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Recent advances in the atmospheric pressure PE-CVD of fluorocarbon films: influence of air and water vapour impurities

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Keywords

Atmospheric Pressure, Dielectric Barrier Discharge (DBD), fluorocarbon films, Plasma-Enhanced Chemical Vapour Deposition (PE-CVD)

Summary

The influence of air and water vapour on the deposition process of fluoropolymers in argon-hexafluoropropene (Ar-C_3F_6) filamentary dielectric barrier discharges was investigated by adding known concentrations of these contaminants to the feed gas. The results obtained show that Ar-C_3F_6 DBDs allow to deposit thin films with a XPS F/C ratio as high as 1.7. Under the experimental conditions investigated, contaminant addition slightly affects the F/C ratio of the coatings, and does not cause appreciable O- and N-uptake, but induces a decrease of the deposition rate. Preliminary

results from the OES investigation of the gas phase and the GC-MS analysis of the gas effluent are also reported.

Introduction

The atmospheric pressure plasma-enhanced chemical vapour deposition (PE-CVD) of fluorocarbon coatings by dielectric barrier discharges (DBDs) has been already investigated by several authors,[1-11] nevertheless, the utilization of atmospheric pressure plasma technologies in this field can be considered still a challenge. Research efforts should be devoted to evaluate if DBDs can actually be advantageous compared to low pressure plasmas for fluoropolymer deposition. For this purpose, besides the fundamental investigation of the PE-CVD in DBDs fed with different fluorocarbons, it is also important to gain insights into the influence of contaminants such as air and water vapour on the deposition process. The presence of these impurities into the atmospheric pressure reactors could have, in fact, a serious detrimental effect on the overall deposition process because it could result in a change of the discharge regime, in a variation of the polymer composition, in oxygen and nitrogen uptake, as well as in deposition rate variation. On the other hand, the knowledge of the highest level of contamination compatible with an acceptable process performance and, consequently, the possibility of depositing fluorocarbon films with the desired properties in contaminated environments could allow to reduce the cost of processes and reactors.

This study is devoted to investigating the influence of contaminants, air and water vapour, on the PECVD of fluoropolymers in DBDs fed with argon and hexafluoropropene (C_3F_6). C_3F_6 is characterized by a relatively low F/C ratio and by the presence of a double bond, which account for its highly polymerizing capability both in low pressure[12-15] and atmospheric pressure plasmas.[1-5, 10, 11] As reported, low pressure hexafluoropropene fed plasmas result in coatings with a maximum F/C ratio of 1.5[12-15] and deposition rates up to 350 nm·min^{-1};[12-14] the C1s XPS signal shows similar densities of CF_3, CF_2, CF and C–CF groups.[12-15] Promising results were also reported at

atmospheric pressure in He-C_3F_6 fed glow DBDs (GDBDs);[1-5, 10, 11] in particular it has been demonstrated that, in spite of the narrow operational window, the deposition process in He-C_3F_6 GDBD is well controlled and reproducible and allows to obtain fluorocarbon films with F/C ratio of 1.5 with deposition rate up to 34 nm·min^{-1}.[10, 11]

In this work the influence of contaminants on the deposition process was investigated by adding controlled amounts of air and water vapour to Ar-C_3F_6 feed gas mixtures. The maximum extent of air and water vapour permissible to preserve the PE-CVD process efficiency in terms of F/C ratio of the coating and deposition rate was defined.

Experimental part

The experimental apparatus consists of a parallel plate electrode (2 mm gas gap) system contained in an airthight Plexiglas box (figure 1). Each electrode (286 cm^2 area) is covered by a double dielectric layer formed by a Al_2O_3 plate (thickness of 0.635 mm) and a quartz plate (thickness of 1.0 mm).

The plasma was generated by applying an AC high voltage (5.7 kV_{p-p}) at 15 kHz by means of a power supply composed of a variable frequency generator (GW Instec GFG-8216A) an audio-amplifier (Outline PA4006) and a high voltage (HV) transformer (Montoux). The electrical characterization was performed with a digital oscilloscope (Tektronix TDS2014); the voltage applied to the electrodes was measured by means of a HV probe (Tektronix P6015A), while the current was evaluated by measuring with a voltage probe (Tektronix P2200) the voltage drop across the 50 Ω resistor in series with the ground electrode.[10, 11]

The gas flow rates were controlled by MKS electronic mass flow controllers (MFC) and the system pressure was monitored by means of a MKS 122 baratron. Feed gas was introduced in the interelectrodic zone through a slit and pumped through a second slit positioned on the opposite side, therefore a longitudinal gas injection was realized.[10, 11] In order to avoid overpressure, the Plexiglas enclosure was slightly pumped with a rotary pump (Pfeiffer). The discharges were fed with Ar-

C_3F_6 (Air Liquide Argon C, Zentek C_3F_6 99% purity). Known concentrations of air, oxygen, nitrogen and water vapour (contaminants) were also added to the feed gas. Deposition processes were preformed with 4 slm Ar flow rate (ϕ_{Ar}) and 0.2 % C_3F_6 concentration, while the [contaminant]/[C_3F_6] feed ratio was increased up to 0.5, 1.0, 0.1, 0.25 for air, nitrogen, oxygen and water vapour, respectively. Before each experiment the Plexiglas chamber was flushed with a high flow rate of argon (6 slm) for 40 min.

Optical emission spectroscopy (OES) was performed by collecting the UV-Vis spectra (200 - 900 nm) with an Optical Multichannel Analyser (OMA) equipped with a monochromator (0.300 m focal length, imaging monochromator ACTON SP-300i, 1200 grooves/mm grating) and a CCD detector (SpectruMM™ 100B, Princeton Instruments).

A stainless steel liquid nitrogen trap, located between the reactor and the rotary pump, allowed to sample the stable species contained in the exhaust gas. Sampling were performed for two hours, then the trap was isolated from the system, the condensate was dissolved in hexane (Fluka, purity ≥ 99.0 %) and analysed by means of gas chromatography (GC) with mass spectrometric (MS) detection. The GC apparatus (GC 8000^Top Thermoquest Corporation) was equipped with an Alltech AT™-1ms capillary column (polydimethylsiloxane 0.25 μm thick stationary phase, length of 30 m, internal diameter of 0.25 mm). The analyses were performed with 2 sccm of He as carrier gas, at 200°C injector temperature and column temperature programmed from 30 to 200°C (2 min at 30 °C, linear heating rate of 10°C·min^{-1}, 5 min at 200°C). Separated products were analysed with a quadrupole mass spectrometer (Voyager, Finnigan, Thermoquest Corporation). Mass spectra were recorded in the *m/z* range 18 – 700 at the standard ionizing electron energy of 70 eV. The products were identified by means of available libraries.[16] The extent of residual C_3F_6 was evaluated by dividing the flow rate of hexafluoropropene in the exhaust of the deposition process, with that collected without plasma ignition.

The chemical composition of the deposited films was investigated by Fourier Transform Infrared Spectroscopy and X-Ray Photoelectron Spectroscopy. A commercial Brucker Equinox 55 FT-IR

interferometer was used to collect infrared absorption spectra of films deposited, while XPS analyses were performed using a Theta Probe spectrometer (Thermo Electron Corporation) equipped with monochromatic Al Ka X-ray source (1486.6 eV) operated at a spot size of 400 µm (corresponding to a power of 100 W). Survey (0-1100 eV) and high resolution spectra (C1s, F1s, O1s, N1s) were recorded at a pass energy of 150 eV and 50 eV, respectively. Spectra were acquired with a take-off angle (TOA) of 37°. The C1s signal for the CF_2 component (292.5 eV) was used as internal standard for the correction of the charging of the samples.[17] Best fitting of the high resolution spectra was performed using Advantage Data Spectrum Processing software (Thermo Electron Corporation).

Coatings wettability was evaluated by static water contact angle (WCA) using a Ramé-Hart manual goniometer (model A-100). Film thickness was evaluated on substrates partially masked during the deposition using an Alpha-Step® 500 KLA Tencor Surface profilometer, while film morphology was investigated by means of Scanning Electron Microscopy (SEM) analyses were using a digital microscope EVO 40XVP (Zeiss).

In order to compare the results obtained under different experimental conditions the chemical and morphological characterization was carried out on films deposited in the middle of the interelectrode region, that is in the region 8–13 cm from the gas entrance inside the discharge area.

Results and Discussion

The first part of the study was devoted to the investigation of the deposition process to define characteristics without contaminants admission in terms of discharge regime, input power, deposition rate and deposit properties.

Respect to pure argon the addition of hexafluoropropene resulted in an intense decrease of the discharge current and in the appearance of non periodical current signal formed by more than one current peak per half-cycle (filamentary discharge).[18, 19] At 0.2 % of C_3F_6 the average power

dissipated into the plasma was 22 ± 2 W, the deposition rate was 56 ± 3 nm·min^{-1} and the deposit was characterized by a XPS F/C ratio of 1.7 and a static WCA of 115 ± 3°. Figure 2 shows the FT-IR spectrum of the coating; the main spectral feature is the broad band between 900 and 1400 cm^{-1} due to the overlap of some CF_x stretching vibration modes.[10-14, 20-25] In particular the shoulder at 1350 cm^{-1} is due to the C–F bonds, the peak at 1238 cm^{-1} with the shoulder at 1187 cm^{-1} are due to CF_2 asymmetric and symmetric stretching, respectively, the peak at 980 cm^{-1} is associated to CF_3 groups. The weak and broad band in between 1650 and 1850 cm^{-1} can be ascribed to the C=C stretching modes. The best fit of the XPS C1s high resolution signal was performed with the following features: CF_3 (294.5 ± 0.2 eV), CF_2 (292.5 ± 0.2 eV), CF (290.1 ± 0.3 eV), C–CF and CF=C (288.0 ± 0.3 eV), C–C (285.0 ± 0.2 eV).[10-15, 25-27] The CF_3 and CF_2 peaks were dominant respect to the others indicating a low branching and crosslinking degree.[15] SEM observations indicated that the coating was smooth and powder free (figure 4a).

The UV-Vis emission spectra of the plasma was characterized by intense Ar emissions,[28] by the emission bands of CF_2 (A^1B_1 - X^1A_1 system)[29-31] and CF ($B^2\Delta$ - $X^2\Pi$ system)[29-31] and by two continua centred at approximately 290 nm and 620 nm, ascribed to CF_2^+ [30, 31] and CF_3 [32, 33], respectively. The amount of unreacted C_3F_6, evaluated by GC-MS, was 59 ± 3 %.

The addition of known quantities of contaminants (i.e. H_2O, O_2, N_2, and air) resulted in a decrease of discharge current and at water and air concentrations of 0.05 and 0.1 %, respectively (corresponding to a Air-to-C_3F_6 and Air-to-H_2O feed ratios of 0.25 and 0.5, respectively), the discharge was not distributed over the entire electrode surface.

As it can be appreciated in figure 3, contaminant addition results in a decrease of the deposition rate but does not affect significantly the XPS F/C ratio of the coating and the oxygen and nitrogen uptake were always lower than 1 %. When the 0.1 % of air was added to the feed, the deposition rate decreased from 56 to 30 nm·min^{-1}, while for water vapour concentration of 0.05 % the deposition rate decreased to 26 nm·min^{-1} (figure 3). Any change of water contact angle was not

detected as a consequence of contaminant addition while a clear variation of film morphology due to the appearance of a slight roughness, more evident for air addition, can be appreciated in figure 4. In order to discriminate the possible different effect on PE-CVD of the two air components, N_2 and O_2, the consequence of independent admission of nitrogen and oxygen was evaluated. A steep decrease of the average power dissipated by DBD from (22 ± 2) W to (16.0 ± 1.6) W was detected when oxygen concentration was increased to 0.02 %; while for nitrogen power reduction was less important, i.e. to (19 ± 2) W for a concentration of 0.2 %. Also the decrease of deposition rate was more intense for oxygen than for nitrogen (figure 3). SEM observation showed that while smooth coatings were obtained for nitrogen containing DBD, oxygen addition increase of the roughness of the deposits (figure 4). As expected, any significant XPS and FT-IR variation of coating chemical composition was observed by adding O_2 and N_2 to the gas feed (figure 3).

Air and water vapour addition does not induce any important variation of the UV-Vis emissions observed without contaminats. When air is added to the feed gas any signals from oxygen containing species were not detected, while intense emissions from the N_2 (Second Positive System) along with the CN violet system band were observed.[29] With water addition the OH emission ($A^2\Sigma^+$ - $X^2\Pi$ system) was detected.[30]

The amount of unreacted monomer was lightly affected by contaminant addition, it resulted equal to (63 ± 3) % and (64 ± 3) % for air and H_2O, respectively.

Conclusions

The deposition of fluoropolymers in Ar-C_3F_6 fed DBDs was studied in highly contamined environment, generated by adding known quantity of air, water vapour, oxygen and nitrogen to the feed gas. The results show that Ar-C_3F_6 DBDs allow to deposit coatings at a deposition rate of 56 $nm \cdot min^{-1}$ and XPS F/C ratio of 1.7 with high CF_2 and CF_3 concentration and low crosslinking degree. Contaminants addition does not appreciably affect coating composition, causes oxygen or

nitrogen uptake lower than 1 % and does not influence the final hydrophobic character of the polymer surface. A decrease of deposition rate and the appearance of a certain surface roughness is observed. The results obtained by separate addition of nitrogen and oxygen to the feed gas allow to suppose that oxygen is the main responsible of power and deposition rate decrease as well as of the appearance of the surface roughness that could be probably related to the etching of the growing polymer.

GC-MS analyses of exhaust gas showed that with contaminant addition, despite the discharge power and deposition rate decreases, the amount of unreacted monomer is similar to that obtained with pure hexafluoropropene.

Acknowledgements

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Figure captions

Figure 1. Schematic of the experimental apparatus.

Figure 2. FT-IR spectrum of film deposited in Ar-C_3F_6 fed FDBD (f = 15 kHz, V_a = 5.7 kV_{p-p}, [C_3F_6] = 0.2 %).

Figure 3. Deposition rate and XPS F/C ratio as a function of the additive concentration in the feed gas (f = 15 kHz, V_a = 5.7 kV_{p-p}, [C_3F_6] = 0.2 %).

Figure 4. SEM images of fluorocarbon film deposited in FDBDs fed with (a) Ar-0.2% C_3F_6, (b) Ar-0.2% C_3F_6-0.1% Air, (c) Ar-0.2% C_3F_6-0.02% O_2, (d) Ar-0.2% C_3F_6-0.08% N_2 (f = 15 kHz, V_a = 5.7 kV_{p-p}).

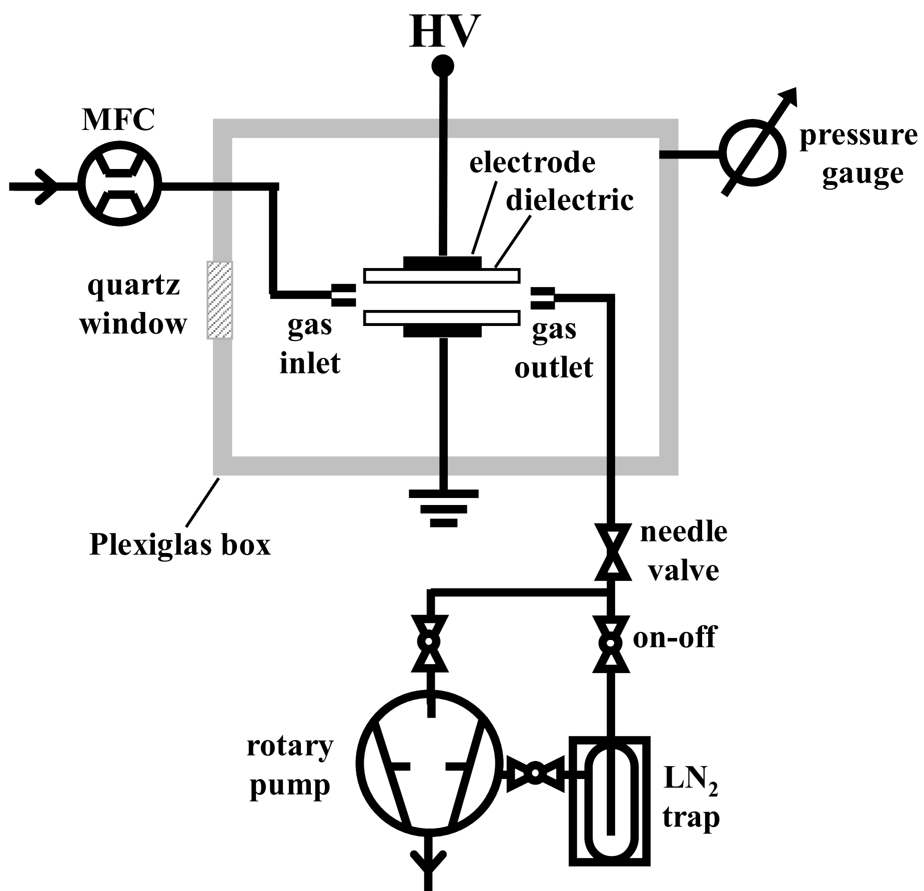

Figure 1

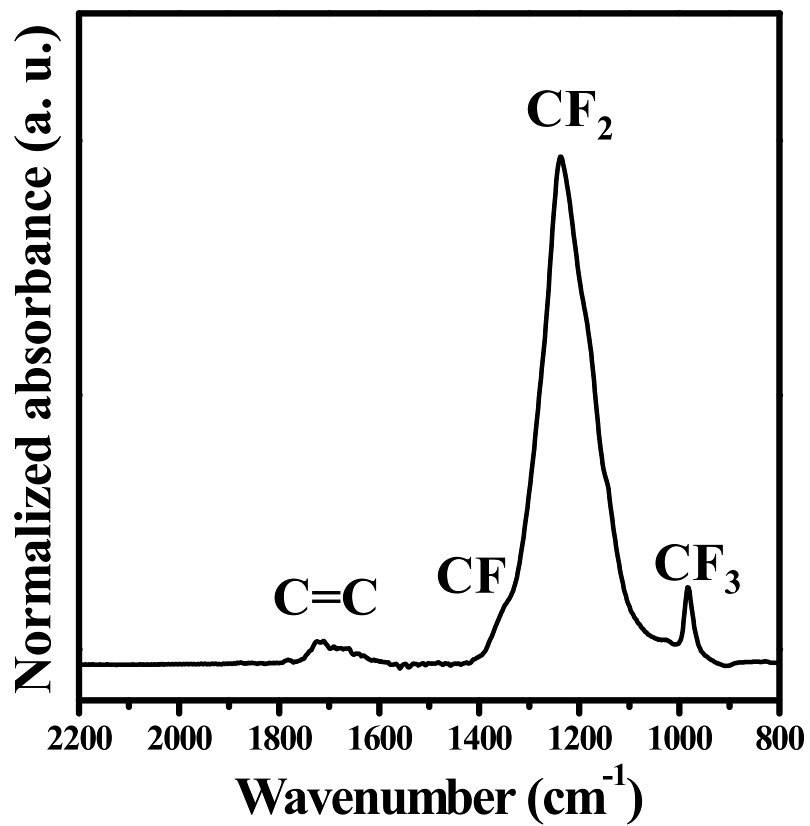

Figure 2

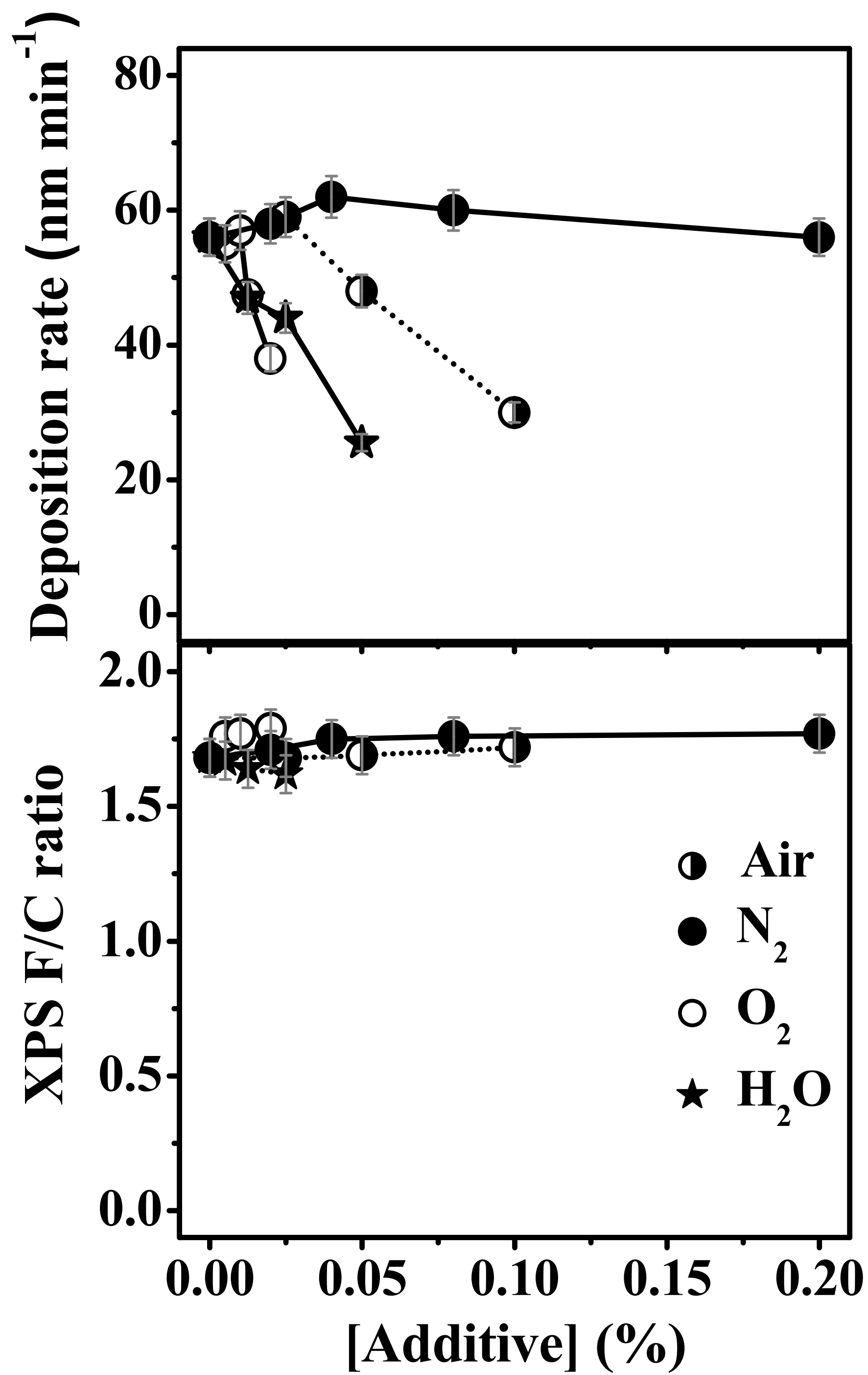

Figure 3

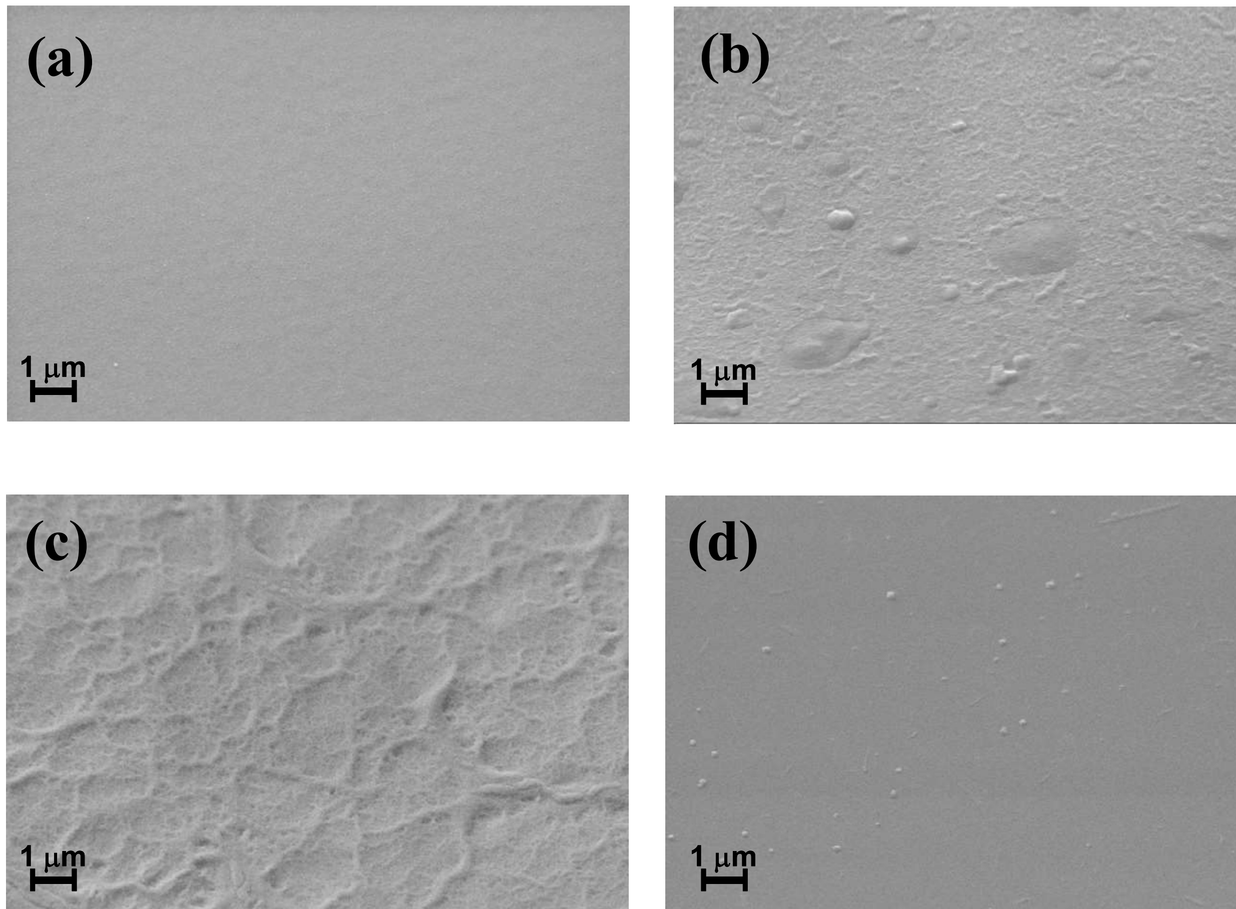

Figure 4

Text for the Table of Contents (300 characters)

The effect of air and water vapour on the fluoropolymers deposition in Ar-C_3F_6 fed FDBDs was investigated with the aim of assessing the highest level of contamination permitted to preserve the process efficiency. Results demonstrate that the gaseous contaminants addition slightly affects the chemical composition of the coatings, but induces a decrease of the deposition rate.