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Autor(en): **Gröning, Pierangelo**

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# Plasma-Polymer Reaction: Etching and Polymerisation

by PIERANGELO GRÖNING

## Abstract

In the last two decades, plasma-polymer reactions have been actively studied because of their unique ability to modify solid surfaces without affecting their bulk properties. This makes plasma treatment also interesting in the field of conservation of archaeological metal objects. Of increasing interest is the conservation of textiles with plasma which can contain cleaning and sterilisation process followed by a deposition process of a protective coating.

In the present contribution we illustrate, with a few examples, how plasmas can react with polymeric (organic) surfaces. We demonstrate a strong gas pressure dependence on the type of chemical reaction on polymer surfaces and discuss the observation in terms of the flux and the kinetic energy of the ions. For the plasma polymerisation we present a "self thickness limited" deposition technique to produce an ultra-thin ( $d \geq 5$  nm [nanometer]) Teflon®-like perfect hydrophobic polymer film. The film has an extremely low surface energy of  $4.2 \text{ mJ/m}^2$  (millijoule per square meter), which is more than four times lower than for Teflon®. The thickness limiting behaviour of the plasma polymerisation is explained by the dualism of etching and polymerisation occurring in fluorocarbon discharges. Such kind of hydrophobic films may be of interest for the conservation of the plasma cleaned archaeological objects to prevent post-oxidation by water adsorption.

## Introduction

The solid surface in a plasma is exposed to a broad spectrum of activated species, as ions, electrons, radicals, and electromagnetic radiation, each of which have an influence on the surface modification. In a chemical sense, the interactions of the polymer with the activated species are implantation reactions of atoms, radical generation, and polymer-forming reactions. Which reaction is initiated by the different species in the plasma depends mainly on the nature of the plasma gas, as well as on the energy level of the plasma and the nature of the polymeric material.

In fluorocarbon sustained discharges both etching and polymerisation can occur, even simultaneously<sup>1,2</sup>. The dominant process depends on the fluorine to carbon atom ratio (F/C) of the monomer of the feed gas. Coburn and Winters<sup>1</sup> found that for polymerisation, the F/C ratio of the feed

monomer must be lower than three. In the presents of hydrogen ( $\text{H}_2$ ) in the discharge, the boundary between polymerisation and etching conditions is displaced to higher F/C ratio, so that  $\text{CF}_4$  can also be used for polymerisation. In this contribution we present a "self thickness limited" deposition of an ultra-thin Teflon®-like polymer film from a  $\text{CF}_4/\text{H}_2$  discharge. Contact angle measurements reveal an extremely low surface energy, four times lower than that of Teflon®. The formation of this ultra-thin polymer film with its extremely low surface energy, its good adhesion to the substrate, and the "self thickness limited" behaviour is explained by the intrinsic dualism of etching and polymerisation of the fluorocarbon discharge.

## Experimental

The treatment of the polymers and the polymerisation were performed in a high vacuum chamber vacuum connected to a spectrometer which enabled surface analysis of the sample without disturbing contaminations from atmospheric contact. The excitation of the plasma is done by microwaves at a frequency of 2.45 GHz (GigaHertz). At pressures lower than  $10^{-2}$  mbar (millibar), the plasma is excited by the electron cyclotron resonance (ECR) condition. The details of this plasma chamber have been published elsewhere<sup>3</sup>. X-ray photoelectron spectroscopy (XPS) was used to analyse the sample surface, a diagnostic tool well-adapted to study surface modifications, since it has a high surface sensitivity.

## Results and Discussion

### Plasma Treatment of Polymers

Figure 1 displays sulphur 2s ( $\text{S}2\text{p}$ ) XPS core-level spectra of plasma treated polyethersulphone (PES) in different gases at very low pressure ( $p = 3 \times 10^{-4}$  mbar). Independent of the gas used, all plasma treated samples show a  $\text{S}2\text{p}$  spectrum where almost the whole signal is shifted to lower binding energy, indicating the reduction of the sulphonic ( $-\text{SO}_2-$ ) group to sulphide ( $-\text{S}-$ ). The amount of sulphide groups present on the PES surface after plasma treatments increases generally with decreasing gas pressure ( $p$ ). For  $p < 10^{-3}$  mbar we observed in the equilibrium state a practi-

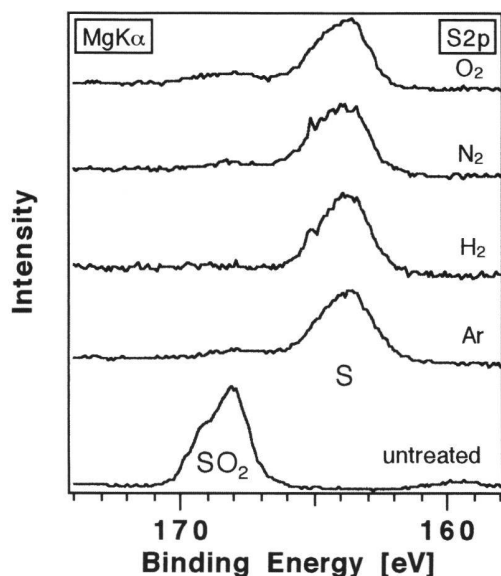


Fig. 1: Sulfur 2p (S2p) XPS spectra of plasma treated PES in different gases ( $p = 3 \times 10^{-4}$  mbar,  $t = 1$  sec.)

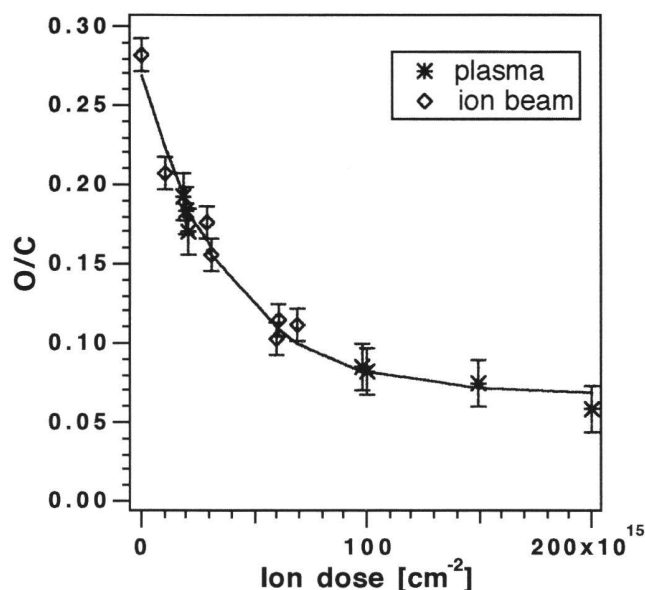


Fig. 2: Oxygen-to-carbon (O/C) atom ratio of the plasma and  $\text{Ar}^+$  ion beam ( $E_K = 10$  eV) treated PMMA surface as a function of the ion dose.

cally total reduction of the sulphonic groups in the probing depth of XPS ( $\sim 10$  nm), whereas for  $p > 10^{-3}$  mbar the amount of sulphide groups decrease with increasing gas pressure. For  $p = 10^{-1}$  mbar sulphide groups are no more observable even after 20 min. of treatment. The reduction of the polar sulphonic group by the plasma is related with the kinetic energy of the ions hitting on the polymer surface. The kinetic energy of the ions hitting on the polymer surface and the ions in the discharge is completely different and given by the difference of the floating potential  $U_f$  of the sample and the plasma potential  $U_p$  ( $E_K = e \cdot (U_p - U_f)$ ). In our plasma chamber, in the pressure range between  $3 \times 10^{-4}$  mbar and  $10^{-1}$  mbar the kinetic energy of the ions interacting with the polymer surface decreases from 22 eV (electron Volt) to 3 eV with increasing pressure. For pressures where the kinetic energy of the ions hitting on the sample is higher than 10 eV the reaction of these ions dominates the modification on the polymer surface. We proved this in the case of *polymethylmethacrylate* (PMMA) by comparing the chemical composition at the surface after plasma and ion beam treatments with different ion doses shown in Figure 2. We conclude that the ions with kinetic energies higher than 10 eV can penetrate the polymer surface and induce ion-dipole interaction, which is stronger and more probable for the high polarity bonds. Once the ion is attracted in the proximity of a high-polarity bond, it can recombine with one of the electrons of the bond. Figure 3 illustrates the ion interaction with the PMMA polymer. In a first step the ion reacts with the partially negatively charged carbonyl oxygen and forms an unstable intermediate state. In a second step the polymer reacts on this modi-

fication by an electron transfer from the neighbouring carbon-carbon (C-C) bond: In the case of PMMA results this in a cleavage and removal of the whole side-chain from the polymer. More about the reaction of the low energetic ions in the plasma with polymer surfaces is described in the references<sup>4-7</sup>.

#### Plasma polymerisation of an ultra-thin Teflon®-like film

As mentioned in the introduction, it is well known that simultaneous etching and polymerisation occur in a fluorocarbon discharge. Using this intrinsic behaviour of the fluorocarbon discharge we found conditions where the polymerisation occurs in a kind of a “self thickness limiting mode”<sup>8</sup>. We tuned the plasma conditions so that polymerisation starts close at the boundary between polymerisation and etching conditions (point I, Fig. 4). With increasing

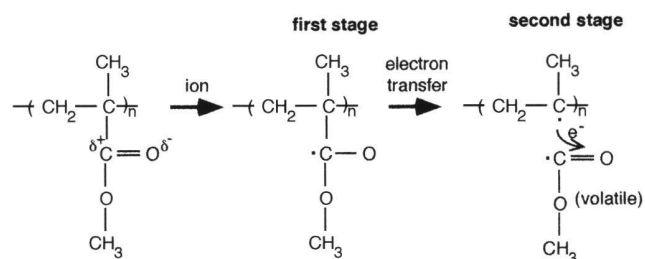


Fig. 3: Schematic illustration of the side-chain scission in PMMA due to low-energy ions.

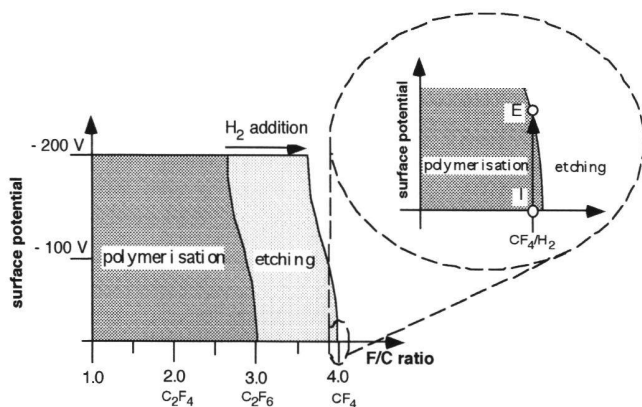


Fig. 4: Schematic illustration of the "self thickness limited" deposition process of the ultra-thin, hydrophobic Teflon®-like film.

thickness, the isolated polymer film becomes negatively charged due to the mobile electrons in the plasma. This negative bias now causes the deposition to come to an equilibrium between polymerisation and etching (point I, Fig. 4). At this point, the growth of the film is stopped (thickness ~ 5 nm) and the deposition process changes from a growth to a treatment mode. During this treatment phase a

fluoridation of the film occurs so that finally 85%  $\text{CF}_2$  functionalities are present in the film visible in the deconvoluted carbon 1s ( $\text{C1s}$ ) XPS spectrum in Fig. 5. The CF component with a content of 9% indicates crosslinks in the film. These crosslinks are important for this ultra-thin film because they allow the formation of a three-dimensional structure of the film, which is essential for its stability. The  $\text{CF}_3$  component indicates endings of the polymer chains. The C-CF component originates from the Ni-polymer interface, indicating a good adhesion of the film. The fluoridation of the film results in a dramatic decrease of the surface energy. Contact angle measurements reveal a surface energy of  $4.2 \text{ mJ/m}^2$ , which is more than four times lower than for Teflon®. This excellent hydrophobic behaviour is demonstrated in Fig. 6 by a droplet of water deposited on a Swiss coin covered with our polymer film. The film was tested as anti-adhesion film for the replication of micro-optical structures, using nickel shim with a very fine surface grating (400 nm periodicity and 140 nm depth) to hot emboss ( $T = 180^\circ\text{C}$ ) polycarbonate (PC) sheet. The covered shim still separated readily from the PC sheet after more than 100 replications and no delamination of the anti-adhesion film was observed, indicating a very good adhesion to the nickel shim.

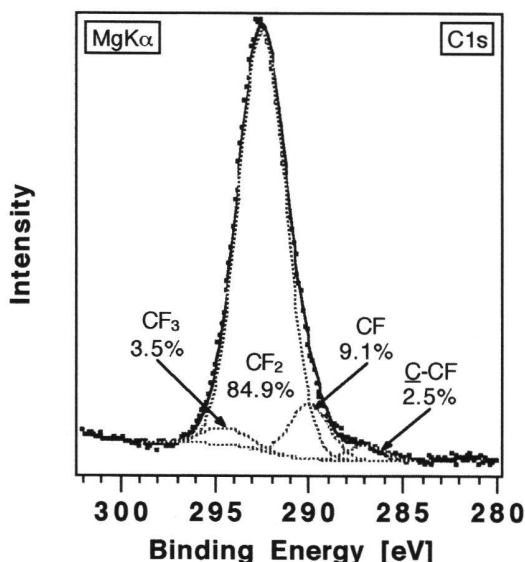


Fig. 5: Deconvoluted Carbon 1s ( $\text{C1s}$ ) XPS spectrum of the plasma polymerised film.

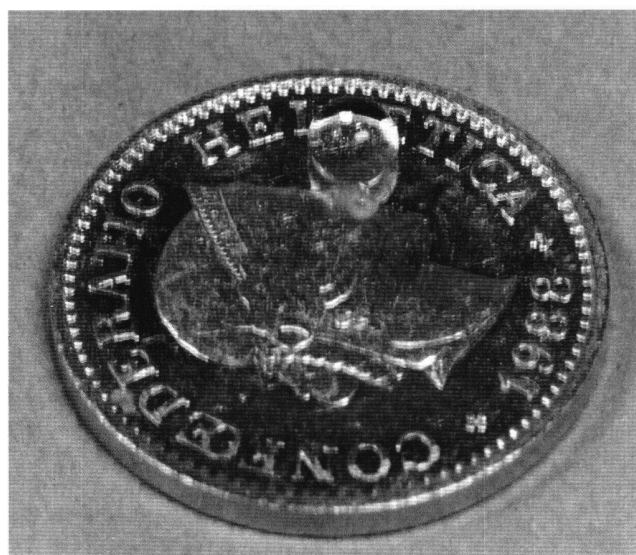


Fig. 6: Drop of water on a Swiss coin covered with the ultra-thin, hydrophobic polymer film.

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