

ON THE FUNCTIONALIZATION OF POLYPROPYLENE WITH CF₄ PLASMA CREATED IN CAPACITIVELY COUPLED RF DISCHARGE

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Key words: Plasma, tetrafluoromethane, plasma functionalization, sputtering, aluminum

Abstract: Hydrophobisation of polypropylene was performed using low pressure weakly ionized plasma of tetrafluoromethane at pressure of 1.0 Pa. Plasma was created in an aluminum discharge chamber by capacitively coupled RF generator at 13.56 MHz and the forward power of 100 W. The powered electrode was made from aluminum and its area was much smaller than the grounded chamber. The plasma density was about $1 \times 10^{16} \text{ m}^{-3}$ and the electron temperature about 3 eV. Samples of polypropylene discs were exposed to plasma for 10 minutes. Before and after the treatment they were analyzed by high-resolution XPS. Apart from the appearance of F-rich functional groups, a few at.% of aluminum was detected on the sample surface after the plasma treatment. The XPS results were explained by weakly etching of the powered electrode during plasma treatment and deposition of sputtered material onto the polymer samples.

Funkcionalizacija polipropilena s CF₄ plazmo ustvarjeni v kapacitivno sklopljeni RF razelektritvi

Ključne besede: Plazma, tetrafluorometan, plazemska funkcionalizacija, razprševanje, aluminij.

Izvilleček: Hidrofobizacijo polipropilena smo izvedli v nizkotlačni šibko ionizirani plazmi iz tetrafluorometana (CF₄) pri tlaku 1,0 Pa. Plazma je bila proizvedena v razelektrivni komori iz aluminija s kapacitivno sklopljenim RF generatorjem pri frekvenci 13,56 MHz in moči 100 W. Elektroda je bila narejena iz aluminija. Njena površina je bila veliko manjša kot površina ozemljene komore. Gostota plazme je bila približno $1 \times 10^{16} \text{ m}^{-3}$ in temperatura elektronov okoli 3 eV. Vzorci polipropilena so bili izpostavljeni CF₄ plazmi za 10 minut. Pred in po izpostavi so bili analizirani z visoko ločljivim XPS. Poleg fluorovih funkcionalnih skupin smo na površini plazemsko obdelanih vzorcih opazili tudi nekaj at.% aluminija. XPS rezultate smo razložili s šibkim jedkanjem napajane elektrode med plazemsko obdelavo in depozicijo tanke plasti razpršenega materiala (Al) na vzorcih polimera.

1. Introduction

Plasma treatment is a popular method for modification of surface properties of different polymers. Surface energy of polymers can be increased using oxygen or nitrogen plasma, or plasma created in a mixture of argon and residual atmosphere (water vapor usually predominates) /1-6/. The surface energy can be decreased, on the other hand, using fluorine-rich plasma. For safety reasons, pure fluorine is often avoided and many researchers apply plasma created in tetrafluoromethane instead. In any case, the surface energy is decreased by formation of a thin film of CF_x functional groups on the polymer surface /7-11/. The functional groups are extremely non-polar so the polymer treated by fluorine plasma becomes highly hydrophobic.

Different discharges are used for creation plasma suitable for hydrophobization of organic materials. They include the RF /12-14/ and MW /15-16/ discharges. The RF discharges can be used in two different modes: i) capacitively coupled and ii) inductively coupled. In capacitively coupled (CC) discharge, plasma is created between two parallel metal electrodes, while in inductively coupled (IC) discharge it is usually created within a coil wound around a tube made from an insulator. The tube is usually cylindrical and made from a glass. Pyrex, quartz and borosilicate glasses are all popular. The coil assures formation of an oscillat-

ing magnetic field inside the tube, which induces an electric field. The electric field is always parallel to the tube, it oscillates with the same frequency as the RF generator, and is rather uniform along the tube, except at the edges of the coil. The induced electric field is 0 at the axes and increases toward the coil as $U = \text{const} \cdot r^2$. The coil is tightly wound around the discharge tube in order to make use of almost all magnetic field. The acceleration of ions in the oscillating induced electric field is neglected at the frequency above, say, 1 MHz due to a large ion mass /17/. The electrons, on the other hand, are well accelerated in the electric field. They transfer a part of their kinetic energy to gaseous molecules at inelastic collisions. Since there is no electrode in IC plasma, no DC biasing occurs. The plasma is slightly positive against the glass wall in order to equalize the fluxes of fast electrons and slow positive ions onto the surface. The plasma potential in IC discharge is estimated as

$$V_p - V_f = -\frac{kT_e}{2e_0} \ln \frac{m_+}{2m_e} \quad (1)$$

Where V_s is the space potential, V_f is the floating potential, k is the Boltzmann constant, T_e is electron temperature, e_0 is the elementary charge, m_+ is the ion mass and m_e is the electron mass. Typical order of magnitude of plasma potential in IC discharges is 10 V.

2. Capacitively coupled plasma

The discharge chamber of our plasma reactor is shown in Fig. 1. The housing is grounded and made from stainless steel while the powered electrode is made from aluminum. Plasma is created in the entire volume of the discharge chamber. The powered electrode is connected to a RF generator via a matching network. The RF generator operates at the standard frequency of 13.56 MHz, and the output power of 100 W. The RF peak - to - peak voltage is about 450 V. Plasma is created in the oscillating electric field between the powered electrode and the ground. At the CF₄ pressure of 1 Pa, the entire volume of the discharge chamber is filled with luminous plasma. Plasma density and electron temperature were estimated with a simple single Langmuir probe mounted into the centre of the plasma reactor. At our discharge parameters the plasma density is about $1 \times 10^{16} \text{ m}^{-3}$ and the electron temperature is about 3 eV. The Debye length is

$$\lambda_D = \sqrt{\frac{\epsilon_0 k T_e}{N e^2}} \quad (2)$$

Here, ϵ_0 is the influence constant, N is the plasma density, while the other symbols were already defined. Taking into account the measured values of plasma density and electron temperature, the Debye length in our plasma is about $1.3 \times 10^{-4} \text{ m}$. The Debye length depends on N and T_e as a square root, so even if the experimental error was a factor of 2, the Debye length would change for only 40%.

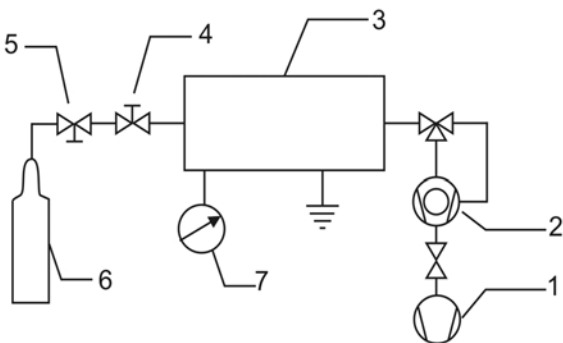


Fig. 1 Discharge chamber

Electrodes in capacitively coupled plasmas acquire a negative potential. The sheath thickness is often said to be “of the order of Debye length”. The thickness is difficult to define since the boundary between the sheath and the unperturbed plasma is not sharp, but it is reasonable to say that it is few times the Debye length. At our conditions the sheath thickness is thus estimated to about 1 mm. The potential is oscillating with the generator frequency. Due to the requirement to equalize the fluxes of fast electrons and slow positive ions from unperturbed plasma onto the boundary of the sheath, the average (let us call it DC) electrode potential is negative against plasma.

The potential in the sheaths appears both at powered and grounded electrode, and depends on the area of the elec-

trodes. Smaller electrodes acquire larger potential sheaths. In the classical work, Chapman /18/ assumes that the sheath voltages vary as $V_1/V_2 = (A_2/A_1)^{1/2}$. This assumption is based on the work performed by Koenig *et al* /19-20/. A 10 - times smaller electrode would thus acquire a 10000 - times larger potential sheath. This effect is used in the conventional RF sputtering systems: the target is always much smaller than the rest of the discharge system. Best results in terms of thin film deposition by RF sputtering are obtained if the mean free path is smaller than the distance between the powered electrode and the substrate holder. In such cases, the sputtered atoms reach the substrate without a collision in the gas phase.

Our experimental system is not at all intended for sputter deposition of thin films, but the basic concepts still apply. Practically all the generator voltage appears as the sheath voltage next to the powered electrode. The sheath voltage oscillates with the generator frequency and so do positive ions appearing in the sheath. The maximum energy of oscillating ions is

$$W_{max} = \frac{1}{2} m v_{max}^2 = \frac{1}{2} m \left(\frac{eE}{m\omega} \right)^2 = \frac{e^2 E^2}{2m\omega^2} \quad (3)$$

and the amplitude is

$$x_{max} = \frac{eE}{m\omega^2} \quad (4)$$

As argued above, almost entire RF voltage drop appears across the sheath next to the powered electrode. The DC self bias is thus little less than half of the peak - to - peak voltage of the RF generator, i.e. about 200V. Assuming the thickness of our sheath is 1mm, and a constant electric field across the sheath (which is definitely not true, but serves as a nice simplification), the oscillating electric field is about 400 V/mm. The ion oscillation amplitude is calculated from equation (4) and is about $6 \times 10^{-5} \text{ m}$ for F⁺ ions, while the maximum energy is calculated from equation (3) and is about 12 eV for the same ions. Lighter ions would gain more energy and would have larger oscillation amplitude, while heavier ions (such as F₂⁺ and CF_x⁺) would gain less energy and would have smaller oscillation amplitude.

Simple calculations performed by equations (3) and (4) give important results. The ions are too heavy to obtain substantial energy at oscillations so the sheath actually acts as a simple DC potential fall across the sheath, i.e. between the unperturbed plasma and the electrode. If the sheath is collisionless (i. e. the sheath thickness is much smaller than the mean free path), the ions are unlikely to lose their kinetic energy within the sheath and bombard the electrode with the kinetic energy of $W_{k+} = eV$, where e is the ion charge (often e_0) and V is the DC potential self bias. In our case, as estimated above, the kinetic energy of ions bombarding the powered electrode is about 200 eV.

The ions thus transfer their energy to the powered electrode. Since their kinetic energy is much larger than the

binding energy of surface and subsurface atoms, they cause the so called radiation damage. Most ion energy is spent for a collision cascade and thus displacement of surface and subsurface atoms. The atoms tend to rearrange so the net effect is heating of the powered electrode. A small part of the ion energy is used for kicking out free electrons from the powered electrode. The electrons are accelerated across the sheath and reach unperturbed plasma with a high energy. In the case of collisionless sheath, the average electron kinetic energy is about 200 eV. Once in unperturbed plasma, the fast electrons are quickly thermalized at elastic collisions with rather slow plasma electrons and contribute to the heating of electrons in plasma.

A small part of the ion kinetic energy is also used for kicking out atoms from the surface of the powered electrode. The effect is called sputtering and is often expressed in the terms of the sputtering coefficient which has been defined as the number of sputtered atoms leaving the electrode per incident ion. Sputtering coefficients have been determined experimentally for a variety of incident ions, kinetic energy, impact angle, surface finish and target materials. For a quick estimation of the sputtering coefficient many authors apply SRIM software package [21-23]. Although the computer simulation may not give extremely accurate results, it is easy to use and represents a quick method for determination of recombination coefficients. The sputtering coefficients for F^+ and C^+ ions on oxidized aluminum electrode are shown in Fig. 2.

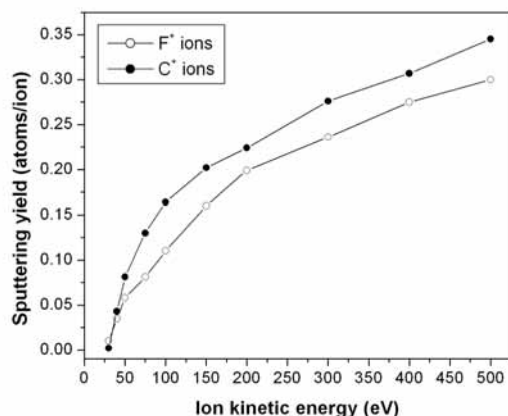


Fig. 2 Sputtering yields for aluminum oxide sputtered by F^+ and C^+ ions

3. Experimental

3.1. Experimental setup

Experiments have been performed in plasma created in the discharge chamber shown in Fig. 1. The chamber is made from aluminum and has inner dimensions $28.5 \times 13.8 \times 23.5 \text{ cm}^3$. There is a flat rectangular powered electrode in the upper part of the chamber as shown in Fig. 1. The dimensions of this electrode are $21 \times 11 \times 2.5$

cm^3 . The area of the chamber wall is thus 2800 cm^2 while the area of the powered electrode is 600 cm^2 .

The electrode is powered by a RF generator via a matching network. The RF generator operates at the industrial frequency of 13.56 MHz and the output power of 100 W. The discharge chamber is an integral part of the experimental system schematically shown in Fig. 3. The system is pumped with a turbomolecular pump with the pumping speed of 250 l/s backed by a two stage oil rotary pump with the nominal pumping speed of $25 \text{ m}^3\text{h}^{-1}$. The turbomolecular pump is mounted about 10 cm apart from the discharge chamber and is connected to the discharge chamber with a stainless steel bellow with the inner diameter of 4.5 cm. The effective pumping speed at the entrance to the discharge chamber at the pressure of 1 Pa is therefore not far from the nominal pumping speed of the turbomolecular pump. Pressure is measured with a baratron attached to the discharge chamber. The ultimate pressure in the system is about 0.01 Pa. Gases are leaked through flowmeters. At current experiments, only one flowmeter that was calibrated for tetrafluormethane was used.

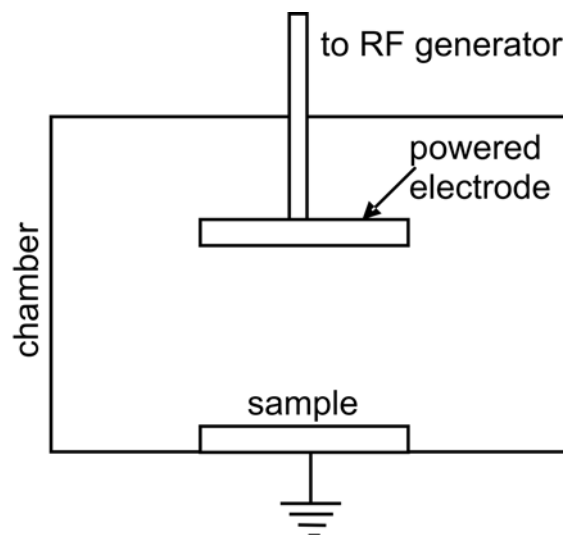


Fig. 3 Experimental set-up: 1 - two-stage rotary pump, 2- turbomolecular pump, 3 - discharge chamber, 4 - flowmeter, 5 - reduction valve, 6 - CF_4 bottle, 7 - pressure gauge

The experiments on the plasma treatment of the polypropylene samples were performed as follows: The discharge chamber was first open to mount a sample onto the bottom of the chamber. The chamber was thus exposed to (humid) air. The chamber was then closed and pumped by the rotary pump to obtain the pressure of few Pa. The turbomolecular pump was turned on and the pressure dropped significantly until after, say half an hour, reached the value of about 0.01 Pa. Tetrafluormethane was then introduced into the discharge chamber to obtain the pressure of 1.0 Pa. The RF generator was turned on for the desired period (in our case the treatment time was 10 minutes).

3.2. XPS analyses

The surface of the samples was analyzed with an XPS instrument TFA XPS Physical Electronics. The base pressure in the XPS analysis chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400- μm spot area with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The energy resolution was about 0.5 eV. Survey-scan spectra were made at a pass energy of 187.85 eV, while the individual high-resolution spectra were taken at a pass energy of 23.5 eV and a 0.1 eV energy step. Since the samples are insulators, we used an additional electron gun to allow for surface neutralization during the measurements. All spectra were referenced to the main C 1s peak of the carbon atoms which was assigned a value of 284.8 eV. The spectra were analyzed by using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer.

4. Results

XPS survey spectrum for an untreated polypropylene (PP) disc is shown in Fig. 4. As expected from the chemical composition of the virgin PP, carbon predominates. The small concentration of oxygen on the untreated sample is probably due to water adsorption. The high resolution C 1s peak for an untreated sample is shown in Fig. 5. The peak is rather uniform – no subpeaks due to carbon bonding with atoms other than C or H are observed. The composition of the surface layer of untreated samples is shown in Table 1. The XPS analyses were performed on 3 samples in order to have some statistics. As expected, no F or anything else was detected on untreated samples, except perhaps some Si whose origin is unknown.

Table 1 Surface composition of the untreated polypropylene sample (three measurements)

Sample	C	O	Si
PP untreated (1 st)	97.4	2.3	0.3
PP untreated (2 nd)	98.9	0.9	0.2
PP untreated (3 rd)	98.4	1.3	0.3

XPS survey spectrum for polypropylene (PP) disc treated by CF₄ plasma is shown in Fig. 6. Apart from the small concentration of O and N, one can observe F in a substantial amount too. The high resolution C 1s peak for plasma treated sample is shown in Fig. 7. The peak now contains several subpeaks due to carbon bonding with F (as well as O and N) atoms, what is an expected feature. More surprising is an appearance of the Al peak which is clearly distinguished from the background. The composition of the surface layer of plasma treated samples is shown in Table 2. Again, the XPS analyses were performed on 3 samples in order to have some statistics.

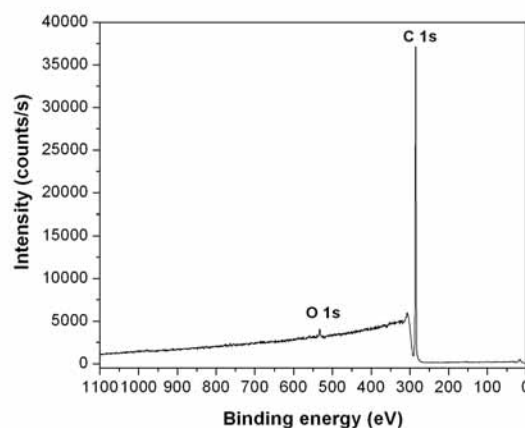


Fig. 4 XPS survey spectrum of the untreated polypropylene sample

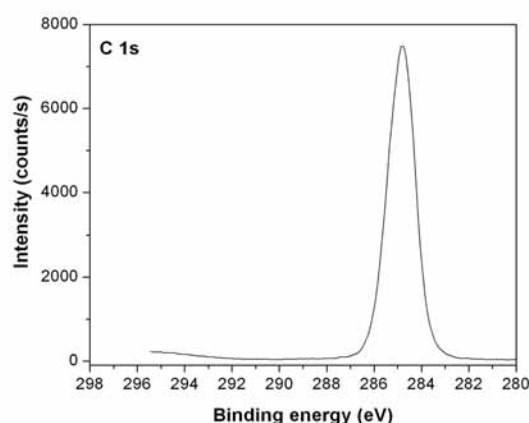


Fig. 5 High-resolution XPS spectrum of C 1s peak of the untreated polypropylene sample

Table 2 Surface composition of the polypropylene sample treated in CF₄ (three measurements)

Sample	C	O	N	Si	F	Al
PP treated in CF ₄ (1 st)	45.1	7.0	2.6	/	36.8	8.6
PP treated in CF ₄ (2 nd)	43.4	6.4	2.0	3.0	38.5	6.7
PP treated in CF ₄ (3 rd)	43.1	5.5	2.4	2.2	39.1	7.6

5. Discussion

The appearance of the F-rich functional groups on the surface of samples treated by CF₄ plasma is expected. Namely, as shown by numerous authors /24-26/, the result of the plasma treatment is a formation of F-rich functional groups on the surface of the PP polymer. Any discussion on the composition, let alone the structure of the surface film, is beyond the scope of this paper.

More interesting is the appearance of aluminum on the surface of plasma treated samples. This is important from both scientific and applied view. Namely, while F-rich functional groups cause a decrease of surface energy and thus the

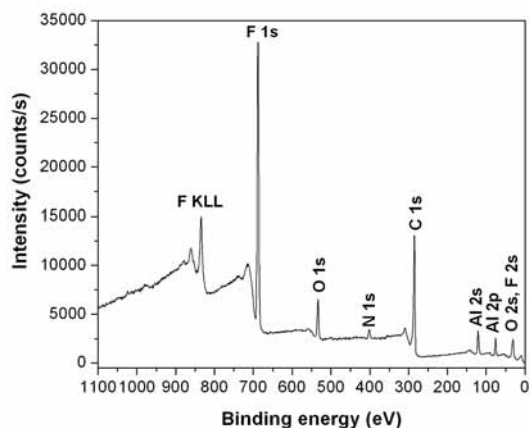


Fig. 6 XPS survey spectrum of the polypropylene sample treated in CF₄ plasma

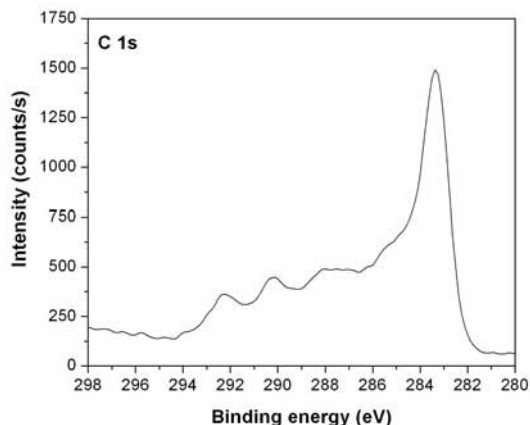


Fig. 7 High-resolution XPS spectrum of C 1s peak of the polypropylene sample treated in CF₄ plasma

decrease of the wettability, aluminum definitely has the opposite effect: metals always have high surface energy and should contribute to an increase of the surface energy.

The appearance of a thin film of aluminum on the sample surface is explained by sputtering of the powered electrode. As already mentioned, almost entire DC self bias occurs at the powered electrode. Let us first consider the type of ions bombarding the powered electrode. The electron temperature is only a few eV. Average electrons are therefore likely to excite CF₄ molecules to a variety of vibrational and rotational states but cannot dissociate or ionize the molecules. Only the fastest electrons are capable of dissociation and ionization. The lowest dissociation energy of about 12.5 eV is found for the reaction CF₄ → CF₃ + F. Since the electron temperature in our plasma is rather low, this reaction probably prevails. Apart from it, dissociation like CF₃ → CF₂ + F seems quite possible, but is definitely less probable. The final concentrations of CF_x molecules should decrease in the following way: CF₄, CF₃, CF₂, CF, C. The concentration of F atoms should be a bit higher than the concentration of CF₃ molecules if F atoms are not lost by some mechanisms. The gas phase loss can be neglected at the pressure of 1 Pa, while there are some

possible mechanisms of the F loss on the surfaces facing plasma. They include heterogeneous surface recombination of F atoms on the walls of the discharge chamber and the powered electrode (reaction F + F → F₂) and substitution of the H atoms on the surface of polypropylene with F atoms (reaction C_xH_y + F → C_xH_(y-1)F). The recombination coefficient for the first reaction is unknown. Namely, to the best of our efforts we could not find literature reporting the recombination coefficient for F atoms on the surface of (surface oxidized) stainless steel or aluminum. However, we can estimate the loss by the other mechanism. Let us estimate a 1% dissociation fraction of CF₄. The partial pressure of F atoms in our plasma is then 0.01 Pa and the corresponding density of F atoms is $n = p_K/kT = 2.4 \times 10^{18} \text{ m}^{-3}$. The resultant flux of F atoms on the PP sample is then $j = \frac{1}{4} n \langle v \rangle$. Assuming the average random velocity of F atoms of 500 m/s the flux is then $j = 3 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$. Taking into account the number of atoms on the surface of solid materials, which is roughly $1 \times 10^{19} \text{ m}^{-2}$ one can clearly see that the loss of F atoms due to substitution of H from polypropylene is negligible.

Let us now estimate the type of ions bombarding our powered electrode. The relevant literature does not report CF₄⁺ ions so the first candidates are CF₃⁺ ions appearing at the reaction CF₄ + e → CF₃⁺ + F + e or at simple ionization of the CF₃ radical. Since the density of CF₄ molecules is much larger than the density of CF₃ molecules and F atoms (let alone CF₂ and CF molecules), we can expect that the CF₃⁺ ions will prevail. These ions are accelerated in the DC sheath and bombard the powered electrode with the kinetic energy of about 200 eV. As soon as an ionized molecule reaches the electrode surface it is dissociated to atoms. On the average, each atom takes about a fourth of the CF₃⁺ ion kinetic energy, i.e. about 50 eV. This is thus the available kinetic energy of each particular atom. As we already mentioned, most of the energy is spent for the electrode heating and a smaller fraction is spent for sputtering. The sputtering coefficients for F and C atoms (or ions) versus the kinetic energy are shown in Fig. 2. At the kinetic energy of 50 eV, the sputtering coefficient for oxidized aluminum is about 0.08. For F⁺ ions with the kinetic energy of 200 eV the coefficient is much larger at around 0.2, but as argued above, the density of F⁺ ions in plasma is much smaller than the density of CF₃⁺ ions so the contribution of F⁺ ions from plasma to the electrode sputtering is easily neglected.

Let us now estimate the etching rate of the powered electrode. If the ion density in unperturbed plasma is $1 \times 10^{16} \text{ m}^{-3}$ the resultant flux of CF₃⁺ ions onto the electrode surface is about $1 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$. Taking into account the sputtering coefficient of 0.08 and the fact that there are 4 atoms in the CF₃ molecule, the powered electrode is etched at the rate of

$$\frac{dx}{dt} = j \frac{S}{N_s} \quad (5)$$

where j is the ion flux, S is the sputtering coefficient and N_s is the atom density in the solid material. Taking into ac-

count the numerical values, i.e. $j = 1 \times 10^{18} \text{ m}^{-2} \text{ s}^{-1}$, $S = 0.08$ and $N = 1 \times 10^{19} \text{ m}^{-2}$, the etching rate is about 10^{-2} monolayers of oxidized aluminum per second. The samples are exposed to plasma for 10 minutes, i.e. 600 s. In this period, the powered electrode is etched for about 2.5 monolayers. The sputtered atoms leave the powered electrode with a small kinetic energy and are deposited on the chamber walls as well as on the surface of the polypropylene samples. Since the area of the samples mounted opposite the powered electrode is much smaller than the area of the powered electrode, we can assume a homogeneous flow of sputtered atoms on the surface of the substrate. The powered electrode is made from aluminum but exposed to air prior to any plasma experiment, so a thin film of oxide is formed on its surface. According to the literature [27-28] the thickness of this native oxide film is several nm, so much more than the thickness of the etched film during our experiments. Since the Al atomic concentration in alumina is 40% the expected thickness of the Al film on the polypropylene surface is $2.5 \times 0.4 = 1$ monolayer. This should be true if the mean free path of the sputtered atoms is larger or close to the distance between the electrode and the sample.

At the pressure of 1 Pa, the mean free path of molecules and atoms is close to 1 cm. The distance between the powered electrode and the samples is about 10 cm. The sputtered atoms are therefore unlikely to go directly towards the sample, but they rather diffuse in the space between the powered electrode and the sample. Since a sample has a much smaller area than the powered electrode, the diffusion should not influence the thickness of the deposited Al film on polypropylene.

Another effect, however, should be addressed before concluding the thickness of the Al film on our samples. The system is pumped by the turbomolecular pump and CF₄ is continuously leaked into the chamber. There is obviously a drift of gas from the entrance port toward the pump. If the geometry of our discharge vessel was cylindrical with the length much longer than the diameter and if the initial gas drift velocity was low, one would be able to calculate the drift velocity of the gas between the electrode and the samples. In our case, however, the discharge vessel has other geometry, and the drift velocity of gas entering the discharge chamber is far from being low. Namely, the gas is leaked into the system through the flowmeter, i.e. an extremely narrow tube. At the exit of the flowmeter, the gas drift velocity is close to the sound velocity, i.e. around 300 m/s. The gas jet expands into the discharge chamber and the drift velocity between the powered electrode and the samples is much smaller than at the entrance, but definitely large enough to push sputtered atoms toward the pump, i.e. away from the samples. For this reason, the thickness of the Al film on the polypropylene is definitely smaller than 2.4 nm, which was calculated ignoring the gas drift. The thickness could be calculated taking into account both the diffusion and the gas drift, but the calculation is definitely beyond the scope of this paper. We can only conclude

that the expected thickness of the Al film on the polypropylene samples is of the order of 0.1 monolayers, or perhaps close to a monolayer.

The upper considerations are sound with the measured XPS survey spectra (Fig. 7). The Al concentration on the sample surface, as calculated from the XPS survey spectrum, is about 7 at.%. If the XPS would measure the composition of the uppermost atomic layer, this would mean that the thickness would be only 0.07 monolayers, i.e. several times smaller than the estimated value, which should be several 0.1 monolayers. This discrepancy is explained by the simple fact that XPS does not measure the concentration of elements in the uppermost layer only, but gives some average over a thicker film, say up to the equivalent of about 10 monolayers. It is clear that the uppermost layer contributes more to the XPS spectrum than the subsurface layers, but it is difficult to calculate the exact thickness of the Al film on the PP samples. Not only the escape depths of photoelectrons, but the surface morphology would have to be taken into account as well.

Let us finally explain the fact that the O concentration on the surface of plasma treated samples is several times larger than on the untreated samples. The most probable explanation for this effect is oxidation of aluminum. Freshly sputter deposited Al is likely to bond oxygen. There are some sources of oxygen atoms (or molecules) in the discharge chamber. The first one is sputtering of the oxidized aluminum, but due to a poor sputtering rate it is easily neglected. The major source of oxygen is a virtual leak originating from desorption of water molecules from the walls of the discharge chamber. The ultimate pressure in our system is about 0.01 Pa. Since the system is never baked prior to plasma experiments, the majority of the residual atmosphere is water vapor. The number of molecules leaving the surface in unit time is estimated using the data on the ultimate pressure and the effective pumping speed:

$$\frac{dN}{dt} = p_0 \frac{S_{\text{eff}}}{kT} \quad (6)$$

where p_0 is the ultimate pressure, S_{eff} is the effective pumping speed, k is Boltzmann constant, T is the gas temperature. Taking into account the numerical values, one can estimate the number of molecules leaving the surface in unit time to $dN/dt = 1 \times 10^{20} \text{ s}^{-1}$. This value is orders of magnitude larger than the number of oxygen atoms entering the discharge volume due to sputtering of the powered electrode (Al₂O₃). The water molecules are oxidative enough, but they also dissociate to H and OH in plasma so they are effective oxidizers.

6. Conclusion

Polypropylene samples were treated by CF₄ plasma created in a capacitively coupled RF discharge. As expected, a thin film of CF_x functional groups appeared on the sample surface during plasma treatment. The concentration of fluorine on plasma treated samples was estimated by XPS

analyses, and it was close to 40 atomic %. Apart from fluorine, a thin film of aluminum was formed on the sample surface as well. The appearance of the Al was explained by sputtering of the powered electrode. The thickness of the Al film on the PP samples was estimated to several 0.1 monolayers from the XPS results. This value was explained taking into account gas phase and surface phenomena. Although the calculations include several simplifications as well as uncertain data, the theoretical calculation is sound with the experimental results.

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