the forming of pleats during deposition.

The best result as we look to the quality of the HMDSO/O_2 plasma polymer film regarding O_2 permeability, was reached at high currents (8 mA); then the flux is reduced to 17 % of the reference value, a non-deposited polypropylene membrane.

In future research it will be interesting to see what higher currents (> 8 mA) will give for results. Better results can be expected after extrapolation the data of several figures, given in this report.

The measurements contain a large amount of inaccuracy. This is caused by poor equipment. We found e.g. large differences in reproducing the same permeability tests with blank substrates, large errors in the thickness measurements, formation of pleats during plasma deposition etc. We recommend that in a follow-up research the system will be improved on these points.

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