Deposition of super-hydrophobic fluorocarbon coatings
in modulated RF glow discharges

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Abstract
Super-hydrophobic coatings have been deposited by means of modulated RF glow discharges fed with tetrafluoroethylene. Film structure and composition analysis, performed by means of ESCA, infrared absorption and X-ray diffraction spectroscopy, have revealed that high retention of monomer structure can be obtained in modulating conditions. Furthermore, the film morphology significantly changes when passing from continuous to modulated plasmas, the latter leading to the growth of uncommon wall-like microstructures. Though it is clear that the roughness can account for the high values of the measured water contact angles (higher than 150°), an attempt to use time resolved optical emission spectroscopy has been carried out to understand the origin of the unusual morphology.

Introduction
In the last decade the deposition of fluorinated coatings by means of modulated RF glow discharges (RFGD) has been widely investigated with interesting results. Power modulation of RF plasma can be simply carried out by triggering the RF power supply with a pulse generator; the result is that the glow consists of alternating periods of plasma on and off states. When dealing with modulated glow discharges, besides the usual experimental parameters (power, pressure, gas flow rate and so on), other factors must be considered to account for the pulse characteristics: the modulation period and the Duty Cycle (DC). If we define \( t_{on} \) and \( t_{off} \) as the pulse time during which the plasma is respectively on or off, the modulation period is the sum of \( t_{on} \) and \( t_{off} \) and DC is the percent of the time during which the plasma is on.

Modulated deposition plasmas allow to obtain a remarkable monomer structure retention degree in the coating. Albeit the kinetics in modulated plasmas have been less investigated than in continuous systems, it is believed that tuning the modulation time parameters, results in strong changes in the plasma composition, thus in coatings completely different from those obtained in continuous regimes.

Furthermore, properties such as low dielectric constant, high flexibility, superior hydrophobic and oleophobic character and very low friction coefficient can be granted by such coatings when properly deposited on different substrates, as well as many applications for textiles, packaging, biomaterials, microelectronics and other industrial areas [1-7].

Though several papers report about the chemistry and morphology of fluorinated coatings deposited in modulated RFGD fed with various compounds (e.g., Hexafluoroproponoxide, Tetrafluoroethylene, Perfluoropropane, Perfluoroaromatic compounds and many others), few
concern the investigation on the plasma phase, to try to better understand and characterise the process itself.

In this contribution we present our last results on the plasma deposition process of super hydrophobic (WCA ≥ 150°, [5]) coatings from modulated glow discharges fed with tetrafluoroethylene (TFE), including a TR-OES (Time Resolved Optical Emission Spectroscopy, [8]) characterization of the plasma. The process studied, besides the super hydrophobicity, features a novel micro structured coating, with a unique "walled" structure. The novelty of the anisotropic structure arising with the process resides in the fact that it is obtained with a single process deposition.

Experimental

The super-hydrophobic fluorinated films have been deposited in the quasi-parallel plate quartz tubular reactor schematised in Figure 1: the RF powered electrode is external and conformal to the reactor shape, and the lower one is internal and connected to ground. In order to modulate the glow discharge the RF generator was externally controlled by means of a programmable home-made pulse generator capable of independent regulation of pulse wave period and duty cycle. During the pulsed deposition processes, the radio-frequency voltage was 100% modulated (the voltage was zero during the t_off period). Polished silicon substrates were processed on the lower electrode and TFE was let in the chamber at 6 sccm and at a pressure of 300 mTorr. The RF power input was set at 30 W.

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical group</th>
<th>BE (eV)</th>
</tr>
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<tbody>
<tr>
<td>C0</td>
<td>C-C</td>
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</tr>
<tr>
<td>C1</td>
<td>C-CF</td>
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</tr>
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<td>CF</td>
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<tr>
<td>C4</td>
<td>CF₃</td>
<td>293.8</td>
</tr>
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</table>

The effect of the modulating parameters, period (20 ± 200 ms) and DC (2 ± 50 %), onto the plasma deposition process, with respect to samples obtained in continuous mode (6 sccm TFE, 300 mTorr, 30 W, DC =100), was investigated by means of film and plasma phase diagnostic tools. X-ray Photoelectron Spectroscopy was carried out with a ESCA PHI 5300 spectrometer for determining the chemical composition of the coatings. The C1s signal has been best-fitted in five components corresponding to carbon bonded to an increasing number of fluorine atoms, according to the parameters reported in table 1.
Complementary information of the chemical composition of the coatings have been obtained by means of FT Infrared Absorption spectroscopy (FTIR) analysis performed in transmission mode, and from X-ray diffraction analysis. Measurement of the static Water Contact Angle (WCA) and Scanning Electron Microscopy were carried out to get information about the wettability and the morphology of the deposited films, respectively. Time-resolved optical emission spectroscopy was accomplished by means of the apparatus described elsewhere [8] (see Figure 1). Briefly, the UV-vis radiation was collected along the reactor axis through a quartz window by means of an optical fiber connected to the OMA III (PAR-EG&G), provided with an intensified gateable multi-diode array detector. The pulse generator, used to modulate the glow discharge, triggers also the OMA detector acquisition and the temporal evolution of the emission intensity of the species of interest can be achieved. Our TR-OES investigation was focused on CF$_2$ radicals (system A$^1$B$_1$-X$^1$A$_1$, 220-280 nm), the only appreciably emitting species detected in the plasma during $t_{on}$. The acquisition has been performed with a detector gate width of 50 μs and an increment delay of 100 μs, and sampling the first 6 ms of the modulation pulse.

Results and Discussion

The effect of modulation onto the plasma deposition of fluorocarbon films has been investigated by changing the DC and the period of the modulating wave, and the results have been compared with that obtained working in continuous mode, using the same experimental parameters (pressure, power and gas flow rate). The measurements of the WCA have shown that hydrophobic coatings were obtained in our experimental conditions. However, when the films were deposited with continuous RFGD or in modulated conditions with DC equal or higher than 10 %, WCA was not greater than 120°, as for conventional polytetrafluoroethylene (PTFE). By reducing the modulation duty cycle to values lower than 10 %, the films exhibited surprisingly high hydrophobic character, as water contact angles values were higher than 150°, and often than 165°. This kind of surface shows very high repellent behaviour towards water. Furthermore, although deeper investigation about surface energy concerns is necessary, potentially these coatings could display excellent oil-repellent properties, and application in fields where non-fouling surfaces are needed can be envisioned. To better understand the source of this phenomenon, both chemical composition and morphology of the film have been investigated. The XPS analysis has revealed fluorine and carbon, with very low concentration of oxygen atoms (less than 3 %), in the coatings. Moreover the fluorine over carbon ratio increases as the DC decreases. In Figure 2 the best-fitted C1s signal of a film deposited in modulated conditions (DC = 5%, period = 100 ms) is reported. Beside the C3 component (CF$_3$), typical of PTFE,
the XPS C1s signal always shows components relative to carbon bonded to a higher (C4) and lower number of fluorine atoms (C2), and to carbon-carbon bonds (C0, C1). With respect to the film deposited in continuous way, films deposited in modulated mode display a lower relative contribution of all the components compared to the C3 one. Moreover, the relative abundance of CF2 moieties has been found to increase when DC is decreased, thus highlighting that the deposition of film with a high teflon-like character (intense CF2 moieties, F/C ratio close to 2) has to be performed at low DC values. These results are confirmed by infrared absorption spectroscopy investigation. In Figure 3 the infrared spectral region of the C-F stretching and bending modes, for three different coatings, has been reported. The spectrum of the film deposited in continuous plasma (Fig. 3 A) displays a strong broad band between 1000 and 1350 cm\(^{-1}\), due to the overlapping of CF\(_x\) stretching modes (x = 1-3); two other important features can be observed: C=C stretching around 1700 cm\(^{-1}\) and the amorphous band at 730 cm\(^{-1}\), characteristic of conventional PTFE. The main differences in the FTIR spectra of films deposited with modulated glow discharges are the reduction of the C=C absorption region and the changes in the CF\(_x\) band. This latter becomes narrower and a sharp absorption band at about 1180 cm\(^{-1}\) originates, likely due to the CF2 symmetric stretching. These results point out to a reduced fragmentation and rearrangement of the monomer in the plasma phase leading to a narrower distribution of the chemical groups contributing to the CF\(_x\) absorption band, as well as to a less crosslinked surface as well. Hence FTIR analysis data are in agreement with XPS ones, thus showing a higher retention of the monomer structure passing from continuous to modulated plasma. These outcomes can be explained with a rather reduced average input energy, or in the selection of a different mechanism pathway, depending on the modulation parameters, leading to a minor fragmentation of the monomer and a higher retention of CF2 unit in the film network.

X-ray Diffraction analyses support the hypothesis that drastic changes in the film structure result from the modulation of the plasma when DC lower than 10 % are used. In fact a diffraction peak at 2\(\Theta\) = 18° is present in the XRD pattern of a sample deposited in modulated conditions (DC = 5% and 100 ms period), which can be ascribed to crystalline PTFE; no peak is present for the coating produced with a continuous plasma [9]. However, the chemical composition of the film, indicating a Teflon-like structure, is not enough to explain their “water-repellent” behaviour when low DC are used. It is well known that water contact angle values are highly dependent on surface roughness, and several models have been developed to explain that dependence. The Wenzel equation (1) correlates the WCA measured on a rough surface, \(\Theta_{\text{WCA}}\), with that of a flat material, \(\Theta_{\text{flat}}\), having the same chemistry, introducing a roughness correction factor \(r (r \neq 1)\).
Since equation 1 foresees higher contact angles when a hydrophobic surface is roughened [10], it has been supposed that roughness is responsible for the super-hydrophobic character of the films deposited in modulated RFGD. For these reasons the surface morphology has been studied by means of SEM and the unusual morphology shown in Figure 4 has been found out: the film surface consists of a net of 0.2±1 μm high wall-like structures. The presence of micro patterns of PTFE composition can be associated to the super hydrophobic properties. In fact, when very thin (200-400Å) differently fluorinated coatings were deposited in continuous mode (WCA≤120° onto flat samples) onto super hydrophobic samples, their WCA value (≥150°) was found unchanged, and the microstructures still observed. The deposition of much thicker planarizing films gave, instead, lower WCA values, and the wall microstructures disappeared.

In order to gain understanding of the deposition process, the plasma phase has been investigated by means of time resolved OES. In particular the time evolution of the CF$_2$ emission intensity, during the $t_{on}$, has been followed for different DC. The CF$_2$ intensity trends in pulsed glow discharge of 100 ms period and duty cycle from 2.5 to 10 %, are reported in Figure 3. The time evolution of CF$_2$ is clearly different when the DC is less than 10 %. When the duty cycle is equal or higher (not shown) than 10 %, an almost linear trend is always observed, at least in the time range considered. If lower DC values are used, the CF$_2$ emission intensity grows till a plateau is reached. More data are needed, obviously, for a complete understanding of the process, but a first hypothesis can be done to explain the CF$_2$ emission intensity trends. The curved behaviour may indicate that two mechanisms, a CF$_2$ formation and a CF$_2$ depletion route, compete in the plasma when DC% is less than 10, while the CF$_2$ formation prevails for higher DC% values. How these different behaviours are reflected in the formation of the microstructures is still under investigation, as well as the growth mechanism and the composition of the wall-like PTFE structures themselves.

**Conclusions**
Super hydrophobic films featuring a unique walled structure with anisotropic profiles and crystalline
characteristics of great interest for many industrial applications have been successfully deposited by means of modulated TFE glow discharges. The use of low (<10%) Duty Cycle values revealed to be crucial for obtaining super hydrophobic (WCA≥150°) coatings, as well as the presence of the unusual microstructures at their surface. TR-OES experiments allowed to distinguish characteristic CF₂ emission intensity trends (and probably reaction paths) during the deposition of super hydrophobic coatings, that could help to understand the deposition mechanism.

Acknowledgements
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