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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

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Abstract

The deposition and etching of plasma-polymerized fluorocarbon thin films were studied in filamentary dielectric barrier discharges (FDBDs) fed with Ar-CF_4-H_2 and Ar-CF_4-O_2 mixtures, respectively. The etching/polymerization competition was investigated as a function of the feed composition.

Hydrogen addition to CF_4 promotes thin films deposition, with a maximum deposition rate at 20 % H_2, and reduces the F/C ratio of the deposit, while the oxygen addition promotes the etching of the plasma-deposited film. It is demonstrated that fluorine atoms can perform the etching of the fluoropolymer also without ion bombardment. The correlation between the trend of the etch rate and the trend of the surface chemical composition of fluoropolymers etched in Ar-CF_4-O_2 mixtures allows to enhance hypotheses on the reaction mechanism and on the role of the different active species involved in plasma-surface interactions.

Keywords: atmospheric pressure cold plasma, dielectric barrier discharge, fluorocarbon film, plasma-enhanced chemical vapour deposition, etching.

1. Introduction

Low pressure fluorocarbon-containing plasmas have been extensively studied in the last decades because of their unique capability to etch several inorganic and organic materials as well as to deposit fluoropolymer thin films, which accounts for their relevance in many technological fields [1,2]. The intrinsic versatility of these plasmas reflects their ability to generate two kinds of reactive species, namely fluorine atoms and CF_x (x = 1, 2, 3) fragments, which are responsible of the etching of many substrates and of the deposition of a wide range of fluorocarbon coatings [1,2].

In the 80's a great interest was devoted to the study of the competition between the deposition and the etching of plasma-deposited fluoropolymer thin films in low pressure fluorocarbon-containing plasmas. This competition was widely investigated in studies related to the dry-etching of silicon and of silicon dioxide for microelectronics applications [3-6], because it was highlighted that the etching and the deposition of thin fluoropolymer layers was responsible for several important characteristics of the etching process [3,6].

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.

The choice of the fluorocarbon is of primary importance, since it is the source of reactive fragments in the plasma, but also the gas additives are important since they can affect the density of CF_x fragments and of F atoms.

The addition of H_2 or of unsaturated molecules, i.e. of fluorine scavengers, reduces fluorine atoms concentration, enhances CF_x densities [1-3,7-12] and consequently promotes thin film deposition. Also the chemical composition of the deposit in terms of the F/C ratio can be tuned by gas additives: less fluorinated and more crosslinked coatings (i.e. coatings characterized by a higher concentration of C-CF and CF groups) are produced at high H_2

content in the feed [1,2,10,12-16]. The trend of the deposition rate is generally characterized by a maximum as a function of the feed composition and of the experimental system utilized; for CF_4-H_2 fed plasmas d'Agostino et al. [7] reported a maximum of deposition rate at 10 % of H_2 in the feed, while Mackie et al. [16] observed the maximum deposition rate at 60 % H_2.

The etching of conventional polymers and of plasma-deposited fluoropolymers can be performed in oxygen and fluorocarbon-containing plasmas [1-3,7,12,17-20]. Egitto et al. [17-19] widely discussed the plasma-assisted etching of several conventional polymers studying the roles played by atomic and molecular oxygen, atomic fluorine, CF_x fragments, ions, energy of metastable species and photons. Starting from an oxygen plasma, generally employed for the ashing of organic materials, they demonstrated that the addition of fluorine-containing gases enhances the number density and/or energies of electrons in the plasma and hence favours the production of oxygen atoms through electron-induced dissociation processes and therefore the polymer etch rates [17,18]. Moreover, it was also demonstrated that the fluorine atoms produced in the discharge participate to the etching mechanism and affect the etch rate [17,18] which, for conventional polymers (e.g. polyimide, polyisoprene, polyethylene, etc.), generally exhibits a maximum at a certain oxygen concentration in the feed.

d'Agostino et al. demonstrated that in fluorocarbon-oxygen mixtures both O and F atoms are etchants of plasma-deposited fluoropolymers through first-order kinetics [11,12] and that the etching mechanism is the same both for high and low crosslinked fluoropolymers, even though the etch rate was significantly lower for high crosslinked films [11]. By increasing the O_2 content in the feed a continuous increase of the etch rate was observed for films characterized by low crosslinking and by a F/C ratio of 2 (the etch rate maximum reported by Egitto et al. [17-19] was not observed), while a maximum at 60 % O_2 was detected for highly crosslinked coatings (F/C ratio of 0.2) [11].

In fluorocarbon fed low pressure plasmas ion bombardment was found to have a crucial role in the etching of organic and inorganic materials as well as in the competition between the etching and the deposition of plasma-deposited fluoropolymers, leading to the so-called ion-assisted chemistry [1-3,21-27]. Fracassi et al. [3] studied the effect of ion bombardment on the plasma-assisted etching and deposition of fluoropolymer films, using a reactor in triode configuration and gas mixtures characterized by different degree of unsaturation. The influence of the ion energy was investigated by simply changing the substrate bias voltage. When the plasma was fed with saturate fluorocarbons (i.e. CF_4) ion-assisted etching was observed and the etch rate increased with the ion energy. By adding to the gas feed an unsaturated compound (i.e. C_2F_4) the deposition dominated over the etching and the deposition rate increased with ion energy, indicating that the growth occurs through the activated growth model (AGM) [1,2,7,11,12], i.e. through the reaction of CF_x fragments with the activated polymer sites generated by ion bombardment. However, beyond a certain ion energy threshold, ion activated etching and/or sputtering of the fluoropolymers occur.

Recently, studies devoted to the utilization of atmospheric pressure non equilibrium plasmas, and in particular of dielectric barrier discharges (DBDs), for surface processing of materials have been published. 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 the knowledge of low pressure fluorocarbon-containing plasmas.

The deposition of fluoropolymers in atmospheric pressure DBDs, both in filamentary and glow regime, have been studied by several authors [28-37]. In particular Vinogradov et al. [32,34,35] reported preliminary results on to the influence of additive gases, i.e. H_2 and O_2, in fluorocarbon-containing filamentary DBDs. They observed that in argon-octafluoropropane fed DBDs, the hydrogen addition results in a consistent increase of the deposition rate, while the addition of small amounts of O_2 to argon-heptafluoropropane and argon-perfluorocyclobutane gas mixtures results in a drastic growth rate decrease. Vinogradov et al.

[32,34,35] widely investigated also the morphology of fluoropolymers deposited in FDBDs fed with argon-fluorocarbon-hydrogen or argon-hydrofluorocarbon mixtures. Smooth films were obtained at low H_2 concentration in the feed or with a hydrofluorocarbon with low hydrogen content, even though dusty-like particles (size in the order of 0.1 – 1 μm) often appeared on the surfaces. A high hydrogen content promotes powder formation and rough surfaces with holes.

Fanelli et al. [36,37] demonstrated that, as observed in low pressure plasmas, with He-C_3F_8-H_2 glow DBDs it is possible to tune the F/C ratio of the coating from 1.5 to 0.6 and to change its crosslinking degree by simply varying the hydrogen concentration in the gas feed. The addition of hydrogen promotes the increase of the deposition rate which is maximum for a fluorocarbon-to-hydrogen feed ratio close to 1.

Several studies reported on the etching of polymers and in particular of photoresist by atmospheric pressure DBDs fed with air or mixtures of noble gases (i.e. He and Ar) and oxygen [38-44]. Yi et al. [42] discussed the etching of photoresist in He-O_2-SF_6 DBDs and observed a steep decrease of the etch rate with increasing the SF_6 concentration in the feed.

Since, as evident from published data, the etching/deposition competition has never been investigated in atmospheric pressure fluorocarbon-containing plasmas, in this paper we report results concerning the deposition and the etching of plasma-polymerized fluorocarbon thin films in filamentary dielectric barrier discharges (FDBDs) fed with Ar-CF_4-H_2 and Ar-CF_4-O_2 mixtures. Possible hypotheses on the reaction mechanisms and on the plasma-surface interactions are presented.

2. Experimental part

The home-made experimental apparatus consists of a parallel plate electrode system (2 mm gas gap) contained in an airtight Plexiglas box (Fig. 1). Each electrode, of 286 cm^2 area

(width of 13.6 cm; length of 21 cm), is covered by a double dielectric layer formed by an 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 (7.6 kV_{p-p}) at 10 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 probe (Tektronix P2200) the voltage drop across a 50 Ω resistor in series with the ground electrode.

The gas flow rates were controlled by MKS electronic mass flow controllers 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) [36,37,45]. 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 atmospheric plasma was fed by 4 slm of argon (Air Liquide Argon C) in mixture with CF_4 (Air Liquide, 100 % purity) and oxygen (Air Liquide Oxygen C) or hydrogen. The total flow rate of reactive gases (CF_4-O_2 or CF_4-H_2) was kept fixed at 24 sccm; the concentrations of O_2 and H_2 with respect to the total flow rate of reactive gas were varied from 0 to 100 %.

The coatings thickness was measured with a profilometer (Tencor Alpha-Step® 500 KLA). To detect the etch rate of plasma-deposited fluoropolymers thickness measurements were performed before and after plasma etching in Ar-CF_4-O_2.

The chemical composition of the deposited films was evaluated by Fourier transform infrared spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS) analyses. A commercial Brucker Equinox 55 Fourier transform infrared interferometer was used to collect the infrared absorption spectra (4 cm^{-1} resolution) of the deposited films. In order to minimize the effects

of carbon dioxide and water vapour, the optical path inside the sample compartment was purged with nitrogen during each measurement.

XPS analyses were performed using a Theta Probe spectrometer (Thermo Electron Corporation) equipped with monochromatic Al K_α X-ray source (1486.6 eV) operated at a spot size of 400 μm corresponding to a power of 100 W. Survey (0 – 1200 eV) and high resolution (C 1s, F 1s and O 1s) spectra were recorded at a pass energy of 150 eV and 50 eV, respectively. All spectra were acquired at a take off angle of 37° with respect to the sample surface. A flood gun was used to balance the surface charging. The C 1s signal for the CF_2 component, with a binding energy of 292.5 eV [46], was used as an internal standard for the correction of the charging of the samples. The F/C ratio was derived from high resolution spectra, considering the area of the C 1s and F 1s peaks. The best fitting of the XPS C1s high resolution spectra was performed using Avantage Data Spectrum Processing software (Thermo Electron Corporation). The full-width at half maximum (FWHM) of each line-shape was allowed to vary between 1.4 – 1.9 eV for the plasma-deposited fluoropolymer and between 1.4 – 2.3 eV for the plasma-etched fluoropolymers.

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). Contact angles were measured on both sides of five 2 μl drops of double distilled water for each sample and the average value was calculated. For contact angle data an uncertainty of ± 3° was assumed.

Scanning electron microscopy (SEM) analyses were carried out by a Zeiss NVISION 40 FIB-SEM (Focused Ion Beam - Scanning Electron Microscope) system to probe the plasma-deposited film topography before and after plasma-etching.

During the plasma processes the substrates were placed on the centre of the lower electrode. XPS and SEM analysis, film thickness evaluations and WCA measurements were performed

on films deposited on glass substrates, while the films for FTIR characterization were deposited on CaF_2 substrates (Crystran).

3. Results and discussion

Fig. 2a shows the trend of the deposition rate in Ar-CF_4-H_2 fed FDBDs vs. the hydrogen concentration in the feed. No fluoropolymer deposition is obtained below 10 % H_2 and a maximum of about 18 nm·min^{-1} is registered at 20 % H_2. At higher H_2 percentages the deposition rate decreases. Since the reactive gas flow rate is fixed, the trend of the deposition rate could be also related to the reduction of the CF_4 concentration in the feed with hydrogen addition. As shown in Fig. 2b, between 20 and 80 % hydrogen concentration, the XPS fluorine concentration decreases and that of carbon increases (the oxygen content is always lower than 2 %). As a consequence, the F/C ratio of the coatings varies from 0.85 to 0.1. This chemical change is also reflected in the WCA which decreases from 100° to 86°, i.e. the surface becomes less hydrophobic by adding hydrogen to the feed. A better characterization of the deposits is achieved by examining the evolution of XPS C1s signals (Fig. 3a). The distribution of the CF_x groups varies with the feed composition: at 20 % H_2 the C1s signal clearly shows four components ascribed to <u>C</u>-CF, CF, CF_2 and CF_3 groups [1,2,10,12-16,36,37]; with increasing the H_2 content the fluorinated components are reduced and the C-C/C-H component at (285.0 ± 0.2) eV becomes the most intense. These results well correlate with the FT-IR spectra shown in Fig. 3b. At 20 % H_2, the main spectral feature is the broad band between 1400 and 900 cm^{-1} due to the stretching vibrations of CF_x [14-16,36,37,47]; the structure of this band suggests the formation of a thin film characterized by a relatively low fluorination degree. With increasing the hydrogen content of the feed a decrease of the signals due to CF_x groups is observed and the CH_x absorptions appear, i.e. the band between 3000 and 2800 cm^{-1} due to the CH stretching and the two absorptions between 1480 and 1370 cm^{-1} from the CH_2 and CH_3 bending [14-16,36,45,47], which are the typical spectral features of

polyethylene-like coatings [45]. In agreement with XPS analyses, at 80 % H_2 CF_x absorptions are negligible. The deposition rate trend and the evolution of the chemical composition of the deposited films are in agreement with the published results on low pressure PE-CVD using fluorinated gas mixtures [7,10,12,13,16].

As shown by SEM analyses (Fig. 4a), under the experimental conditions utilized, the coatings were characterized by a certain roughness and by the presence of some globules with a diameter of some hundreds of nm, likely due to the filamentary character of the discharge, no powders and pin-hole were detected. These results are quite different from those of Vinogradov et al. [32,34] who obtained abundant powder and holes at high hydrogen concentrations in the feed. The coatings appear quite different from those obtained by Liu et al. [48-51] who in low pressure glow DBDs deposited very high quality uniform films. In this case the uniform glow-like DBD undoubtedly has a crucial role in the growth of uniform coatings with controlled microstructure and roughness.

The dry etching of the film deposited in Ar-CF_4-20 % H_2 was investigated in Ar-CF_4-O_2 fed DBDs. Fig. 5 shows that the etch rate continuously increases as a function of the O_2 content in the feed, as found in low pressure plasmas for low crosslinked plasma-deposited fluoropolymers [11]. As shown by the SEM images reported in Fig. 4, the morphology of the film is not appreciably affected by the plasma-etching. Without oxygen, an etch rate of 7 $nm \cdot min^{-1}$ is detected indicating that, as in low pressure plasmas [3,11], the etching of fluoropolymers occurs also for reaction with fluorine atoms. Oxygen addition increases the capability of the plasma to etch the fluoropolymer and without CF_4 (i.e. with Ar-O_2 fed FDBDs) the etch rate increases up to 62 $nm \cdot min^{-1}$. Since at atmospheric pressure the ion bombardment is negligible, these results demonstrate that the plasma-deposited fluoropolymers can be etched by the fluorine atoms also without ion bombardment (i.e. pure chemical etching) and allow to claim that the competition between etching and deposition in fluorocarbon-fed plasmas exists also at atmospheric pressure. In analogy with the low

pressure case, this competition must be duly considered when dealing with dry etching or deposition processes. It is also important to highlight that in this work the etch rate maximum as a function of the oxygen content in the feed, reported by Egitto et al. [17-19] for conventional polymers in low pressure plasma, was not observed. This diversity could be likely due to the different chemical structure of the plasma-deposited coating respect to the conventional polymers utilized by Egitto et al. [17-19]. In fact, in reference 11, it was demonstrated that in low pressure plasmas the trend of etch rate vs. the oxygen addition depends on the chemical structure of the fluoropolymer to be etched: a continuous increase of etch rate was reported for films with high crosslinking and a trend with a maximum for films with low crosslinking. The difference between the results reported in this article and the trends of Egitto et al. [17-19] could also be ascribed to the fact that in atmospheric plasma DBDs atomic oxygen concentration could not be affected by the addition of fluorine-containing compounds to the feed gas. Further investigations are necessary to clarify this point.

The XPS analyses of the etched polymer surface (Fig. 6) show that the oxygen concentration increases from 2 % for the as-deposited fluoropolymer up to 14 % after etching with 100 % O_2, while the F percent decreases from 58 % to 38 %. It is important to highlight that the fluorine content of the etched surfaces is higher with respect to the as-deposited polymer up to 20 % O_2 in the feed. A different trend is observed for the carbon, in fact, C atoms percent is always higher for the as-deposited film and increases from 41 % to 50 % with the O_2 content in the feed.

The detailed XPS C1s signals and the results of curve fitting of the etched surfaces are shown in Fig. 7 and in table 1. Without O_2, the relative concentration of CF_2 and CF_3 significantly increases respect to the as deposited film, indicating the grafting of fluorinated fragments (i.e. CF_2 and CF_3) and/or of fluorine atoms. When oxygen is added to the feed gas, the contribution of oxygen-containing functionalities has to be considered in the curve fitting and

in fact with increasing the oxygen concentration from 0 % to 100 % the relative density of the peak no. 1 increases for the clear contribution of CO groups, and a small quantity of O$\underline{C}F_3$ is detected at 50% O_2. The abundance of the peaks no. 2 and 3 remains almost constant. This oxygen uptake is a clear evidence of reactions of oxidation which occur on the etched surface and, in agreement with the results reported by Wydeven et al. [20] for low pressure plasma, induces to assume that fluoropolymer etching is not a simple depolymerization reaction, but a complex reaction including polymer oxidation. These authors compared the dry etching of crosslinked plasma-polymerized tetrafluoroethylene (PPTFE) and of conventional polytetrafluoroethylene (PTFE) downstream of a 13.56 MHz high pressure O_2 fed plasma. Any change in C1s and F1s signal was not reported for the PTFE, while for the PPTFE the presence of C-O and CF_xO groups was detected, as found in our case. Wydeven et al. proposed that when reacting with oxygen atoms, PTFE undergoes a simple depolymerization reaction, while chain scission, oxidation and network rearrangement must be claimed for the PPTFE.

4. Conclusion

The deposition and the etching of plasma-polymerized fluorocarbon thin films were studied in filamentary dielectric barrier discharges (FDBDs) fed with Ar-CF_4-H_2 and Ar-CF_4-O_2 mixtures, respectively. Both processes are very similar to those in low pressure plasmas. The addition of hydrogen to the fluorocarbon enhances the deposition rate, which is maximized at 20 % H_2, and induces a decrease of the F/C ratio of the film. The addition of oxygen always favours the etching of the plasma-deposited fluoropolymer which reacts also with fluorine atoms without ion bombardment. The contemporaneous presence of fluorine atoms (polymer etchants) and CF_x fragments (polymer building blocks) indicates that the etching-deposition competition in fluorocarbon-fed plasmas occurs also at atmospheric pressure, and therefore it

must be considered also in the plasma assisted dry etching processes performed with fluorocarbon containing plasmas.

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Figure captions

Fig. 1. Schematic of the DBD reactor.

Fig. 2. Ar-CF_4-H_2 FDBDs: (a) deposition rate and (b) XPS F and C atomic percent as a function of the H_2 percent.

Fig. 3. (a) XPS C1s region and (b) normalized FT-IR spectra of fluorocarbon films deposited in Ar-CF_4-H_2 FDBDs as a function of the H_2 percent.

Fig. 4. SEM images of the fluoropolymer deposited at 20 % H_2 (a), plasma-etched at 100 % O_2 (b). Images are acquired at a tilt angle of 30°.

Fig. 5. Etch rate of plasma-deposited fluoropolymer as a function of the oxygen percent in Ar-CF_4-O_2.

Fig. 6. XPS atomic percent of a plasma-deposited film etched in Ar-CF_4-O_2 FDBDs as a function of the oxygen percent.

Fig. 7. Best fit of the XPS C1s signals of fluoropolymer deposited in Ar-CF_4-20% H_2 FDBD and after etching in Ar-CF_4-O_2 FDBDs.