Optical Emission Spectroscopy of Argon-Fluorocarbon-Oxygen Fed Atmospheric Pressure Dielectric Barrier Discharges

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Summary

Atmospheric pressure Filamentary Dielectric Barrier Discharges (FDBDs) fed with argon, a fluorocarbon compound (i.e. CF_4, C_3F_8, C_3F_6 and c-C_4F_8) and O_2 were investigated by Optical Emission Spectroscopy (OES). The Ultra Violet-Visible (UV-Vis) spectra of the plasma in argon-fluorocarbon mixtures are characterized by narrow signals from Ar atoms, CF_2 and CF fragments and by two continua due to CF_2^+ and CF_3. O_2 addition to the feed gas reduces the emissions of fluorocarbon fragments and results in the appearance of an intense narrow emission at 193 nm and of a broad continuum centred at 290 nm ascribed to ArF and Ar_2F excimers, respectively. Any signal from F atoms was not detected under the experimental conditions investigated even though the plasma contains F atoms since the dry etching of silicon substrates, a typical process driven by F atoms, was observed. Some possible explanations of this phenomenon are presented.

1 Introduction

Fluorocarbon-containing plasmas have been extensively studied in last decades because of their intrinsic versatility, namely the unique capability to etch several inorganic and organic materials as well as to deposit fluoropolymer thin films, which accounts for their technological relevance in a wide range of applications.[1, 2]

The first studies of fluorocarbon fed low pressure plasmas date back to the 70's, when tetrafluoromethane started to be utilized in microelectronics for dry etching processes of silicon and silicon dioxide; for almost two decades the employment of plasma processes in this field was the principal issue of the great deal of work produced. Quite quickly, besides the need for continuous improvements in microelectronic processing, there was a demand for *in situ* plasma diagnostics with the aim of gaining insights into the gas phase and plasma-surface interactions for process understanding and control. Optical Emission Spectroscopy (OES) of the plasma phase demonstrated to be a powerful diagnostic tool due to its non-intrusive nature and to the ease of integration into production equipments.[1-3] OES, in fact, is a highly sensitive diagnostics which allows identification and monitoring of species emitting in the ultra violet-visible (UV-Vis) region. However, it has the limit to be truly representative only of the excited state population. The actinometric approach, known as Actinometric Optical Emission Spectroscopy (AOES), set up by Coburn et al.[4, 5] and d'Agostino et al.,[6-8] under particular conditions overcomes this limit allowing the estimation of the relative concentration of emitting species in the ground state.

Recently, many investigations have focused on the utilization of atmospheric pressure non equilibrium plasmas, and in particular of dielectric barrier discharges (DBDs), in fields traditionally dominated by low pressure plasmas. Also fluorocarbon-containing DBDs, both in filamentary and glow regime, have been studied, even though the state of the art can be still considered at its early stages if fundamental and applicative aspects as well as plasma diagnostics are considered.[9-17]

In this paper new results of OES investigation of filamentary dielectric barrier discharges fed by argon in mixture with O_2 and several fluorocarbons, such as tetrafluoromethane (CF_4),

octafluoropropane (C_3F_8), hexafluoropropene (C_3F_6) and octafluorocyclobutane (c-C_4F_8) are reported. Assignments for the most important emission signals are discussed along with the effect on the emission spectra of the O_2 addition to the gas feed.

1.1 OES of low pressure fluorocarbon-containing plasmas

The main emissions observed by OES in low pressure fluorocarbon fed plasmas are the atomic fluorine lines (e.g. at 703.7 nm),[4, 5, 18] and the emission bands in the spectral range 200 - 400 nm, due to the CF_2 $A^1B_1 – X^1A_1$ transition,[8, 19-22] and to the CF $A^2\Sigma – X^2\Pi$ and $B^2\Delta – X^2\Pi$ systems.[6-8, 21, 22] Two continua emissions are also reported. The first one, centred at 290 nm, was assigned by d'Agostino et al. to CF_2^+ ($4b_2 – 6a_1$).[1, 2, 8] It probably originates from the $4b_2$ state of CF_2^+ which undergoes a transition to $6a_1$, which is highly C-F antibonding and weakly F-F bonding. The second continuum, at approximately 600 nm, was assigned by Flamm to CF_3 radicals,[23] which undergo a transition from an electronically excited state to a repulsive lower state yielding CF_2 and F.[23, 24]

Several studies on fluorocarbon fed plasmas, for both dry etching and fluoropolymer deposition, correlate the AOES density trends of F atoms and CF_x fragments with etching/deposition rates and surface chemical composition with the aim of understanding the reaction mechanisms and plasma-surface interactions.[4-8, 22, 25-29] It was stated that the F-to-CF_x concentrations ratio in the gas phase[1, 2] is the key parameter of low pressure fluorocarbon-containing plasmas, since F atoms and CF_x fragments trigger the etching of many substrates and the deposition of a wide range of fluorocarbon coatings, respectively. This allowed to outline the role of the reactive gas, and in particular of its F/C ratio, that of additives, namely O_2, H_2 or unsaturated molecules, and the effect of input power, pressure and discharge regime (i.e. continuous and modulated). The ultimate goal was to predict and control the effects of the experimental conditions on the plasma processes.[1, 2]

The choice of the monomer is of primary importance, since it is the source of reactive fragments;[1, 2] but also additives have a crucial role. The addition of H_2 or unsaturates, i.e. fluorine scavengers, enhances CF_x densities and reduces F atoms concentration,[1, 2, 25, 26] while O_2 addition increases the

density of F atoms and lowers that of CF_x. In fact, in this case OES investigation allowed to observe that O_2 addition enhances emissions of F atoms, O atoms and of various CO and CO_2 systems, while CF_x signals are reduced.[6, 7, 26, 27, 30, 31]

1.2 OES of atmospheric pressure fluorocarbon-containing plasmas

One of the first studies on fluorocarbon containing DBDs was reported by Yokoyama et al.[9] in a pioneering work on the deposition of thin films in helium-tetrafluoroethylene fed atmospheric pressure glow discharges (APGDs). Kogoma et al.[10, 11] extended these preliminary results showing the increase of the CF_2 emission intensity ($A^1B_1 - X^1A_1$ system) as a function of the discharge power. The authors supposed that, as in low pressure plasmas, CF_2 plays a key role in the deposition mechanism.[11]

I. Vinogradov et al.[12-14] performed the gas phase investigation of filamentary DBDs (FDBDs) fed with argon and different fluorocarbons (i.e. CF_4, C_2F_6, $C_2H_2F_4$, C_3F_8, C_3HF_7 and c-C_4F_8) by means of UV and Fourier Transform infrared (FT-IR) absorption spectroscopy, and UV-Vis emission spectroscopy. Along with Ar emission lines, the CF_2 band and the CF_3 continuum were detected by OES measurements, while any signal from F atoms and CF fragments was not observed. With decreasing F/C ratio of the fluorocarbon, the intensity of the CF_3 continuum emission decreased, while the concentration of CF_2, evaluated by UV absorption, had a maximum for octafluorocyclobutane (c-C_4F_8) and decreased upon O_2 addition. Any correlation between the CF_2 density in the gas phase and deposition rate was not found as instead reported in low pressure plasmas.

Recently, new results of the optical emission spectroscopic investigation of fluorocarbon-containing helium glow DBDs (GDBDs) have been published.[15-17] The emission spectra for CF_4, CHF_3, C_2F_6 and C_3F_8 were compared[17] in order to identify the most important emitting species. By varying the H_2 content in He-C_3F_8-H_2 fed GDBDs, reproducible trends were detected for F, H, CF_2 and CH emissions and a steep increase of the H/F and CH/CF_2 intensity ratios was observed.[15, 16]

2 Experimental part

The experimental apparatus consists of a parallel plate electrode system (2 mm gas gap) contained in an airthight Plexiglas box (figure 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 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 (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 voltage probe (Tektronix P2200) the voltage drop across a 50 Ω resistor in series with the ground electrode.

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, therefore a longitudinal gas injection was realized.[15-17] The working pressure was kept constant at 1 atm; in order to avoid overpressure, the Plexiglas enclosure was slightly pumped by a rotary pump (Pfeiffer).

The atmospheric plasma was fed by argon (Air Liquide Argon C) in mixture with O_2 (Air Liquide Oxygen C) and a fluorocarbon compound: CF_4 (Air Liquide, 100 % purity), C_3F_6 (Fluorochem, 99% purity), C_3F_8 (Fluorochem, 99% purity) and c-C_4F_8 (Fluorochem, 99% purity). Discharges were fed with various mixtures, keeping constant the Ar flow rate (ϕ_{Ar}) at 4 slm and, hence, since the concentration of reactive gases was lower than 0.6 % the gas residence time in the interelectrode zone can be considered constant. The total flow rate of reactive gases (fluorocarbon and O_2) was

kept fixed at 24 sccm for CF_4-O_2, 8 sccm for both C_3F_6-O_2 and C_3F_8-O_2, 6 sccm for c-C_4F_8-O_2. O_2 concentration with respect to the total flow rate of reactive gas was varied from 0 to 100 %.

Optical emission spectroscopy (OES) was performed in the UV-Vis range 180 - 850 nm using an Optical Multichannel Analyser (OMA). The radiation emitted by the DBD was collected through a side view-quartz window by means of a 3 m optical fiber bundle to an ACTON SP-300i air-monochromator (0.300 m focal length imaging monochromator, 0.1 nm resolution at 435.8 nm) equipped with a 1200 grooves/mm grating (blazing wavelength of 300 nm, dispersion of 2.7 nm/mm) and a CCD detector (SpectruMM^{TM} 120B, Princeton Instruments) consisting of 1024 × 122 imaging pixels (24 × 24 μm pixel area) cooled by a Peltier-effect thermoelectric cooler (-15°C operating temperature). Spectra were collected with an entrance slit of 80 μm that allowed to obtain a nominal bandwidth of 0.238 nm. The optical fiber bundle was positioned at (100.5 ± 0.5) mm from the gas entrance in the interelectrode zone and centred with respect to the gas gap. To exclude the interference of second order signals, in the wavelength range 450 – 850 nm the spectra were registered using a long pass filter (cut-off wavelength of 450 nm).

Some experiments were performed by positioning a partially masked silicon substrate (1, 0, 0 – CZ, P-type) of about 1 cm^2 on the centre of the lower electrode for etch rate evaluation in Ar-CF_4-O_2 fed plasmas.

3. Results and Discussion

The filamentary DBDs fed with argon-fluorocarbon-oxygen mixtures are characterized by numerous intense emissions from Ar atoms and weak atomic oxygen lines at 777.4 nm and 844.6 nm.[32] The main emissions due to the atoms and polyatomic fragments identified are listed in Table 1.

Figure 2 shows the typical emission spectra in the wavelength ranges 180 – 380 nm of C_3F_6-O_2 fed plasmas. Without O_2, the most important features are the signals due to the CF $A^2\Sigma - X^2\Pi$ and CF_2

$A^1B_1 - X^1A_1$ systems[19-22, 29, 33] and the two broad continua in the wavelength range 220 – 360 nm and 540 – 720 nm, ascribed to CF_2^+[1, 8] and CF_3, respectively.[13, 14, 17, 23, 24] At 30 % O_2 addition, several signals due to oxygen-containing species along with an emission at 193 nm are detected. In particular, weak oxygen atomic lines,[32] the CO third and forth positive systems bands and the CO^+ first negative system[33] appear. The CF and CF_2 signals are still visible, even though a slight variation of the structure of the continuum between 220 and 360 nm is observed. At 90 % O_2 addition the CF, CF_2, CF_2^+, CO, and CO^+ features disappear, the emission at 193 nm becomes very intense and a new continuum centred at 290 nm appears. The ArO auroral green band ($2^1\Sigma^+$-$1^1\Sigma^+$, $1^1\Pi$ transitions) at 557.7 nm[34-36] is also present. Without C_3F_6, the spectra is composed by emissions of argon, weak emissions of O atoms, an intense emission from OH (3064 Å system)[33] and the ArO auroral green band. The second Positive System of N_2,[33] related to air contaminations in the reaction chamber, was detected under all the experimental conditions explored.

The presence of the new continuum centred at 290 nm and definitely evident at an O_2 concentration of 90 % could explain the slight variation of the CF_2^+ emission (220 – 360 nm) observed at 30% O_2, reasonably due to the overlap of the two continua. A careful investigation of published data allows to ascribe the narrow emission at 193 nm and the broad continuum peaked at 290 nm to ArF,[34, 35, 37-44] and Ar_2F [35, 40, 41, 44-49] excimers, respectively. Excimer emission is a topic not sufficiently investigated in fluorocarbon fed DBDs even though it is well-known that dielectric barrier discharges are suitable for efficient production of high intensity VUV (vacuum ultra violet) and UV radiation from excimers, namely excited dimers or trimers, which make them widely utilized in excimer lamps.[51-55]

DBDs couple nonequilibrium conditions to atmospheric pressure operation which allow to fulfil the two main requirements for efficient excimer generation, namely a reasonably high electron energy (5 – 10 eV) for efficient excitation or ionization of excimer precursors and high collision rates providing fast excimer formation reactions.[51-55] As a consequence, each microdischarge acts as an

intense source of VUV-UV radiation. Moreover the conditions generated in a filamentary DBD, in terms of electron energies (1 – 10 eV) and densities (10^{14} cm^{-3}), were demonstrated to be comparable to those of discharge pumped excimer lasers.[51-55] Excimer emissions from filamentary DBDs has been found to be very similar to those observed with other excitation techniques traditionally used for excimers generation and study, e.g. high energy electron beams, α-particles, protons, synchrotron radiation (X-ray or VUV radiation), pulsed discharges, transverse volume (TSV) discharges, microwave discharges.[51-55]

The most studied and best understood excimers are the rare gas dimers He_2, Ne_2, Ar_2, Xe_2[34] and the rare gas-halides ArF, KrF, XeCl, XeF which, in particular, exhibit stimulated emission and therefore are used in excimer lasers.[34, 37] Rare gas-halide excimers radiate in a narrow VUV or UV band by undergoing a transition ($B^2\Sigma^+_{1/2} - X^2\Sigma^+_{1/2}$) from a bound ion-pair electronically excited state to an unbound covalent ground state that dissociates into neutral atoms.[34, 37-39] For ArF this transition is responsible for the intense signal peaked at 193 nm.[35, 37, 39-44]

In electron-beam excited Ar-F_2 mixtures and laser media two main reaction pathways, leading to the formation of ArF excimer, have been reported:[37, 40, 43, 44]

i) an ionic channel, i.e. a three-body reaction in which Ar^+ and F^- recombines in the presence of an argon atom;
ii) a neutral channel, namely a harpoon reaction between an excited argon atoms and F_2.

Because the ionic channel requires a three-body collision, the high pressure of DBDs is generally found to favour excimer production[37] and enhance the reaction rate of excimer formation.

The triatomic Ar_2F excimer emits a structureless broadband continuum centred at 290 nm, due to the transitions from an electronically bound ionic excited state (2^2B_2), characterized by an isosceles triangular geometry, to repulsive covalent lower states (1^2A_1 and 1^2B_2) which rapidly dissociates into ground state atoms.[35, 40, 41, 46, 48, 49] This emission, observed in electron-beam excited high pressure Ar-F_2 and Ar-NF_3 mixtures as well as in high pressure Ar-F_2 excimer lasers,[40, 41, 43-48] was always associated to the ArF signal. Both experimental evidence and theoretical calculations

indicate the third-body reaction of ArF with two Ar atoms as the dominant Ar_2F formation process,[40, 48] which therefore can be considered a possible pathway for non radiative quenching of ArF excimer. Ar_2F emission becomes more prominent at high noble gas partial pressures when clustering reactions are expected to be important.[40, 48, 50]

In this work, in agreement with published data the full width at half maximum (FWHM) of ArF at 193 nm is approximately 2.6 nm,[34, 35, 37-44] while the FWHM of the structureless Ar_2F continuum is about 60 nm.[40, 41, 45-49] An unknown system is overimposed to the continuum between 250 and 260 nm; moreover a confident identification of the emitting signal responsible of the shoulder at 340 nm and visible at 30 % O_2 was not achieved.

A deeper analysis of the ArF band (figure 3) allows to observe the presence of weak absorptions ascribed to the Schumann-Runge system ($B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$) of O_2.[56-60] These absorptions are due to the O_2 present both in the DBD reactor and in the optical path inside the monochromator (not under vacuum). The latter contribution is expected to be more important since in the monochromator the O_2 concentration is about 20 % (air) and therefore much higher than in the DBD (0.6 % maximum). It is important to report that if the spectrum at 100% O_2 (no C_3F_6) is collected with dielectric surfaces contaminated by fluoropolymers coming from previous experiments, intense ArF and Ar_2F emissions are detected due to the release in the DBD gap of F atoms and fluorocarbon fragments from the dielectric surfaces.

In figure 4 the emission spectra (180 - 380 nm) as a function of the O_2 content in the feed, for the different fluorocarbons investigated in this work, are compared (each spectrum is normalized to its maximum). The spectral features are highly influenced both by the fluorocarbons utilized, by their fluorine-to-carbon ratio, in particular, and by the O_2 content. Without O_2 addition excimer signals are evident only for CF_4 (F/C = 4) and C_3F_8 (F/C = 2.7) and the emissions of CF, CF_2, and CF_2^+ become more important by decreasing the F-to-C ratio, i.e. CF_4> C_3F_8> C_3F_6 = c-C_4F_8, as expected if the general concentration trend in low pressure plasmas are considered.[1, 2] Similar trends are obtained as a function of O_2 addition: i.e. the lower is the fluorine-to-carbon ratio of the

fluorocarbon the higher is the amount of O_2 necessary to decrease the emissions of CF and CF_2 below the detection limit. For CF_4, 10 % O_2 is sufficient to completely eliminate CF_x emissions and to have a spectrum dominated by ArF and Ar_2F features (CO and CO^+ emissions have never detected), with C_3F_8 O_2 concentration must be increased to 50%, while with C_3F_6 and c-C_4F_8 O_2 concentration must be increased up to 90 %. It must be recalled that the experiments of Figure 4 have been performed with different flow rate for each fluorocarbon in order to obtain the same maximum potential production of CF_x fragments i.e. 24 sccm for CF_4, 8 sccm for C_3F_8 and C_3F_6, 6 sccm for c-C_4F_8 since the molecules of fluorocarbon utilized are characterized by different amounts of CF_x (i.e. 1 for CF_4, 3 for C_3F_8 and C_3F_6, 4 for cC_4F_8). Similar trends have been obtained utilizing the same flow rate of each fluorocarbon (2 sccm) in the feed gas.

The excimer emissions in the VUV and UV region must be duly taken into consideration when fluorine containing DBD are utilized for surface treatment since the VUV-UV radiation can affect the processes as well as result in surface modification, in particular when polymer different than polypropylene (PP) and polyethylene (PE) are considered, as widely discussed for low pressure plasma.[61]

Since the complete absence of F atoms emission in fluorocarbon containing plasmas was surprising, the presence of F atoms was tested by evaluating the etch rate of silicon substrates in CF_4-O_2. It is well known, in fact, that in fluorocarbon-oxygen plasmas, silicon surfaces can be etched only by F atoms, also without ion bombardment (O atoms or CF_x radicals are not silicon etchants).[1, 2] Figure 5 clearly shows that the silicon substrate is etched in CF_4-O_2 containing FDBD and therefore F atoms are contained into the discharge but they do not emit. If we consider that F atom excitation occurs through electron impact collisions, the emission depends not only by F atom density but also on the overlap between the excitation cross section and the electron energy distribution function (EEDF). Consequently, the lack of emission of F atoms could be due to a lower density of electrons with energy equal or higher than the excitation threshold energy of F atoms (between 14.37 and

14.75 eV, as a function of the transition considered[32]). The following consideration support this hypothesis:

- the emission of O atoms at 774.4 and 844.6 nm, with excitation threshold energy of 10.74 and 10.99 eV, respectively,[32] and therefore lower than that of F atom, are always very weak although in plasma containing high amount of O_2 the concentration of O atoms is expected to be high;
- Any emission of helium, with excitation threshold energy ranging from 22.72 and 23.07 eV,[32] was never detected under similar experimental conditions also if the 24 sccm of the CF_4-O_2 mixture in argon were totally replaced by 24 sccm of He.

In conclusion, it is reasonable to assume that any emission from F atoms is not detected under the experimental conditions utilized in this study because the high energy tail of the EEDF (Electron Energy Distribution Function) is scarcely populated. This could be a consequence of different effects also acting contemporaneously, e.g. excitation frequency and gas feed composition. For instance intense F atoms emissions (and higher silicon etch rate) were reported by Nagata et al.[67] for DBDs fed with He-CF_4-O_2 mixtures at higher excitation frequency (13.56 MHz), while F atom emissions were observed in the same frequency region of the present work (15 – 30 kHz) but in helium-fluorocarbon containing DBDs.[15-17]

The comparison between the absolute emission trend of ArF excimer and silicon etch rate in Figure 5 evidences some analogy with published results concerning silicon etching in CF_4-O_2 low pressure plasma.[27] By plotting the silicon etch rate and the F atom concentration vs. the O_2 content of the gas feed, it was realized that the two maxima do not coincide (the maximum of F atoms concentration is at higher O_2 concentration than that one of the etch rate) for the competition between the etching reaction of F atoms and silicon oxidation due to O atoms. Since in the data plotted in figure 5 a similar shift is shown between etch rate and ArF excimer emission, it would be interesting in a future work to investigate the relationship between ArF emission and F atoms

concentration in the gas phase, to see whether ArF emission can be utilized to represent F atoms concentration.

Conclusion

Atmospheric pressure filamentary DBDs fed by argon in mixture with O_2 and several fluorocarbons (i.e. CF_4, C_3F_8, C_3F_6 and c-C_4F_8) were investigated by Optical Emission Spectroscopy. The most relevant spectral features detected are due to Ar, CF_2, CF, CF_2^+ (continuum), CF_3 (continuum), and eventually CO, and CO^+. A signal due to ArF excimer at 193 nm and a continuum centred at 290 nm ascribed to Ar_2F excimer were also found. O_2 addition to the feed gas affects the spectral features as a function of the fluorine-to-carbon ratio of the fluorocarbon. The higher is the fluorine-to-carbon ratio of the fluorocarbon the lower the O_2 concentration necessary to reduce the emission of CF_x fragments below the detection limit. Even though any emission from F atoms was not detected under the experimental conditions investigated, it was demonstrated that CF_4-O_2 fed FDBDs are able to etch a silicon substrate, i.e. to perform a typical process driven by F atoms also without ion bombardment, as in low pressure plasmas. It seemed reasonable to assume that the lack of emissions of F atoms could be due to a lower density of electrons with energy equal or higher than the excitation threshold energy of F atoms.

The comparison between the absolute emission trend of ArF excimer and silicon etch rate evidences some analogy with published results concerning silicon etching in CF_4-O_2 low pressure plasmas. In a future work the relationship between ArF emission and F atoms concentration in the gas phase will be investigated with the aim of evaluating whether the ArF emission can be representative of the F atoms concentration.

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Figure Captions

Figure 1**.** Schematic of the DBD reactor.

Figure 2. Emission spectra of Ar-C_3F_6-O_2 fed FDBD as a function of the O_2 concentration in the feed in the wavelength range 180 – 380 nm (spectra are normalized to their maximum).

Figure 3. Details of the ArF bands centred at 193 nm in C_3F_6 – 90 % O_2 fed Ar FDBD. Some of the absorptions of the Schumann-Runge system ($B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$) of O_2 are indicated.

Figure 4. Emission spectra of FDBDs fed with argon, O_2 and different fluorocarbons (CF_4, C_3F_8, C_3F_6, c-C_4F_8) as a function of the [O_2] in the feed ([O_2] = 0, 10, 50, 90 %).

Figure 5. ArF excimer emission and Silicon etch rate in Ar-CF_4-O_2 FDBD as a function of O_2 percent.

Table 1. Identified emitting species in argon-flurocarbon-oxygen FDBDs.

Emitting specie	Transition	Wavelength (nm)	Ref.
CF	$A^2\Sigma - X^2\Pi$	220 – 265	21, 29, 33, 62
CF_2	$A^1B_1 - X^1A_1$	240 – 360	19-22, 29, 33, 63
CF_2^+	$4b_2 - 6a_1$, continuum	220 – 360	1, 8
CF_3	Continuum	540 – 720	14, 17, 23, 24, 64-66
ArF	$B^2\Sigma^+_{1/2} - X^2\Sigma^+_{1/2}$	193	34, 35, 37-44
Ar_2F	$2^2B_2 - 1^2A_1$, 1^2B_2, continuum	290	35, 40, 41, 43-49
ArO	$2^1\Sigma^+$-$1^1\Sigma^+$, $1^1\Pi$	557.7	34-36
CO	$b^3\Sigma - a^3\Pi$, 3rd positive system	185 – 225	6, 7, 33
	$A^1\Pi - X^1\Sigma$, 4th positive system	280 – 350	6, 7, 33
CO^+	$B^2\Sigma - X^2\Sigma$, 1st negative system	215 – 260	6, 7, 33
N_2	$C^3\Pi_u - B^3\Pi_g$, 2nd positive system	330 – 460	33
OH	$A^2\Sigma^+ - X^2\Pi$, 3064 Å system	300 – 320	33
Ar	4s $[1½]^0$ – 4p´ [1½]	706.7	32
	4s $[1½]^0$ – 4p´ [1½]	738.4	32
	4s´ $[½]^0$ – 4p´ [½]	750.4	32
	4s $[1½]^0$ – 4p [2½]	811.5	32
	4s´ $[½]^0$ – 4p´ [½]	826.5	32
O	3s $^5S^0$ – 3p ^5P	774.4	32
	3s $^3S^0$ – 3p ^3P	844.6	32

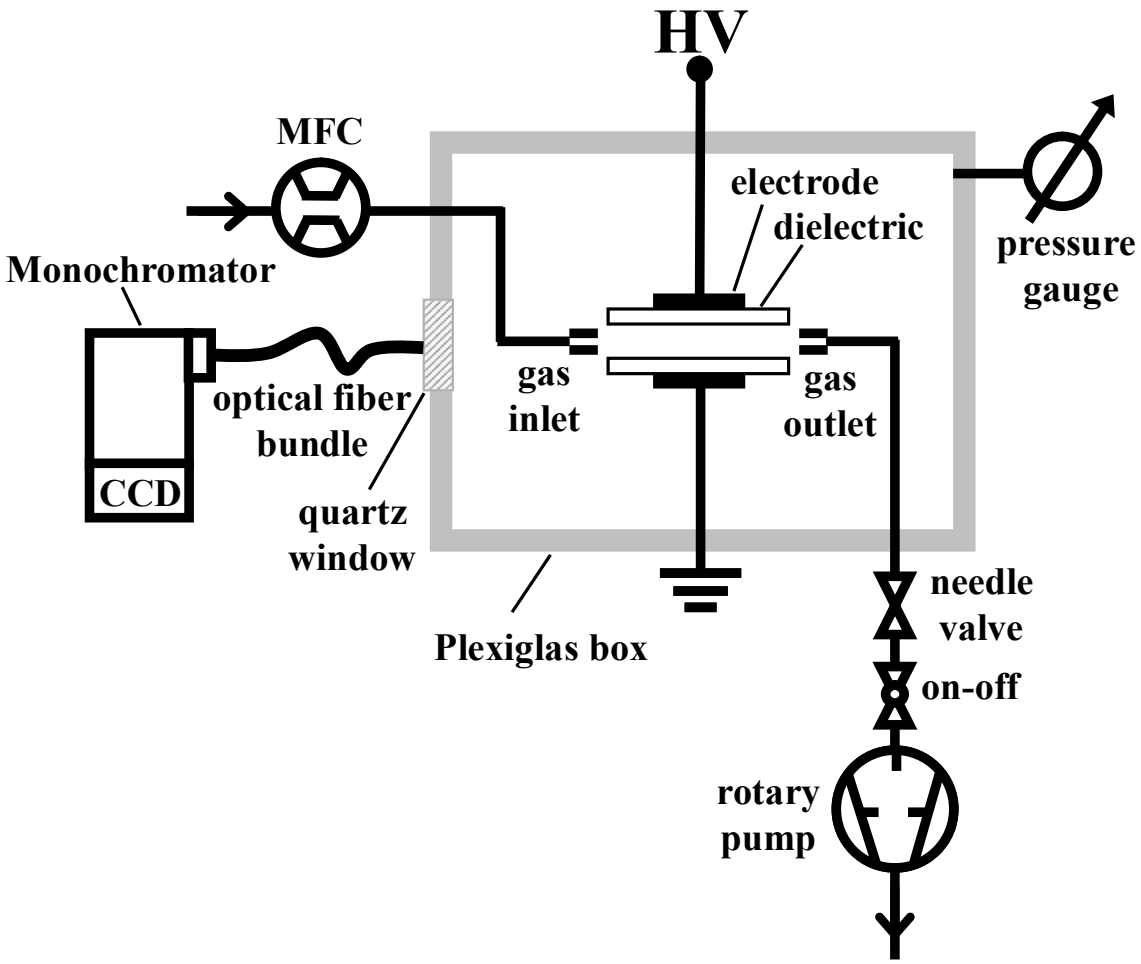
HV
MFC
Monochromator
electrode
dielectric
pressure
gauge
optical fiber
bundle
CCD
quartz
window
gas
inlet
gas
outlet
Plexiglas box
needle
valve
on-off
rotary
pump

Figure 1

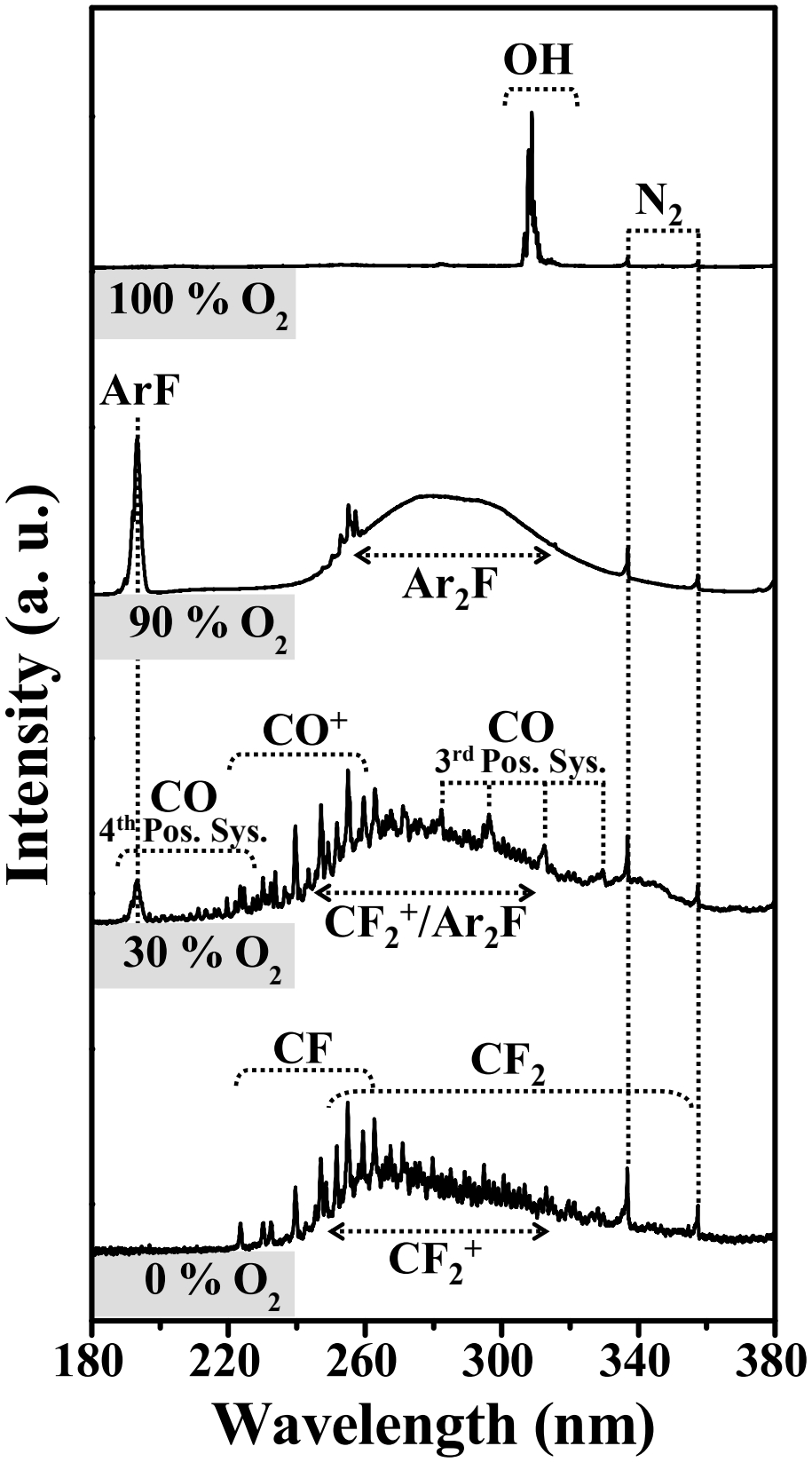
OH
N2
100 % O2
ArF
Ar2F
90 % O2
CO+
CO
3rd Pos. Sys.
CO
4th Pos. Sys.
CF2+/Ar2F
30 % O2
CF
CF2
CF2+
0 % O2
Intensity (a. u.)
180
220
260
300
340
380
Wavelength (nm)

Figure 2

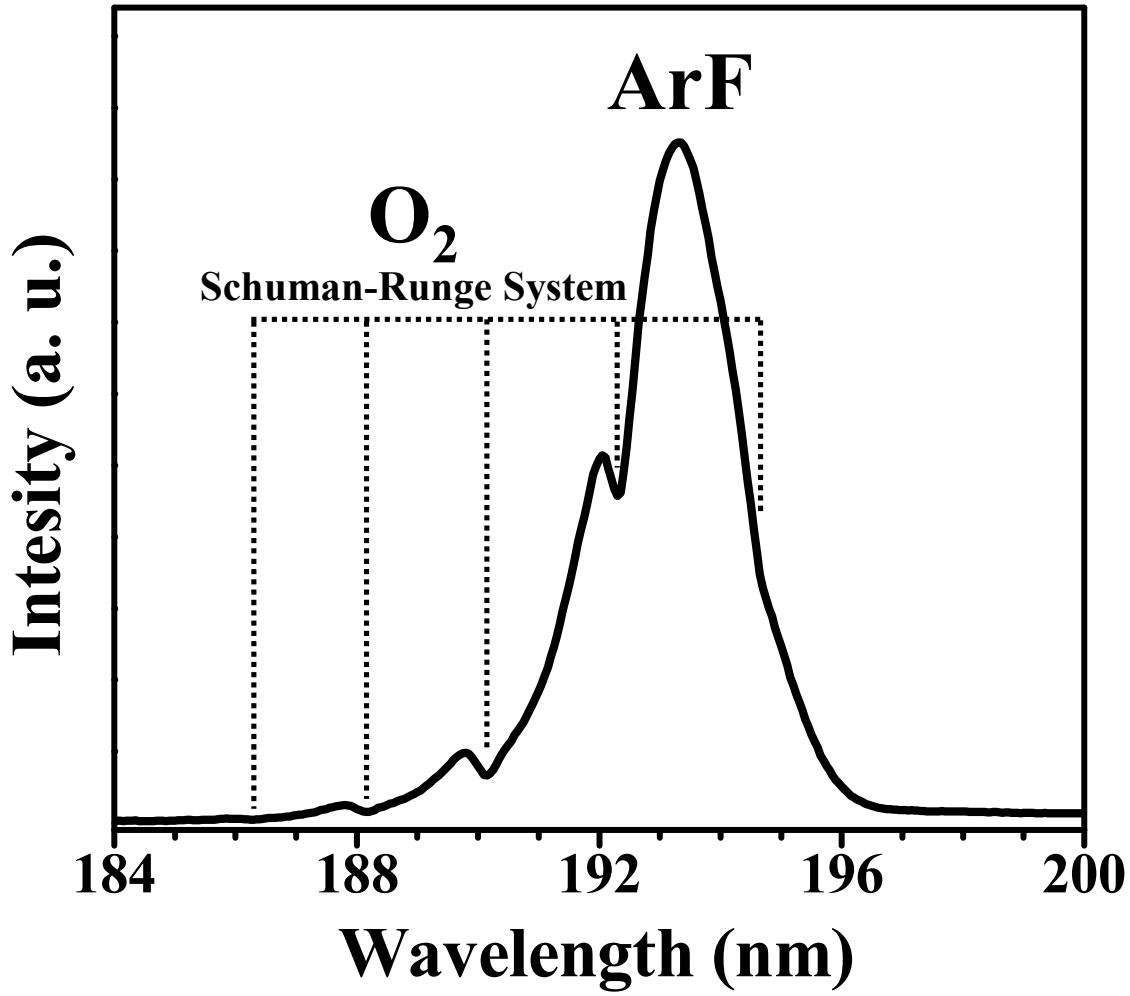
ArF
O2
Schuman-Runge System
Intesity (a. u.)
184
188
192
196
200
Wavelength (nm)

Figure 3

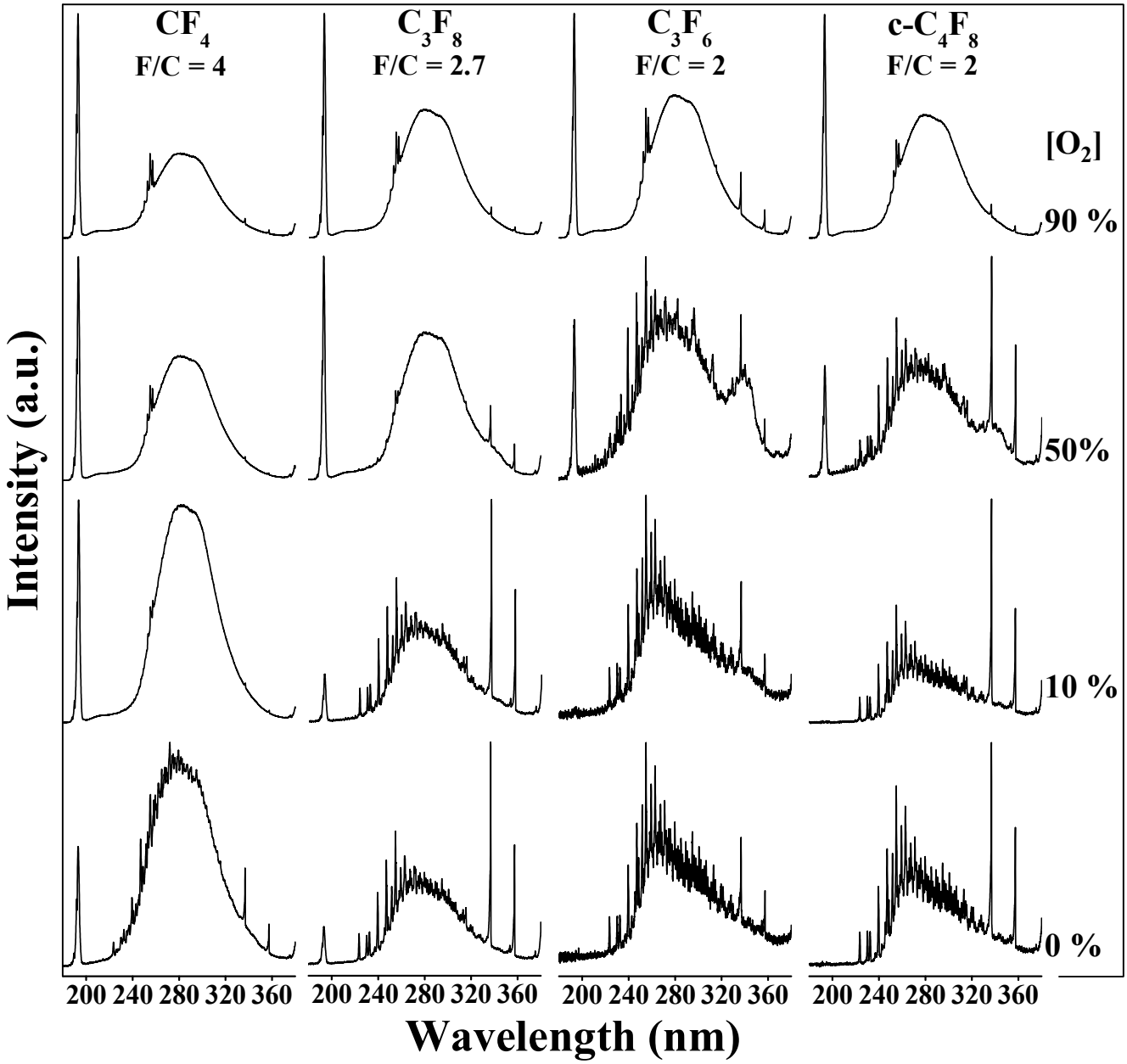
CF4
F/C = 4
C3F8
F/C = 2.7
C3F6
F/C = 2
c-C4F8
F/C = 2
[O2]
90 %
50%
10 %
0 %
Intensity (a.u.)
200 240 280 320 360
200 240 280 320 360
200 240 280 320 360
200 240 280 320 360
Wavelength (nm)

Figure 4

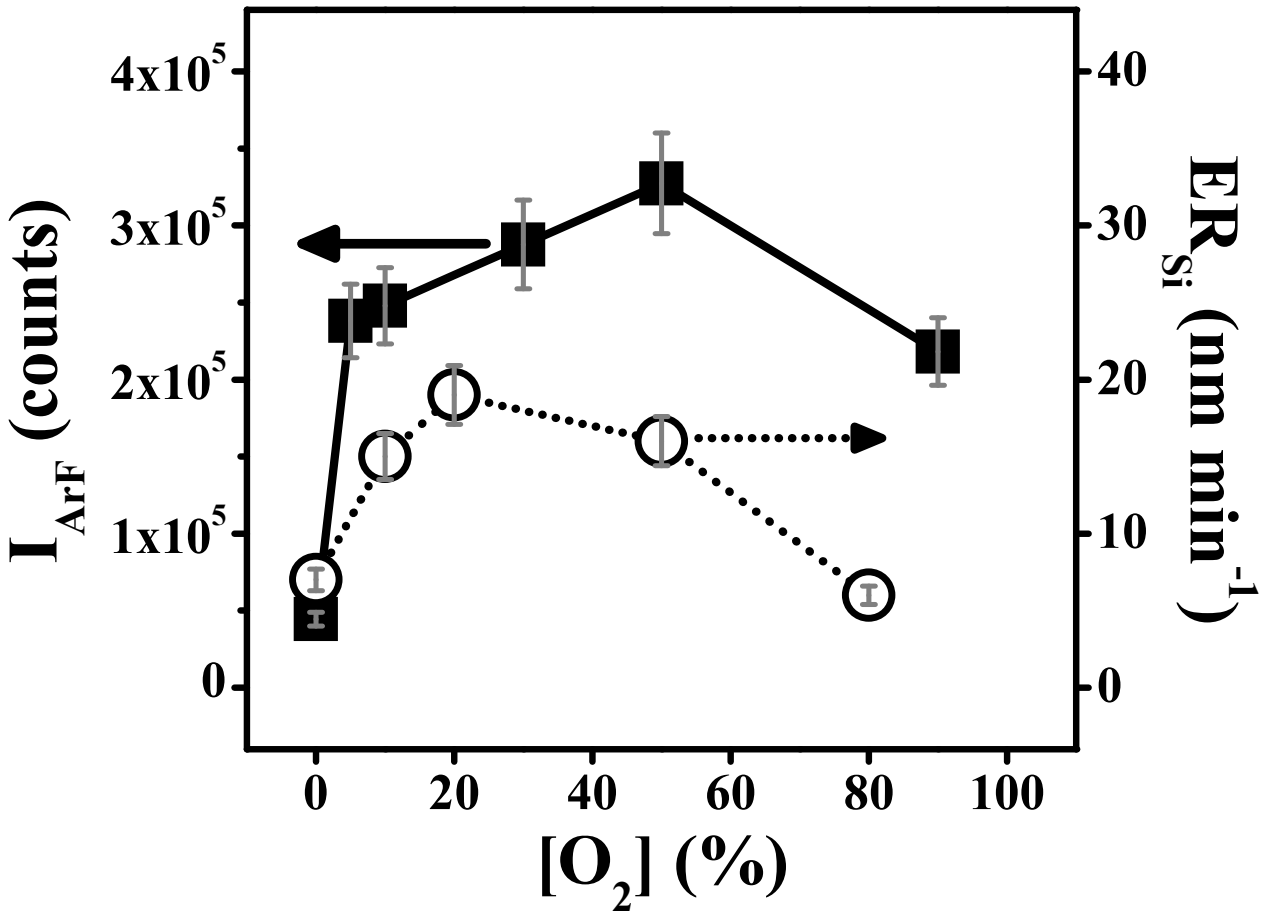
4x10^5
3x10^5
2x10^5
1x10^5
0
I_ArF (counts)
40
30
20
10
0
ER_Si (nm min^-1)
0
20
40
60
80
100
[O_2] (%)

Figure 5

Figure and Text for the Table of Contents

UV-Vis emission spectra of atmospheric pressure filamentary DBDs fed with argon, a fluorocarbon compound (i.e. CF_4, C_3F_8, C_3F_6 and c-C_4F_8) and O_2 were investigated by OES. O_2 addition to the feed gas reduces the emissions of fluorocarbon fragments (i.e. CF, CF_2, CF_2^+, CF_3) and, as shown in the Figure, results in the appearance of an intense narrow emission at 193 nm and of a broad continuum centred at 290 nm ascribed to ArF and Ar_2F excimers, respectively