Deposition of Super-Hydrophobic and Oleophobic Fluorocarbon Films in Radio Frequency Glow Discharges

L. Laguardia,[*1] *D. Ricci,*[1] *E. Vassallo,*[1] *A. Cremona,*[1] *E. Mesto,*[2] *F. Grezzi,*[1] *F. Dellera*[1]

Fluorocarbon films using a monomer, 1H, 1H, 2H-perfluoro–1-dodecene were deposited in a continuous radio frequency (RF) glow discharge, the process was carried out in a parallel-plate RF discharge onto stainless steel reactor in order to produce coating with a water-and oil–repellent surface. Fourier-Transform Infrared spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS) revealed that the films obtained contain mainly perfluoromethylene (CF_2) species. Film wettability was tested using water and hydrocarbon liquids for contact angle measurements, furthermore surface energy was also calculated. Oil-repellency was found to increase as the amount of CF_2 species increases in the film structure. Film morphology was studied by Atomic Force Microscopy (AFM), films showing an usual morphology from that typical of Plasma Polymerised Fluorocarbon (PPFC) films. The combination of the low surface energy coating and the surface morphology produces materials which are both water and oil repellency.

Keywords: fluoropolymer; glow-discharge; oil-repellency; surface energy; water-repellency

Introduction

Fluorocarbon films (CFx) obtained by plasma enhanced chemical vapour deposition (PECVD) in continuous process are attractive materials applied in various fields for their outstanding properties: good adhesion to organic and inorganic substrates,[1] the presence of low intermolecular forces, which give rise to relatively inert surfaces with extremely low free energy,[2] biocompatibility,[3] a low friction coefficient.[4] Thin films with a tuneable F/C ratio can be deposited in glow discharge with many different fluorinated monomers, such as fluoroalkyls, fluorohydroalkyls, cyclofluoroalkyls, fluorobenzene, as pure feed or in mixture with various additives.[5] The feed supplies the plasma phase with CF_x radicals, F atoms, and with charged particles. CF_x radicals are the building blocks for the polymeric deposits. The relative abundance of these active species are affected not only by monomer feed but also by input power, pressure, feed additives, etc.[6]

Films derived from many fluoromonomers show excellent hydrophobicity,[7] but few studies have specifically examined oleophobicity.

Conventionally, plasma polymerization of fluorocarbon films has been accomplished using a low molecular mass monomer, such as C_2F_6,[8] C_4F_8.[9] A few research groups have investigated higher molecular mass monomers to produce a film dominated by CF_2 species.

In our work, continuous R.F. glow discharge fed with 1H, 1H, 2H-perfluoro-1-dodecene monomer was used to deposit CF_x films on silicon substrate to produce water and oil- repellent surfaces.

[1] Istituto di Fisica del Plasma ENEA-CNR-EURATOM, Milano, Italy
E-mail: Laguardia@ifp.cnr.it
[2] Università degli Studi di Bari, Dipartimento Geomineralogico, Italy

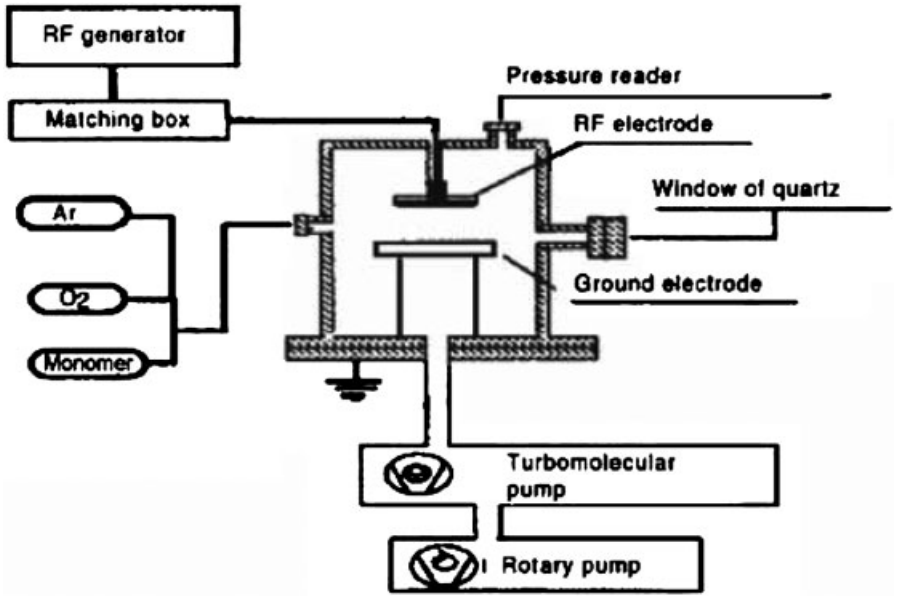

Figure 1.
Schematic representation of the apparatus for the fluorocarbon films deposition.

Experimental Part

Thin fluorocarbon films were obtained by 1H,1H, 2H-perfluoro-1-dodecene plasma deposition in continuous modes. The films were deposited both on Si(100) single side lapped wafer and double-side lapped wafer for the FT-IR analyses. Before deposition, the wafer was cut in pieces (about 2×2 cm^2), washed in acetone and ethanol and dried under a air flow.

The processes were carried out in cylindrical parallel plate stainless steel reactors, with the upper electrode powered and the lower one grounded. The plasma was ignited at 13.56 MHz power supply. The long chain fluorocarbon monomer 1H,1H, 2H-perfluoro-1-dodecene consisted of a fully fluorinated carbon chain with a vinyl end group and was used for all film depositions. This liquid monomer was placed in a vessel that was connected directly to the inlet of the reactor. RF power was varied from 6 to 50 W and the deposition time was held at 15 min. The base pressure was 0.009 Torr and the process pressure was fixed at 0.05, 0.1 and 0.2 Torr.

A chemical analysis of the film was performed using a FT-IR by means of Spectrum One of the Perkin Elmer. Further chemical analysis was performed using XPS by using a non-monochromatized Mg anode X-ray source ($h\nu = 1253.6$ eV) VSW model TA10 and a hemispherical analyzer, VSW model CLASS 100 equipped with a single channel detector, operated in the constant pass energy mode. The survey scans were acquired with an overall

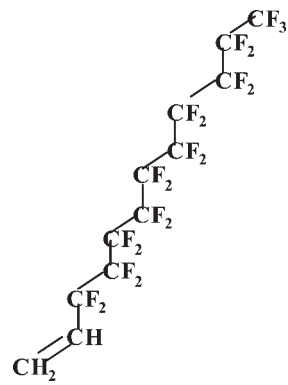

Figure 2.
Chemical structure of the 1H,1H, 2H-perfluoro-1-dodecene used for plasma polymerization.

experimental resolution of about 2 eV and with a take-off angle of 0°. The core line levels spectra were acquired with an overall experimental resolution of about 0.8 eV. All spectra were referenced to the same energy scale determined by calibrating the Ag $3d_{5/2}$ line at 368.3 eV[8] previously determined using a polycrystalline Ag sample.

The core levels fit was performed through a Voigt profile including a Lorentzian function (accounting for lifetime broadening) and a Gaussian function (accounting for the finite instrumental resolution). The fitting routine included also a Shirley background, mimicking the secondary electron background.

For each element, the relative atomic concentration of the species was estimated by using the areas below the prominent spectral lines and after normalization to the atomic sensitivity factors[9] regardless of the specific chemical state. We remark, that in the present work the main issues deal with the relative trends and not with the absolute values of the concentrations. This justifies the use of sensitivity factors related to a spectrometer other than ours.

The base pressure in the analysis chamber was always $\sim 7^{*}10^{-6}$ Torr. The samples were measured before every ion sputtering (as received samples), and after 10 min of Ar sputtering (primary beam energy 3 keV; primary current ≈ 1 μA) for removing the surface contaminated layers due to exposure to the air.

Distilled water and diiodomethane contact angle (θ), of the films surface, was measured using a Data Physics contact angle instrument with the sessile drop technique.

Surface energies of the films were compared using the Owens Went method.[12]

$$W_{sl} = 2(\gamma_{sv}^{d} + \gamma_{lv}^{d})^{\frac{1}{2}} + 2(\gamma_{sv}^{p} \cdot \gamma_{lv}^{p})^{\frac{1}{2}}$$

where γ_{sv}^{d} and γ_{lv}^{d} are the dispersive contribution to the surface energy of solid and liquid components respectively, and γ_{sv}^{p} and γ_{lv}^{p} are the polar contribution to the surface energy of solid and liquid components.

Surface morphology of the films deposited was studied using AFM, investigation was perforemd using a Nano-R2 system of Pacific Nanotecnology in close contact mode.

Results and discussion

Film Composition

Film chemical composition as a function of input power was observed by XPS and FT-IR analysis. XPS analysis reveled that the films were composed predominantly of florine and carbon. The XPS C_{1s} spectra were fitted by the peaks shown in Table 1. The corresponding assignments were showed.

The Fig. (3) shows the best-fitted C1s signal of a fluorocarbon film deposited at 0.2 Torr and at 10W and 50W respectively. The importance of the CF_2 component over the other ones is evident. The film also

Table 1.
Assignment of the C_{1s} components of fluorocarbon film and the energy separation $\Delta C_i - C'_i$, between components corresponding to different "forms" of carbon (i) and the component corresponding to non –functionalized aliphatic carbons (i′).[13]

Component numberf on fitted C1s spectrum	$\Delta C_i - C'_i$,	Carbon group assignment
1	8.7 ± 0.2 eV	CF_3
2	7.3 ± 0.2 eV	CF_3–$\underline{C}F_2$–
3	6.6 ± 0.2 eV	–($\underline{C}F_2$–$\underline{C}F_2$)–
4	4.9 ± 0.2 eV	–$\underline{C}F$–CF_2–
5	3.7 ± 0.2 eV	–$\underline{C}$–F–
6	2.6 ± 0.2 eV	–$\underline{C}$–CF_2
7	1.5 ± 0.2 eV	–$\underline{C}$–CF–
8	0.00 ± 0.2 eV	–$\underline{C}$–C–
9	−1.3 ± 0.2 eV	Conjugated carbons

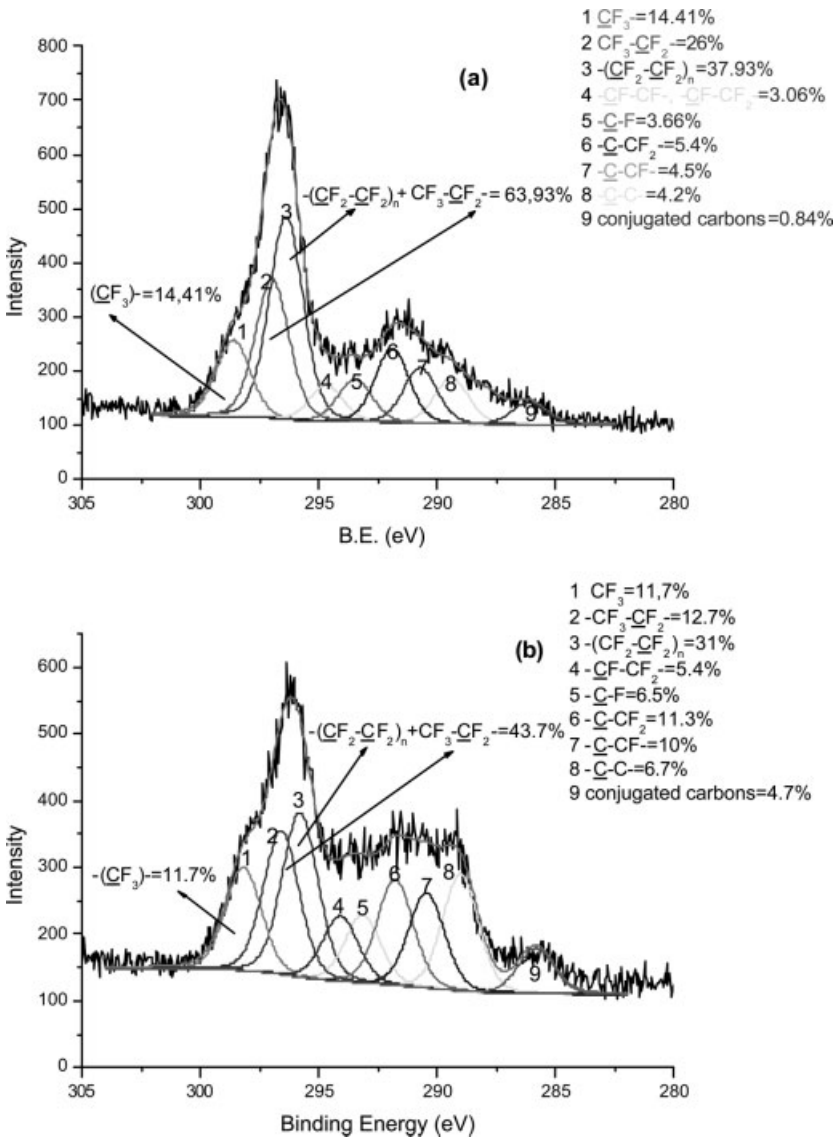

Figure 3.
XPS C1s signal for a coating deposited at 0.2 Torr, 10W (a) and 50W (b).

shows a slightly higher concentration of CF_3 closer to the surface. CF_x area percentages determined by the curve fitting[14] of the C1s spectra are reported in the figure. XPS analysis reveled that relative contribution of the CF_2 component increases markedly as the RF power decreases from 50W to 10W, a similar behavior is found for the CF_3 contribution.

The effect of pressure on the film chemical composition has been observed: $\underline{C}F_3$, CF_3-$\underline{C}F_2$ and $\underline{C}F_2$ content in the film increases progressively while the trend of the C-C is opposite when the pressure increases. These results point out a low monomer fragmentation at higher pressure.

Figure 5 shows the FT-IR spectra of the films deposited at two different

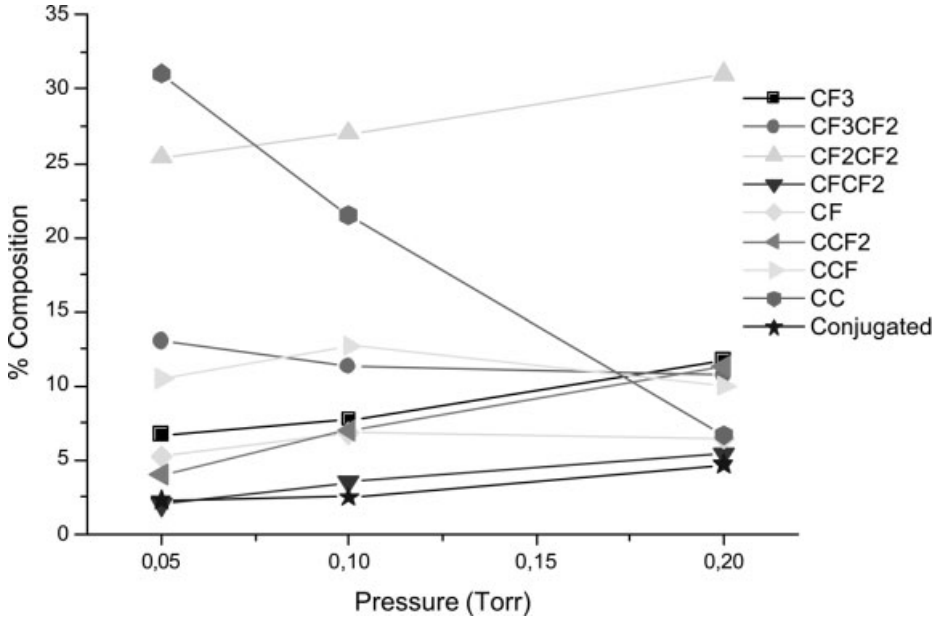

Figure 4.
CF_x percentage as a function of pressure for films deposited at 10W.

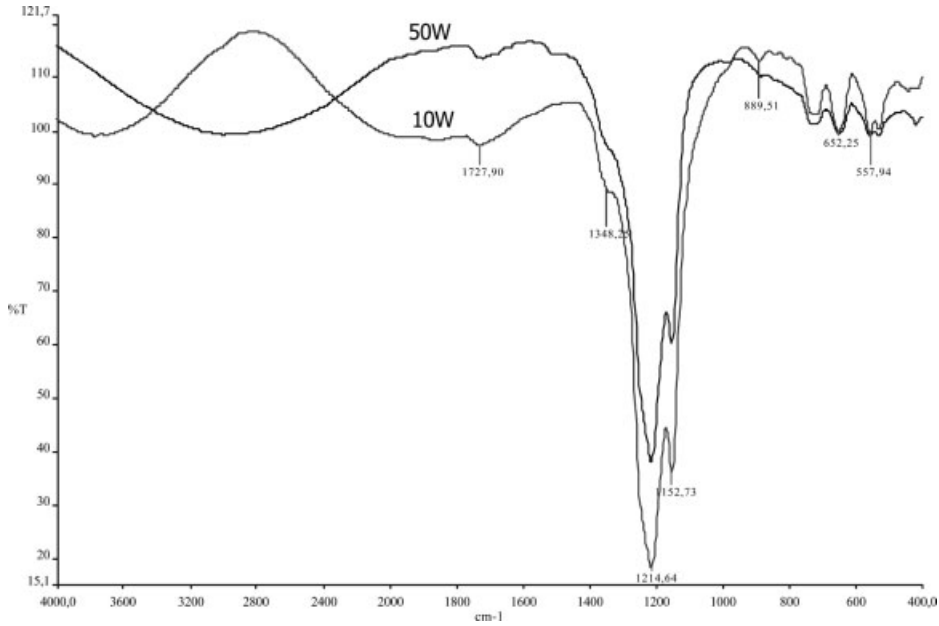

Figure 5.
FT-IR spectra of films deposited for 15 min and at 0.1 Torr, input power are 50W and 10W respectively.

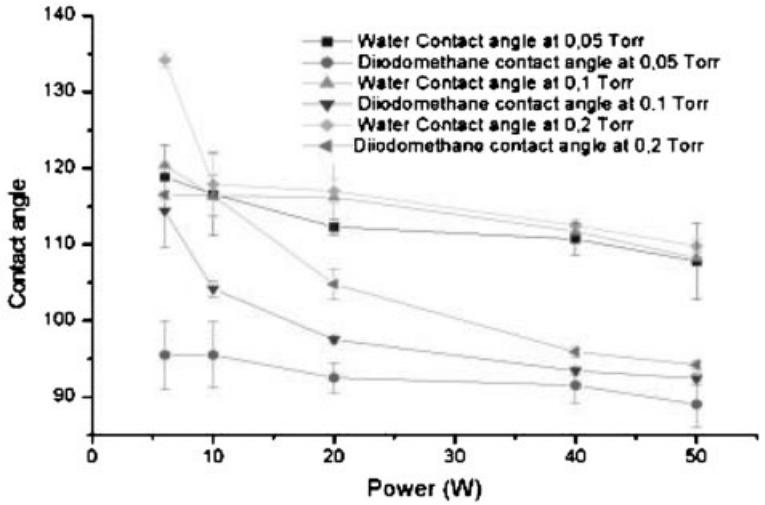

Figure 6.
Contact angle measurements for the films deposited at various RF power.

powers, both spectrum present the same contributions. The band in the 1700–1850 cm^{-1} region, where both C=O and C=C groups originate absorptions.[15] The absorption band between 1400 and 1000 cm^{-1} region, where most of the CF_x vibrations are relevated, producing the principal feature of plasma polymerized fluorocarbon.[16] Peaks at 1214,64 and 1152,73 cm^{-1}[17,18,19] are assigned to CF_2 asymmetric and symmetric stretching vibrations, respectively. Another significant feature characterizing deposited film is the absorption of 1348,25 cm^{-1}, assigned to CF stretching.[17] Finally, the bands at 652,25 and 557,94 cm^{-1}, are due to CF_2 wagging mode.[20] Comparing the spectrum of the films deposited at 50W with that one

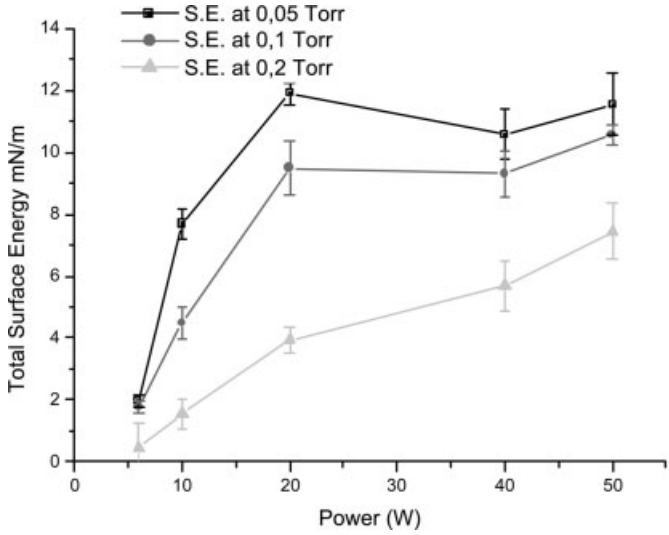

Figure 7.
Total surface energy for the films deposited in RF glow discharge as a function of the power using Owens-Wendt method, water and diiodomethane were used as test liquids.

deposited at 10W, the CF_2 symmetric stretching becomes narrowed and sharpened. It should also be noticed that power lowering results in films with major CF_3 groups and this feature is highlighted by the slight broadening of the peak at 889,51 cm^{-1}.[20] These data are confirmed by XPS data ones.

Contact Angles and Surface Energy

The water contact angle on the coated surfaces ranged from 107° to 134°, hence contact angles of the hydrocarbon liquids varies from 89° to 116°. The high contact angle for water (134°) and diiodomethane (116°) was for film deposited using only 6W of power. So that films show hydrophobicity and oleophobicity, trend of these properties were attributed to variation content of CF_2 and CF_3 on the films.[21]

The total surface energy, calculated using Owens-Wendt method, showed in Figure 6.

The surface energy decreases for films deposited at low RF power and high pressure, however with a purely dispersive component. For the films deposited at 10W and 0.2 Torr a total surface energy of 0,45 mN/m was calculated (γ^d_{sv} 0.33 mN/m, γ^p_{sv} 0,12 mN/m), while for the films deposited at 50W a total surface energy of 7.44 mN/m (γ^d_{sv} 7.24 mN/m, γ^p_{sv} 0,2 mN/m) was determined. Evidently an increase in the amount of CF_2 and CF_3 species on the surface of the films will decrease the surface energy.[22]

Film Morphology

AFM analysis of the film reveals an usual morphology for fluorocarbon film.[23] Fig. 7 shows a surface characterized by globules uniformly distributed, with average roughness (Ra) of 2.8 nm (estimated for 50×50 μm area). The structures have an average size of 8 μm in width and 7 nm in high. This globular morphology and its dimension indicates the low monomer fragmentation during the plasma process.

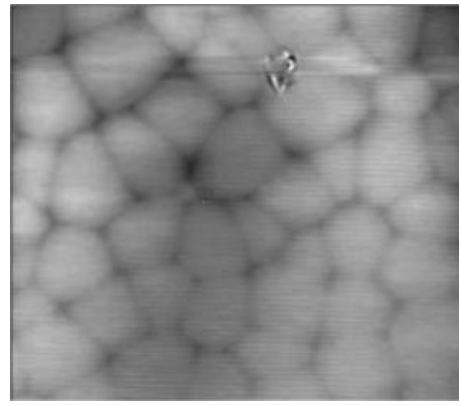

Figure 8.
AFM image (50×50 μm) of fluorocarbon film deposited on silicon wafer at 10W and 0.1 Torr.

Conclusion

Plasma polymerization of 1H, 1H, 2H-perfluoro –1-dodecene films with very high CF_2 content were deposited. As input power decreases and the pressure increases it is possible to obtained higher structural retention of the CF_2 chain of the precursor, and films with both water and oil repellency character with a very low surface energy. By the morphological evaluation, the surface of the films shows the typical globules of the fluorocarbons. The combination between high content of CFx nonpolar groups (which are at the base of the hydrophobic character) and a globular morphology is responsible of the hydrophobicity and oleophobicity showed by Plasma Polymerised Fluorocarbon films.

[1] V. Panchalingingam, B. Poon, H. H. Huo, C. R. Savage, R. C. Eberart, *J. Biomat. Sci. Polym.* Ed., **1993**, *5*, 131.
[2] S. J. Limb, K. K. Gleason, D. J. Edell, E. F. Gleason, *J. Vac. Sci. Tech.* A, **1997**, *15*, 1814.
[3] S. R. Coulson, I. S. Woodward, S. A. Brewer, C. Willis, J. P. B. Badyal, *Chem. Mater.*, **2000**, *12*, 2031.
[4] S. J. Limb, K. K. S. Lau, D. J. Edell, E. F. Gleason, K. K. Gleason, *Plasmas and Polymers*, **1999**, *4*, 21.
[5] A. Hozumi, O. Takai, *Thin Solid Film* **1997**, *303*, 222.
[6] R. D'Agostino, F. Cramarossa, F. fracassi, F. Illuzzi, in: *Plasma Depositins, Treatment, and etching of Polymers*, R. d'Agostino, Eds., Academic Press, Sand Diego, **1990**, pp. 95–162, Chapter 2.
[7] P. Favia, G. Cicala, A. Micelle, F. Palombo, P. Rossigni, R. d'Agostino, *Surface And Coating Technology* **2003**, *169–170*, 609–612.
[8] R. D'Agostino, *Plasma Polymerization, Treatment, and Eching of Fluoropolytmers*, Academic, San Diego, CA, **1990**, pp. 95–161

[9] E. J. Winder, and K. K. Gleason, *J. Appl. Polym. Sci.* **2000**, *78*, 842.
[10] R. Romand, M. Roubin, J. P. Deloume, *J. Electron Spectrosc. Relat. Phenom.*, **1978**, 229.
[11] J. F. Moulder, W. F. Stckle, P. E. Sobol, K. D. Bomben. in *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics Inc., Minnesota, **1995**.
[12] F. Arefi-Khonsari, M. Tatoulian, N. Shahidzadeh, J. Amouroux, R. D'Agostino et al., *Plasma Processing of Polymers*, 165–207
[13] G. Beamson, and D. Briggs, in *High Resolution XPS of organic polymers (The Scienta ESCA 300 Database)*, Wiley, Chichester **1992**.
[14] G. Nansè, E. Papirer, P. Fioux, F. Moguet, and A. Tressaud PII: S0008-6223(96) 00094-95.
[15] S. R. Coulson, I. S. Woodward, J. P. S. Badyal, S. A. Brewer, and C. Willis, *Langmuir* **2000**, *16*, 6287.
[16] R. D'Agostino, F. Cramarossa, F. Fracassi, *Plasma Polymerization of Fluorocarbons*, Academic, San Diego, CA, **1990**.
[17] W. K. Fishes, and J. C. Corelli, *J. Polym. Sci., Polym. Chem.* **1981**, *19*, 2466.
[18] L. Martinu, H. Biederman, and J. Nedbal, *Thin Solid Films* **1986**, *136*, 11.
[19] K. S. Shen, Y. N. Chang, J. L. Her, and J. Y. Lai, *Proc. of the 8th international Symposium on Plasma Chemistry, ISPC-8, Tokio,* **1987**, p. 1340.
[20] H. Gigengak, and H. Hinze, *Phys. Stat. Sol.* **1971**, *A 8*, 513.
[21] N. Inagaki, S. Tasaka, and Y. Takami, *J. Appl. Polym. Sci.* **1990**, *41*, 965.
[22] S. Sicurdsson, and R. Shishoo, *J. Appl. Polym. Sci.* **1997**, *66*, 159.
[23] R. Chen, V. Gorelik, and M. S. Silverstein, *J. Appl. Polym. Sci.* **1995**, *56*, 615.

