Accepted manuscript.
Link to publisher version with DOI: https://doi.org/10.1179/1743294411Y.0000000043

Full citation information: Fiorenza Fanelli, Surface processing of materials with fluorocarbon fed atmospheric pressure dielectric barrier discharges, *Surface Engineering* (Vol 28, Issue no 2) 28, 83–86. Copyright © 2012 Institute of Materials, Minerals and Mining Published by Maney on behalf of the Institute. DOI: 10.1179/1743294411Y.0000000043.

Surface processing of materials with fluorocarbon fed atmospheric pressure dielectric barrier discharges

F. Fanelli

Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro – IMIP CNR, via Orabona 4, 70126 Bari, Italy

Abstract

Nowadays atmospheric pressure cold plasmas, in particular in dielectric barrier discharge (DBD) configuration, attract significant interest in the field of surface processing of materials. Also fluorocarbon-containing DBDs have been studied, but the state of the art in this field is at its early stages especially if compared to low pressure plasmas, which have been widely and successfully employed for the etching of inorganic and organic materials, for the deposition of fluoropolymers, as well as for the treatment of synthetic and natural polymers. This contribution will provide an overview of our recent studies on fluorocarbon-containing DBDs and will present results on the deposition of fluoropolymers concerning the tuning of the chemical composition of the deposits, the etching-deposition competition, and the influence of feed gas contaminants (i.e. air and water vapour).

Keywords: atmospheric pressure cold plasma, dielectric barrier discharge, fluorocarbon, fluoropolymers, plasma-enhanced chemical vapor deposition.

1 Introduction

In recent years atmospheric pressure cold plasmas have attracted an increased attention in the field of surface modification of materials. The absence of vacuum equipments is expected to result in some benefits, e.g. the reduction costs of processes and reactors, as well as in the easier integration into continuous production lines.

The dielectric barrier discharge (DBD) is a very popular experimental methodology to establish non-equilibrium plasma conditions at atmospheric pressure. DBD generation simply requires the presence of at least one dielectric layer located in the current path between the metal electrodes in order to prevent arc transition, and the utilization of alternated current (AC) high voltage (HV) power supplies in the typical frequency range 0.5–500 kHz.[1,2] Recently efforts have been directed to evaluate if, for some specific applications (e.g. polymer treatment, thin film deposition, plasma-etching or plasma-cleaning, etc.), DBDs can be competitive with respect to the well established low pressure plasma technology.

In last decades low pressure fluorocarbon-containing glow discharges have been extensively studied because of their intrinsic versatility, namely the unique capability to etch several inorganic and organic materials, to deposit fluoropolymer thin films, as well as to graft specific chemical functionalities onto polymeric surfaces.[3,4] This accounts for their technological relevance in a wide range of applications. The intrinsic versatility of these plasmas is related to their unique ability to generate two kinds of reactive species, namely fluorine atoms and CF_x (x = 1, 2 and 3) fragments, which are responsible of the etching of many substrates and of the deposition of a wide range of fluorocarbon thin films.

In particular, concerning the low pressure PE-CVD (plasma-enhanced chemical vapour deposition) of fluoropolymers the possibility of tuning the chemical composition (i.e. F/C ratio and crosslinking degree), the morphology and wettability of the coatings has been widely demonstrated.[3,4]

A great interest was also devoted to the study of the competition between the deposition and the etching of plasma-deposited thin films in low pressure fluorocarbon-containing plasmas.[5,6] It was demonstrated that by changing the experimental conditions, e.g. input power, pressure, substrate bias, substrate temperature and gas feed composition, it is possible to change the concentration of fluorine atoms and of CF_x fragments as well as the extent of ion bombardment, and therefore the etching and polymerizing behaviour of the discharge.[5,6] The employment of a multidiagnostic approach which couples the investigation of both the surface properties and the gas phase composition allowed gaining insights into the plasma-surface interactions as well as into the deposition/etching mechanism.

Recently, many studies on the PE-CVD of fluorocarbon thin films in atmospheric pressure DBDs have been published by several authors. One of the first investigations was reported by Yokoyama et al.[7] which used tetrafluoroethylene (C_2F_4) in mixture with high flow rates of helium; coatings with a F/C ratio in the range 1.4–1.7 were obtained with deposition rates as high as 2 μm h^{-1}. Afterwards, Vinogradov et al.[8,9] and Fanelli et al.[10-13] studied the deposition of thin films in DBDs fed with different fluorocarbons, e.g. CF_4, C_2F_6, C_3F_8, C_3HF_7 and c-C_4F_8; the investigation of the plasma phase was performed by means of different spectroscopic techniques.

This contribution will provide an overview of our recent studies on fluorocarbon-containing DBDs; in particular the possibility of tuning of the chemical composition of the deposits, the etching-deposition competition, and the influence of feed gas contaminants (air and water vapour) will be discussed. The results obtained through different diagnostic techniques of the plasma phase and of the deposits allow to highlight interesting aspects of the fluorocarbon plasma chemistry at atmospheric pressure.

2 Experimental

The experimental apparatus (Figure 1) consists of a parallel plate electrode system (2-5 mm gas gap) contained in an airtight Plexiglas box. Each electrode (area of 9 cm^2 or 286 cm^2) is covered by a double dielectric layer formed by a Al_2O_3 plate and a quartz plate.[10-12] The plasma was generated by applying an AC high voltage (≤ 8 kV_{p-p}) in the frequency range 10-30 kHz by means of a power supply composed of a variable frequency generator (GW Instec GFG-8216A), an audio-amplifier (Outline PA4006) and a HV transformer (Montoux).
Gas flow rates were controlled by MKS electronic mass flow controllers (MFC) and the system pressure was monitored by means of a MKS capacitive gauge. The feed gas was introduced in the interelectrodic zone through a slit and pumped through a second slit positioned on the opposite side (longitudinal gas injection). The working pressure was kept constant at 1 atm; the Plexiglas enclosure was slightly pumped by a rotary pump (Pfeiffer) in order to avoid overpressure.
The feed gas was composed by 4 slm of helium or argon in mixture with CF_4-H_2, CF_4-O_2 C_3F_8-H_2, C_3F_6, C_3F_6-Air and C_3F_6-H_2O. [10-12]
The optical emission spectroscopy (OES) investigation was performed in the UV-Vis region (180 – 850 nm) using an Optical Multichannel Analyser equipped with a monochromator (SP-300i ACTON) and a CCD intensified detector (SpectruMM^{TM} 100B, Princeton Instruments).
XPS analyses were performed using a Theta Probe spectrometer (Thermo Electron Corporation) as reported in reff. 10 - 12. 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. [10-12] The F/C ratio was derived from high resolution spectra considering the area of the C1s and F1s peaks.
The wettability of deposited coatings was determined by static water contact angle (WCA) measurements carried out using a Ramé-Hart manual goniometer (model A-100).
Film thickness was evaluated on substrates which were partially masked during the deposition using an Alpha-Step1 500 KLA Tencor surface profilometer, while surface morphology was assessed by means of scanning electron microscopy (SEM) analyses using a digital microscope EVO 40XVP (Zeiss).

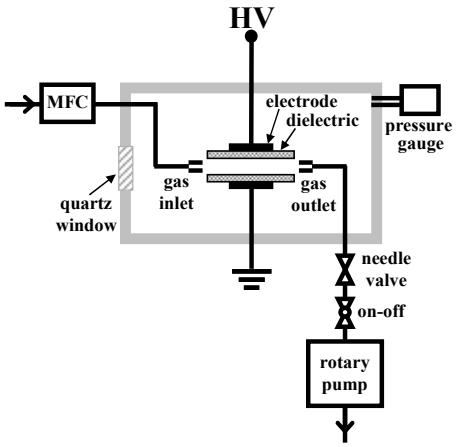

Fig. 1: *DBD reactor.*

3 Results and Discussion

3.1 Tuning of the chemical composition of the fluoropolymer

The study of He–C_3F_8–H_2 fed DBDs[10] showed that by simply varying the H_2 concentration in the feed (i.e. with increasing the $[C_3F_8]/[H_2]$ feed ratio from 0 to 2) it is possible to tune the XPS F/C ratio of the coating from 1.5 to 0.6 (Figure 2), and, hence, its wettability, as reported for low pressure plasmas. The investigation of these DBDs by means of OES allowed detecting the features due to He, F and H atoms as well as to CF_2 ($A_1\ B^1$–$X_1\ A^1$ system), CF_2^+ (continuum at

about 290 nm), and CH ($A^2\Delta$–$X^2\Pi$ system).[10] The OES results were correlated to the properties of the deposited film and, in fact, as shown in Figure 2 the F/C ratio of the coatings decreases with the H_2 content in the feed, which in turn results in an increase of the CH/CF_2 emission intensity ratio. It can be hence concluded that also in the case atmospheric pressure plasmas OES is a powerful in situ diagnostic technique for process control.

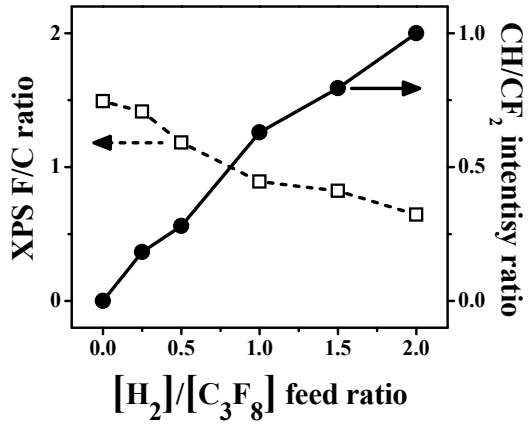

Fig. 2: *XPS F/C ratio and CH/CF_2 emission intensity ratio as a function of the $[H_2]/[C_3F_8]$ feed ratio in He-C_3F_8-H_2 DBDs.*

3.2 Competition between deposition and etching of fluorocarbon thin films

The competition between the deposition and the etching of fluorocarbon thin films was investigated in atmospheric pressure DBDs fed by Ar–CF_4–H_2 and Ar–CF_4–O_2 mixtures.[12]. This is a very interesting topic debated in the 80s by the scientific community involved in the study of the dry-etching of silicon and of silicon dioxide for microelectronics.[5,6]

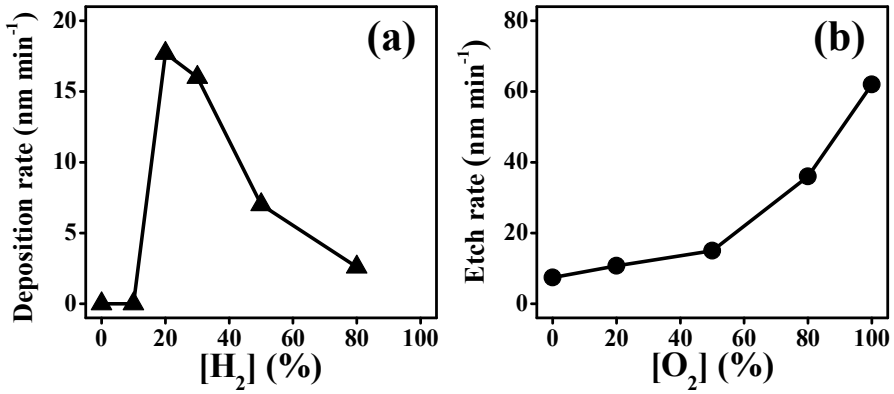

Fig. 3: *(a) Deposition rate as a function of the H_2 content in Ar-CF_4-H_2; (b) etch rate of plasma-deposited fluoropolymers as a function of the O_2 content in Ar-CF_4-O_2 (O_2 and H_2 concentrations are calculated with respect to the total flow rate of reactive gas, CF_4–O_2 or CF_4–H_2).*

In Figure 3(a) it is shown that H_2 addition to CF_4 promotes thin film deposition; no deposition is obtained below 10% H_2 and a deposition rate maximum (about 18 nm min^{-1}) is registered at 20% H_2. The dry etching of the fluoropolymer was investigated by exposing a film deposited in Ar–CF_4–20% H_2 to Ar–CF_4–O_2 fed DBDs. To detect the etch rate of plasma-deposited fluoropolymers thickness measurements were performed before and after plasma-etching. As expected O_2 addition

enhances the etching (Figure 3(b)). Without oxygen, an etch rate of 7 nm min^{-1} is registered indicating that, as in low pressure plasmas, fluoropolymers can be etched by fluorine atoms. Since at atmospheric pressure the effect of ion bombardment is negligible, it is possible to conclude that the plasma-deposited fluoropolymers can be etched by the fluorine atoms through pure chemical reactions (i.e. pure chemical etching). These results indicate that in fluorocarbon fed DBDs the CF_x fragments are responsible of the film growth (i.e. plasma polymerization) and the fluorine atoms act as etchants of the growing film (i.e. dry etching): this is the deposition–etching competition.

3.3 Effect of gas impurities on the PE-CVD of fluoropolymers

In spite of the interesting results reported on the PE-CVD of fluorocarbon coatings by DBDs, the utilization of atmospheric pressure plasma technologies in this field can still be considered a challenge. Besides the fundamental investigation, 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 in 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 polymer composition, in oxygen and nitrogen uptake, as well as in variations of the deposition rate. On the other hand, the possibility of depositing fluorocarbon films with the desired properties in contaminated environments could allow reduction in the cost of processes and reactors.
We investigated the influence of feed gas contaminants on the deposition process by adding controlled amounts of air and water vapour to Ar-0.2% C_3F_6 gas mixtures up to [Air]/[C_3F_6] and [H_2O]/[C_3F_6] feed ratios of 0.5 and 0.25, respectively.[12]

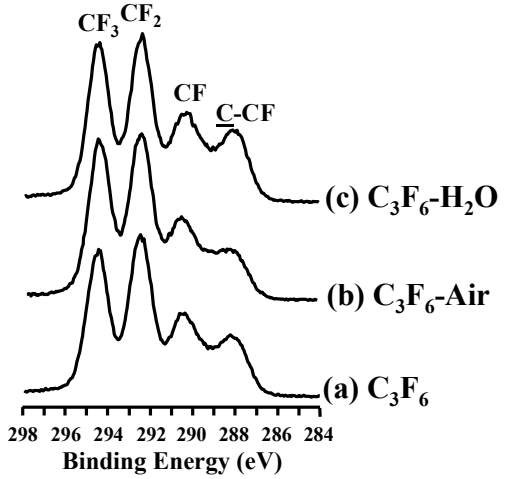

Fig. 4: *XPS C1s signal of fluorocarbon thin films deposited in DBDs fed by (a) Ar-0.2 % C_3F_6, (b) Ar-0.2 % C_3F_6-0.1% Air ([Air]/[C_3F_6] feed ratio of 0.5), and (c) Ar-0.2 % C_3F_6-0.05% H_2O ([H_2O]/[C_3F_6] of 0.25) mixtures.*

The results show that Ar-C_3F_6 DBDs allow depositing coatings at a deposition rate of 56 nm min^{-1} and XPS F/C ratio of 1.7. The fluoropolymer is characterized by high CF_2 and CF_3 concentration and low cross-linking degree as shown by the XPS C1s signal in Figure 4. Contaminants addition does not appreciably affect coating composition (Figure 4) and wettability, and does not cause appreciable O- and N-uptake (lower than 1%); however it induces a decrease of the deposition rate (to 30 nm min^{-1} and 26 nm min^{-1} at 0.1% Air and 0.05% H_2O in the feed, respectively) and the appearance of a certain surface roughness likely due to etching reactions. The fact that the contaminants addition does not affect the chemical composition of the deposited film corroborates the hypothesis that feed contaminants do not change the nature of the film precursors, but could be

responsible of a decrease of the their concentration and hence of the deposition rate. Further studies will be performed in order to confirm this hypothesis.

4 Conclusions

Our studies on the PE-CVD of thin films by fluorocarbon-containing DBDs allowed highlighting that as widely demonstrated for low pressure plasmas, also at atmospheric pressure it is possible to tune the chemical composition and properties of the deposited fluoropolymer by simply changing the feed gas composition. At the same time OES confirmed to be a powerful and reliable diagnostic technique for in situ and online process monitoring; as shown for instance in the case of He-C_3F_8-H_2 DBDs with increasing the H_2 content in the feed a decrease of the F/C ratio of the coatings occurs along with an increase of the CH/CF_2 emission intensity ratio. As observed in low pressure plasmas, also in atmospheric pressure DBDs the competition between the deposition and the etching of plasma-deposited fluoropolymers exists; our results on Ar-CF_4-H_2 and Ar-CF_4-O_2 feeds allow claiming that in a fluorocarbon-containing DBD the fluorocarbon radicals are responsible of the film growth and the fluorine atoms etch the growing film. Finally, if C_3F_6 is used as PE-CVD precursor, the deposition process performance remains acceptable in terms of chemical composition of the coating also at relatively high air and water vapour concentration in the reactor.

Acknowledgements:

The author would like to express her deepest gratitude to Prof. Riccardo d'Agostino and Prof. Francesco Fracassi (University of Bari Aldo Moro, Bari, Italy) for the guidance and the many inspiring and valuable discussions. The author gratefully acknowledges also Mr. Savino Cosmai for the technical assistance. This research has received financial support from Regione Puglia ("Accordo di programma quadro ricerca scientifica, II atto integrativo", project n. 51 "LIPP").

Bibliography

1. Kogelschatz, U.: 'Dielectric-barrier Discharges: Their history, discharge physics, and industrial applications', *Plasma Chem. Plasma Process.*, 2003, **23**, 1–46.
2. Fridman, A.; Chirokov, A.; Gutsol, A.: 'Non-thermal atmospheric pressure discharges', *J. Phys. D Appl. Phys.*, 2005, **38**, R1–R24.
3. d'Agostino, R.; Cramarossa, F.; Fracassi F.; Illuzzi, F.: 'Plasma polymerization of fluorocarbons', in 'Plasma deposition, treatment and etching of polymers' (ed. R. d'Agostino), 95-162; 1990, New York, Academic Press.
4. d'Agostino, R.: "PE-CVD of polymer films: mechanisms, chemistry and diagnostics', in 'Plasma processing of polymers' (ed. d'Agostino et al.), NATO ASI Series, E: Applied Science, Vol. 346, 3–46; 1997, Dordrecht, Kluwer Academic Publishers.
5. Fracassi, F.; Occhiello, E.; Coburn, J.W.: 'Effect of ion bombardment on the plasma-assisted etching and deposition of plasma perfluoropolymer thin films', *J. Appl. Phys.*, 1987, **62**, 3980–3981.
6. Egitto, F.D.: 'Plasma etching and modification of organic polymers', *Pure Appl. Chem.*, 1990, **62**, 1699–1708.
7. Yokoyama, T.; Kogoma, M.; Kanazawa, S.; Moriwaki, T.; Okazaki, S.: 'The improvement of the atmospheric pressure glow plasma method and the deposition of organic films', *J. Phys. D Appl. Phys.*, 1990, **23**, 374–377.

8. Vinogradov, I.P.; Dinkelmann, A.; Lunk, A.: ‘Measurement of the absolute CF_2 concentration in a dielectric barrier discharge running in argon/fluorocarbon mixtures’, *J. Phys. D Appl. Phys.*, 2004, **27**, 3000–3007.
9. Vinogradov, I.P.; Lunk, A.: ‘Spectroscopic diagnostics of DBD in Ar/fluorocarbon mixtures – correlation between plasma parameters and properties of deposited polymer films’, *Plasma Process. Polym.*, 2005, **2**, 201–208.
10. Fanelli, F.; d’Agostino, R.; Fracassi, F.: ‘Atmospheric pressure PE-CVD of fluorocarbon thin films by means of glow dielectric barrier discharges’, *Plasma Process. Polym.*, 2007, **4**, 797–805.
11. Fanelli, F.; Di Renzo, G.; Fracassi, F.; d’Agostino, R.: ‘Recent advances in the atmospheric pressure PECVD of fluorocarbon films from glow dielectric barrier discharges: influence of air and water vapour impurities’, *Plasma Process. Polym.*, 2009, **6**, S503–S507.
12. Fanelli, F.; Fracassi, F.; d’Agostino, R.: ‘Deposition and etching of fluorocarbon thin films in atmospheric pressure DBDs fed with Ar-CF_4-H_2 and Ar-CF_4-O_2 mixtures’, *Surf. Coat. Technol.*, 2010, **204**, 1779–1784.
13. Fanelli, F.: ‘Thin film deposition and surface modification with atmospheric pressure dielectric barrier discharges’, *Surf. Coat. Technol.*, 2010, **206**, 1536–1543.