Synthesis and Characterization of Teflon-Like Macromolecular Structures from Dodecafluorocyclohexane and Octadecafluorodecalin Under RF-Cold-Plasma Conditions

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ABSTRACT: The chemical inertness, thermal stability, and low dielectric constant characteristics of polytetrafluoroethylene make this polymer very attractive for advanced technology applications. Current production technologies are not adequate for the deposition of often desired, thin-layer Teflon coatings. In this article the synthesis and characterization of Teflon-like macromolecular structures from dodecafluorocyclohexane and octadecafluorodecaline vapors under RF-cold-plasma conditions is discussed. It was demonstrated, based on high-resolution ESCA, ATR-FTIR, and LD-FT-ICR-MS investigations, that the deposited Teflon-like layers are built of CF, CF₂, CF₃, and *ex situ* origin C—O groups with an over 60% fluorine content, and that they have a branched and/or crosslinked nature. These structures have a relatively high thermal stability (340°C) and are characterized by a low dielectric constant (2.1). Plasma-enhanced coatings of Teflon-like layers can be performed at room temperatures at large substrate areas. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1627–1639, 1999

Key words: plasma; electrical discharge; Teflon; dielectric constant; PECVD

INTRODUCTION

Polytetrafluoroethylene (Teflon; PTFE) has properties, including chemical inertness, thermal stability, low coefficient of friction, low dielectric constant (1.9–2.1), low surface energy, and relatively low permeability for most gases,¹ which can hardly be matched by other polymers. These characteristics suggests that Teflon coatings could be used in a variety of applications, including medical implants, barrier and protective coatings for optical quality surfaces, corrosion resistance, and interlayer dielectrics for microelectronics, just to name a few. The application of dielectric materials with significantly lower dielectric constants than that of silicon dioxide or fluorinated silicon dioxide, for instance, would result in substantial diminution of propagation delay, cross-coupling noise between adjacent lines, and power consumption. The extremely high interest in the field of low dielectric constant and thermally stable materials is clearly emphasized by the contributions presented at recent international conference dedicated to this subject.²

Conventional Teflon-production technologies do not allow the deposition of thin-layer Teflon materials due to their insolubility and infusible nature. The thermal decomposition of these ma-

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terials starts at about 400°C without melting. Most of the Teflon-based final materials are created by sintering prepolymers under relatively high temperature and pressure environments. These technologies obviously exclude the use of thermally sensitive substrates (for example, thermoplastics) from coating applications.

Plasma-enhanced chemical vapor deposition (PECVD) has extensively been used for depositing fluorocarbon polymers on various substrates.^{3–11} The starting components include both monomericand nonmonomeric-type fluorocarbon derivatives. It has been shown that these approaches performed mainly by using continuous-wave (CW) PECVD techniques resulted in macromolecular layers with a stoichiometry where the F/C ratios were usually much lower than 2. This clearly reflects the presence of unsaturation, trapped free radicals, and the existence of CF functionalities in the structures of plasma-generated macromolecular layers. These structural particularities are suspected to be responsible for dielectric loss and ageing effects. On the other hand, the presence at the same time, of a totally linear CF_2 -based macromolecular structure (for example, conventional polytetrafluorethylene) would exhibit moderate surface adhesion characteristics (for example, poor adhesion of metallic layers deposited on Teflon substrate surfaces).

The ideal approach for avoiding the generation of undesired characteristics, while maintaining useful properties, would be to succeed in synthesizing high fluorine content (60% or higher) macromolecular layers with a precise control of the relative ratios of CF_x composing units.

Timmons's pioneering work¹² has demonstrated in the early 1990s that pulsed PECVD can be a solution to these problems. By starting from hexafluoropropylene oxide (HFPO), it was demonstrated that under controlled duty-on/duty-off cycle conditions, high-fluorine-content fluorocarbon macromolecular layers can be synthesized with predominant CF₂ units. Similar data have been reported later by Limb at al.¹³

Recently, it has been suggested that cyclic aromatic fluorocarbons like hexafluorobenzene undergo ring-opening processes under cold plasma conditions rather than defluorination mechanisms.¹⁴ Benzene and acetylene also behave similarly under plasma conditions.¹⁵ Both compounds generate macromolecular structures under plasma environments without releasing significant amounts of hydrogen. These findings suggest that perfluorinated cyclic fluorocarbons might result in high-fluorine-content macromolecular layers under similar plasma environments.

In this contribution, the formation of Teflonlike (TL) structures, by starting from dodecafluorocyclohexane (DC) and octadecafluorodecalin (OD), under radio frequency (RF)-cold-plasma conditions is investigated. The starting components were analyzed by gas chromatographymass spectroscopy (GC-MS) and the deposited films by PECVD were characterized using attenuated total reflection-Fourier transform infrared (ATR-FTIR), laser desorption (LD)-MS, electron spectroscopy for chemical analysis (ESCA), differential thermal analysis-thermogravimetric (DTA-TG), and atomic force microscopy (AFM) techniques (described in the experimental section) to elucidate the nature of the macromolecular layers generated under plasma conditions.

EXPERIMENTAL

Materials

Aldrich DC (98%) and OD (mixture of cis and trans, 95%) fluorocarbons were used in all experiments. High-purity argon and oxygen were purchased from Liquid Carbonic and were used during the reactor decontamination processes.

Methods

The electron impact (30 and 50 eV) molecular fragmentation of DC and OD were monitored using the GC–MS technique (GC, Carlo Erba Fractovap 4162; MS, Kratos, MS × 25. Experimental conditions: column-fused silica; length, 40 m; ID, 0.32 mm; Coating, 0.25 μ m of 5% phenyl and 95% vinyl polysiloxane; injector/splitter temperature, 40°C; temperature profile of the column, 5 min, 40°C, then heated up to 280°C at a rate of 15°C/min). Gas chromatography was performed to insure that only OD and DC were examined by electron impact.

The relative surface atomic compositions and the nature and the relative ratios of nonequivalent carbon (C1s) linkages of plasma-generated macromolecular layers were analyzed using X-ray photoelectron spectroscopy (ESCA). A Perkin– Elmer Physical Electronics 0 5400 Small Area Spectrometer was used in all investigations (Mg source, 15 kV; 300 W; angle, 45°; deconvolution of high-resolution diagrams were performed using Perkin–Elmer software and an Apollo Domain 3500 computer). Untreated and plasma-treated substrates were vacuum-dried overnight.

ATR-FTIR evaluations of virgin and DC- and OD-plasma exposed samples were carried out with the aid of a ATI-Mattson, Research Series instrument, provided with a Graseby Special Benchmark Series ATR in-compartment P/N 11160 unit. All infrared (IR) investigations were performed under a nitrogen atmosphere supplied from a gas-flow controlled liquid nitrogen tank. Identification of surface functionalities were carried out in the $600-4000 \text{ cm}^{-1}$ wave number range with 250 scans for each sample.

Laser desorption Fourier transform ion cyclotron resonance mass spectroscopy (LD-FT-ICR-MS) investigations were performed on the DC- and OD-origin plasma-generated macromolecular layers using a Finnigan FT-MS Newstar system (Madison, WI) operating at 3.0 tesla with the standard dual-trap configuration, as previously reported.¹⁶ Experimental control and data interpretation were accomplished by use of Odyssey software running on Sun Microsystem (Mountain View, CA) computer station. The plasmacoated sample-holder discs were positioned, with the aid of an automatic insertion probe, approximately 3 mm away from the source trap plate of the ion cyclotron resonance (ICR) cell. The source pressure was less than 3.0×10^{-7} torr (uncorrected ion gauge reading) for all mass evaluations. A Tachisto CO_2 (Needham, MA) laser beam ($\lambda =$ 10.6 μ m, power = 10⁶-10⁸ watts/cm², and pulse width = 40-80 ns) was fired at the sample disc, producing a spot size of approximately 1 mm². We exclusively trapped the negative ions as they are readily formed during the analyses of the polymers. The source trap plate was set 0.0 V, and the back trap plate (conductance limit) was held at -9.0 V with the probe held at -3.0 V for 60 μ s, after which both trapping plates were set to -3.0V for 2.5 s so that the pseudomolecular ions could equilibrate in the cell. After 30 ms, ions were excited by use of linear sweep excitation prior to detection. One zero fill was performed prior to Fourier transformation.

The surface roughness of TL layers were evaluated using a Digital Instruments Nanoscope III atomic force microscope (experimental conditions: scan rate, 2.654 Hz; sampling number, 510).

The comparative wetting characteristics of virgin and plasma-coated substrates were estimated using static contact angle measurements. An NRC contact angle goniometer (Model 100-00; Rame'-hart Inc.) was used under the experimental conditions of a 0.05-mL sessile water droplet; contact angles were evaluated from the average of five readings.

The presence of free radicals in the plasmadeposited Teflon-like films were measured by electron spin resonance (ESR) technique. A Bruker ESP 300E instrument was employed for free-radical concentration measurements (DC-origin macromolecular structures were deposited on 2-mm diameter quartz rods and placed into standard ESR quartz tubing for free radical concentration evaluation).

The dielectric constants of TL layers were determined from capacitance-voltage measurements using the mercury droplet technique.

Plasma Reactor

The deposition of TL was performed in a specially designed plasma reactor (Fig. 1) provided with thermostating capabilities (in the range of 25-250°C) both for the reaction chamber and the monomer reservoir, and for the connecting stainless steel line. The reactor is composed of a cylindrical stainless steel reaction chamber (Fig. 1, 9), in which a 20-cm diameter and 0.8-cm thick (lower) (14) grounded electrode and identical dimensions in the upper region (7), stainless steel electrodes are located. The upper electrode is connected to the RF-power supply. Both electrodes are removable, which facilitates post-plasma cleaning operations. The lower electrode is also a part of the vacuum line (15) through its supporting conical shaped and circularly perforated stainless steel tubing (17). The evacuation of the chamber is performed uniformly through the narrow gap (3 mm) existing between the lower electrode and the bottom of the reaction chamber. The upper electrode is directly connected to the threaded end of the vacuum-tight metal-ceramic feed through (4), which assures both the insulation of the RF-power line from the reactor and the dissipation of the RF-power to the electrodes. The space between the upper electrode and the upper wall of the reaction chamber (5) is occupied by three 1-cm-thick and 20-cm-diameter Pyrex-glass removable disks (6). These discs insulate the electrode from the stainless steel top of the reactor and allow the adjustment of the electrode gap. The reactor volume located outside of the perimeter of the electrodes is occupied by two Pyrexglass cylinders (8) provided with 4 symmetrically



Figure 1 Thermostated Plasma Reactor: (a) stainless steel feed through for gas and monomer supply; (2) shower-type circular gas mixing chamber; (3) stainless steel bolts for closing the reactor hermetically; (4) metal-ceramic feed through for connecting RF-power supply; (5) stainless steel upper wall of the cylindrical reactor; (6) Pyrex glass, 20-cm-diameter and 8-mm-thick removable insulating discs; (7) stainless steel, 200 mm, upper electrode; (8) ID = 210 mm, OD = 226 mm, and ID = 234 mm, and OD = 250 mm, and 117-mm-height Pyrex glass cylinders; (9) stainless steel cylindrical reactor wall; (10) glass wool insulation; (11) protective aluminum wall; (12) four symmetrically located port hole connections with built-in optically smooth quartz windows; (13) electrical heating elements; (14) lower, grounded stainless steel electrode; (15) 1-in.-diameter stainless steel vacuum line; (16) large capacity vacuum valve. Liquid and gas feeding system in Detail A: (1) 13-mm-thick copper jacket; (2) stainless steel liquid reservoir; (3), (5), and (9) VCR connectors; (4), and (7) stainless steel needle valve; (6) stainless steel 6-mm ID connecting tubing; (8) gas supply connection.

located through holes (12) for diagnostic purposes. This reactor configuration substantially eliminates the nonplasma zones of the gas environment and considerably reduces the radial diffusion of the plasma species, consequently leading to a more uniform plasma exposure of the substrates (electrodes). As a result, a uniform surface treatment and deposition processes (6-10% film thickness variation) can be achieved. The removable top part of the reactor vacuum seals the reaction chamber with the aid of a copper

gasket and fastening bolts (3). This part of the reactor also accommodates a narrow circular gasmixing chamber (2) provided with a shower-type, 0.5-mm-diameter orifice system and with a gas and monomer supply connection (1). This gas supply configuration assures an uniform penetration and flow of the gases and vapors through the reaction zone. The entire reactor is thermostated by electric heaters attached to the outside surface of the chamber and embedded in an aluminumsheet-protected (11) glass-wool blanket (10) for



Figure 2 50 eV MS electron energy fragmentation pattern of dodecafluorocyclohexane.

avoiding extensive thermal energy loss. Four symmetrically positioned stainless steel, port hole tubings are connected and welded through the insulating blanket to the reactor wall for diagnostic purposes. These portholes are provided with exchangeable, optically smooth, quartz windows.

The monomer reservoir (2), valve (4), and the connecting stainless steel tubing (6) (Fig. 1A) are embedded in two shape-designed, 1-cm-thick copper jackets (1) provided with controlled electric heaters for processing low volatility chemicals. The vapor supply assemblage is composed of a reservoir (2), VCR connectors (3, 5, and 9), needle valves (4 and 7), and connecting tubing (6 and 8). The entire system is insulated using a glass-wool blanket coating.

Plasma Processing

All experiments were preceded by a cleaning procedure by heating up the reactor to 200°C and igniting oxygen-plasma (200 W; 250 mT; 5 sccm) for 10 min in order to remove possible contaminants from earlier plasma reactions. In a typical experiment an 8-in. silicon wafer substrate is placed on the substrate holder (lower electrode), and then the reaction chamber is closed and evacuated to base pressure level.

In the next step, the reactor and the vapor supply reservoir are thermostated to the desired temperature, and by operating the corresponding needle valve system and the large capacity valve, the working pressure of the preselected perfluorinated compound is established in the reactor. The plasma state is then initiated by dissipating RF power to the electrodes and sustained for the predetermined time period. At the end of the reaction, the chamber is evacuated to base pressure, followed by repressurizing the system to atmospheric conditions. The TL-coated substrate is then removed and stored under open laboratory conditions until the analytical experiments are started. During the plasma deposition processes, the following experimental conditions were employed.

- Substrates: aluminum foil, silicon wafer, Whatman-1 filter paper, stainless steel discs.
- Starting components: DC or OD.
- Base pressure in the reactor: 50 mTorr.
- Vapor pressure in the absence of plasma: 200 mTorr.
- Pressure in the presence of plasma: 210–220 mTorr.
- Temperature of the reactor and vapor supplying reservoir system when depositing from DC: 70°C.
- Temperature of the reactor and vapor supplying reservoir system when depositing from OD: 70°C.
- RF-power dissipated to the electrodes: 100 W.
- Reaction time: 0.5–10 min.

RESULTS AND DISCUSSIONS

It has been shown in previous contributions that low-energy-electron MS fragmentation patterns of gases and vapors allow us to predict the nature of predominant fragments resulting from the RFplasma processing of similar components.^{17–20} It also has been suggested that due to the nonspecific nature of the electron-initiated ionization processes (the low degrees of ionization of cold plasmas also include the ionization of the neutral



Figure 3 50 eV MS electron energy fragmentation pattern of octadecafluorodecalin.



Figure 4 High-resolution deconvoluted ESCA spectrum of dodecafluorocyclohexaneand octadecafluorodecalin-origin macromolecular structures.

molecular fragments), the ion patterns reflect the relative ratios of neutral species as well. The major ion molecular species resulting from the 30 eV electron energy MS fragmentation of DC and OD are presented in Figures 2 and 3. In both cases, the C_3F_5 ionic species have the highest relative concentrations. However, it should be noticed

that the fragmentation mechanisms of OD also result in significant amounts of C_6F_9 and C_7F_{11} components. It should be mentioned that the (30 eV MS) fragmentation patterns of DC and OD did not change substantially with 50 or 70 eV.

Survey ESCA data indicate that the DC- and OD-origin plasma-generated macromolecular



Figure 5 ATR–FTIR spectrum of conventional Teflon, and differential ATR–FTIR spectra of dodecafluorocyclohexane- and octadecafluorodecalin-origin networks.

structures have a high fluorine concentration (F > 60%; O < 5%) and a very similar relative surface atomic composition. The high-resolution ESCA diagrams of these structures exhibit also an advanced similarity (Fig. 4). All assignments of C- and F-containing functionalities has been performed based on the spectra of the following model compounds: $-(^{a}CHF-CH_{2})$, 287.9 eV; $-(^{a}CF_{2}-CH_{2})_{n}$, 290.9 eV; $-(^{a}CF_{2}-CF_{2})_{n}$, 292.5 eV; $-[^{a}CF(^{c}CF_{3})-^{b}CF_{2})_{x}-(^{c}CF_{2}-CF_{2})_{n}$, 289.8, $^{b}291.8$, and $^{c}293.8$ eV; $^{a}CF_{3}-[(O-^{b}CF(^{c}CF)_{3}-^{d}CF_{2})_{n}-(O-^{e}CF_{2})_{m}]_{x}-O-CF_{3}$, $^{a}295.2$, $^{b}291.4$, $^{c}293.8$, $^{d}293.23$, and $^{e}294.1$ eV; and $-[CH_{2}-CH(OCO-^{a}CF_{2})]_{n}$, $^{a}292.65$ eV.²¹ It should be noticed that CH_{x} containing units have also been included into the model compounds due to the possible formation of unsaturated bond adjacent to the CF_{x} units and to the absence of binding energy data for these kind of compounds.

By analyzing the DC- and OD-origin high-resolution ESCA diagrams, the following conclusions can be drawn. The CF_2 component of the macromolecular structures is the dominant unit representing about 60% of all carbon- and fluorinebased functionalities. The presence of CF_3 and CFgroups indicate that the plasma-induced molecular fragmentation processes are accompanied by defluorination and refluorination mechanisms. However, the small C—C bond contribution allow us to suggest that the defluorination reactions, which could lead to the total removal of the fluorine atoms from some of the carbon atoms, have a very low intensity. The possible presence of C—O groups or other C-, O-, and F-atom-based linkages might be related to *ex situ* post-plasma oxidation processes developed under open laboratory conditions. These reactions are initiated by plasmagenerated free radical centers and are common mechanisms during the deposition and surface functionalization processes.

The IR signature of DC- and OD-origin macromolecular structures were analyzed using ATR mode from layers deposited on aluminum substrates (Reynolds, heavy duty aluminum foil). Due to the fact that, usually, all aluminum substrates have a thin oxide layer on their surfaces and which strongly absorbs in the 1000–1070 cm^{-1} and 760–800 cm^{-1} wave number region, the differential spectra of plasma polymers were recorded by subtracting the ATR spectrum of the aluminum substrate from the ATR spectra of DCand OD-origin macromolecular layers deposited on aluminum substrates.



Figure 6 Influence of (a) RF power and (b) deposition time on the IR signature of dodecafluorocyclohexane-origin macromolecular structures.

The ATR–FTIR spectrum of Teflon and the spectra of DC and OD-origin plasma generated macromolecular structures are presented in Figure 5. It can be observed that the IR diagram of the conventional polymer exhibits two very strong absorptions at 1200 and 1141 cm⁻¹, which are characteristic C—F vibrations of high-molecular-weight fluorocarbons, and a low intensity doublet (780 and 724 cm⁻¹), peculiar for symmetric and asymmetric absorption of CF₃ belonging to CF_3 —CF₂-type structures. Perfluorinated poly-

meric structures are easily recognizable due to the intense absorption in the $1100-1400 \text{ cm}^{-1}$ wave number region and by the lack of any significant vibration at frequencies higher than 1350 cm⁻¹.²² The ATR–FTIR spectra of DC- and ODorigin macromolecular structures exhibit similar absorption in both region characteristic for polymeric perfluorocarbon structures, as follows: a very intense doublet at 1228 and 1184 cm⁻¹ (C—F vibration from CF_x) and a fairly intense doublet at 835 and 724 cm⁻¹). It also can be



Figure 7 Negative ion LD–FT—ICR—MS spectra of dodecafluorocyclohexane- and octadecafluorodecalin-plasma deposited macromolecular networks.

noticed that the spectrum of DC-based structure exhibit the 835 cm⁻¹ vibration as a shoulder and that the OD-origin macromolecular structure present weak C-H (2950 cm⁻¹) and a medium C = 0 (1710 cm⁻¹) absorption. These spectral differences might be explained by a more intense fragmentation and defluorination mechanisms and, consequently, by the presence of significant, ex situ, free-radical-mediated, post-plasma oxidation processes, which accompany the OD-based plasma chemistry. The existence of a more intense $720-850 \text{ cm}^{-1}$ doublet region in the plasma-polymer spectra allow us to suggest that these macromolecular structures have a branched and/or crosslinked nature and composed of CF_{2} , CF, and CF_3 units.

Figure 6 shows the influence of the RF-power and deposition time on the patterns of the differential ATR-FTIR spectra of DC-origin macromolecular structures. One cannot detect significant differences in the IR signatures. This allow us to suggest that the formation of the macromolecular networks is based on a plasma-induced fragmentation mechanism, which is not significantly influenced by the RF power and reaction time between the explored limits.

MS analysis of DC- and OD-origin macromolecular layers (Fig. 7) bring more information on the nature of the plasma-deposited structures. It should be mentioned that during the LD-FT-ICR-MS analyses, resolving powers in excess of 3000, M/delta M, were achieved; therefore, the ¹³C isotopes can be considered well resolved and can consequently be used in support of the suggested elemental formulae. It can be observed, for instance, that the ion identified at m/z = 769 Da could be attributed both to $C_{15}F_{31}$ and $C_{34}F_{19}$. Ultrahigh mass accuracy could distinguish between these two possibilities due to the fact that the fluorine has a slight mass defect of -0.0016Da²³; however, this was not possible owning to the actual resolution level. Isotope abundance, at

m/z	Relative Abundance	$\begin{array}{c} \mathrm{C}_{x}\mathrm{F}_{y} \\ y/x \end{array}$	Formulae
CF			
0 ₆ r ₁₂ 220	1 680	1 1	CF
040	4.009	1.1	$C_{10}\Gamma_{11}$
343	3.12	1.0	$C_8 r_{13}$
367	6.108	1.3	$C_{10}F_{13}$
377	8.949	1.0	$C_{14}F_{14}$
401	10.748	0.68	$C_{16}F_{11}$
451	12.504	0.76	$C_{17}F_{13}$
537	13.294	0.71	$C_{21}F_{15}$
599	11.022	0.74	$C_{23}F_{17}$
623	13.687	0.68	$C_{25}F_{17}$
709	9.079	0.65	$C_{29}F_{19}$
881	2.294	0.621	$C_{37}F_{23}$
$C_{10}F_{18}$			
305	25.573	1.37	C_8F_{11}
317	22.157	1.22	C_9F_{11}
355	26.932	1.44	C_9F_{13}
374	100.00	1.55	C_9F_{14}
381	29.311	1.87	C_8F_{15}

Table IIons Identified in the DC- and OD-MSSpectra

the same time, can help to distinguish between these two possibilities; the isotope with one ^{13}C , observed at one Da higher, for an ion containing 15 carbon atoms is expected to be about 17% (1.1% ^{13}C per carbon atom²⁴), whereas the ^{13}C contribution for an ion composed of 34 carbons is theoretically about 37%. The measured value of 35% (see Fig. 7, expansion region), for the isotope at m/z = 770 Da, supports the existence of $C_{34}F_{19}$ structure. Moreover, the existence of most of the lower mass ions cannot be explained using molecular formulae similar to $C_{15}F_{31}$ as their fluorine contents would be too high (higher than 2n+ 2). For example, the ions observed 12 and 24 Da lower at 757 and 745, respectively, would have to originate from $C_{14}F_{31}$ and $C_{13}F_{31}$. In a similar fashion, one can assign the molecular formula to the ions observed in the LD-FT-ICR-MS of the OD-origin macromolecular layer (Fig. 7, bottom). The base peak at 347 Da was attributed to the presence of $[C_9F_{14}]^{--}$ species. The C_9 isotope contribution from a C_9 species observed at 375 Da is expected to be 9.9%, and a value of 12% was measured supporting our assignments. All majorintensity negative ions have been identified in the DC and OD MS spectra; some of them and their relative abundance, and their y/x (C_xF_y) ratios, are presented in Table I.

These data substantiate the ESCA and ATR– FTIR findings that both plasma-generated layers are branched and crosslinked networks based on CF_2 , CF, and CF_3 units. The high fluorine contents of these structures can be explained by the extensive presence of CF_3 groups in the plasmagenerated macromolecular structures. Some de-



Figure 8 DTA–TG diagram of dodecafluorocyclohexane-origin macromolecular structure.



Figure 9 AFM image of Whatman-1 filter paper.

fluorination reactions also could occur during the laser evaporation processes; however, the intensities of these mechanisms would not affect significantly the MS-ion composition.

The high thermal stability of DC and OD macromolecular structures also reflects the perfluorinated and crosslinked nature of these compounds. Thermal analysis (DTA–TG) of plasma-deposited layers, carried out in nitrogen atmosphere, indicate that these structures are stable at temperatures as high as 340°C. A typical DTA–TG diagram of DC-layer is presented in Figure 8. One can observe that no considerable weight loss is recorded until around 340°C, and that at 500°C 15% of the sample is still present.

These structures can be deposited uniformly on large substrate areas (for example, 8-in. silicon wafer) and in a fairly large temperature range of the substrate. Depositions performed at 25 and 200°C substrate temperatures resulted in similar macromolecular structures. This is a significant finding because it opens up possibilities for surface coating of thermally sensitive substrates, like polymeric materials. Consequently, hydrophobic or dielectric layers can be deposited on conventional polymeric surfaces.



Figure 10 AFM image of dodecafluorocyclohexane-RF-plasma-coated Whatman-1 filter paper.

AFM images of untreated and DC–RF-plasma exposed (temperature of the substrate holder: 25°C; 100 W; 200 mT; 10 min) Whatman-1 paper are presented in Figures 9 and 10.²⁵ One can observe that the fibrous surface morphology of the paper is replaced by a smooth surface as a result of the plasma coating.



Figure 11 Influence of treatment time on the surface atomic composition of dodecafluorocyclohexane-RFplasma-coated Whatman-1 filter paper.

The relative surface atomic compositions of DC-discharge coated paper samples resulting from various plasma exposures show that treatment times of 30 s and higher result in an almost identical atomic concentrations (Fig. 11). The high fluorine contents of all plasma-treated samples indicate the presence of a very efficient coating. This substantiates the ATR-FTIR findings that a stable reaction mechanism controls the deposition process, and that short treatment times (for example, 30 s) are sufficient for creating a total surface coating.

Contact angle evaluations of DC-plasmacoated paper resulting from various treatment times (Fig. 12) clearly indicate that plasma exposures as short as 30 s are high enough to reach an extremely high contact angle value (120°). Longer treatment times do not significantly influence the contact angle, which allows us to suggest that even under very short plasma exposure conditions a total coating of the paper surface has been achieved. The hydrophobic nature of the plasmacoated surfaces is quite stable. Contact angle evaluations performed on samples resulting from different treatment times and stored under open laboratory conditions (Fig. 13) show that the elapsed time does not dramatically influence the surface wettability. It can be observed that samples resulted from treatment times longer than 1 min indicate almost identical contact angle changes during the storing period, and that after 20 min, the contact angle values are still around 115°. DC-plasma coated Whatman-1 paper substrates prepared under 5-min treatment time conditions exhibited a contact angle higher than 112°, even after a 4-month storing period. Contact



Figure 12 Influence of treatment time on the contact angle values of the dodecafluorocyclohexane-RF-plasma-coated Whatman-1 filter paper.



Figure 13 Influence of treatment time on the stability in time of dodecafluorocyclohexane-plasma-polymer-coated Whatman-1 filter paper.

angle evaluations performed on DC- and ODplasma coated silicon wafers show 120° in comparison to 30° characteristic of untreated silicon wafer.

ESR measurements performed on DC-plasmacoated quartz rods show no detectable free-radical concentrations. This might be explained by the presence of a free-radical quenching mechanisms under open laboratory conditions and by the existence of a very low concentration of trapped free radicals in the bulk of the deposited layers. The high fluorine contents of the macromolecular layers is in good agreement with the very low freeradical concentration. Both DC- and OD-origin layers exhibited a dielectric constant around 2.1.

CONCLUSIONS

DC- and OD-RF-plasma environments are proper for surface-coating of various nature, large area substrates with high-fluorine-content (> 60%) macromolecular thin films.

High-resolution ESCA, ATR-FTIR, and LD-FT—ICR—MS investigations performed on the plasma-generated layers indicate the presence of a branched and/or crosslinked macromolecular network based on CF, CF₂, and CF₃ units. The C—O based functionalities present in the structures of the plasma-films are related to *ex situ*, post-plasma oxidation mechanisms. These reactions are mediated probably by plasma-generated free-radicals.

The DC- and OD-plasmas deposited structures have a relatively high thermal stability (340°C)

and are characterized by a low dielectric constant (2.1). Surface coatings can be developed in a wide temperature range, including room-temperature environments. This opens up possibilities for the deposition of barrier layers on thermally sensitive substrates (for example, organic polymers). Applications of these findings are envisaged for creating barrier coatings and for depositing low dielectric constant layers.

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