



Effect of VUV radiation and reactive hydrogen atoms on depletion of fluorine from polytetrafluoroethylene surface

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ABSTRACT

Modification of polytetrafluoroethylene (PTFE) surface upon treatment with reactive species from hydrogen plasma (ions, neutral atoms, and UV/VUV) as well as synergistic effects are presented and explained. PTFE samples were either directly exposed to hydrogen plasma or separately to UV/VUV radiation or atomic hydrogen, and the resulting evolution of the surface composition was determined by X-ray photoelectron spectroscopy. High-density plasma was created by an inductively-coupled radiofrequency discharge in the H-mode. Samples placed in specially designed holders were covered with various optical windows (magnesium fluoride, quartz glass, or borosilicate glass), to allow for separate treatments with either VUV, UV or visible radiation. Rapid fluorine depletion was observed either at a direct exposure to plasma or to VUV; however, the best results were observed at a combined treatment with VUV/UV and atomic hydrogen. For direct treatment, a minimum in the F/C ratio was observed at the shortest time of 1 s. The F/C dropped from 2.2 to 0.4, whereas at longer times it increased to 1. For treatment with UV/VUV and for the combined treatment with UV/VUV and atoms, the F/C decreased with treatment time and stabilized at 0.6 and 0.4, respectively. Exposure to the afterglow did not result in significant modification.

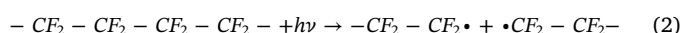
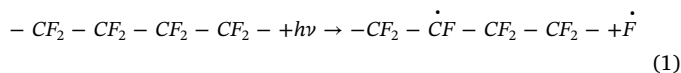
1. Introduction

Plasmas are often used for improving surface wettability of polymeric materials [1]. Reactive species formed in plasma such as ions, neutral atoms, metastables, electrons, and UV/VUV radiation play an important role in polymer surface modification [2–4]. By choosing a different configuration of the discharge system and different discharge parameters, it is possible to manipulate the type and density of plasma radicals and ions to which polymer is exposed, and consequently, influence the degree of a polymer surface modification. In some studies, it was found that a single type of plasma species (often atoms in the ground state) already causes modification of a polymer surface, but many authors agree that synergistic effects are often much more important [5–8].

The wettability of most polymers is increased by a brief treatment with oxygen plasma [9]. Although the exact mechanisms on the atomic scale are still unclear, it is generally accepted that the reactive oxygen plasma species interact chemically with the polymer surface causing functionalization with polar functional groups [10]. Such a treatment, however, is rather insufficient in the case of fluorinated polymers because the treatment with oxygen plasma often leads to etching rather

than functionalization [11–13].

Nevertheless, it has been shown by several authors that the PTFE surface layer can be modified significantly using plasmas containing hydrogen that causes depletion of fluorine from the surface of PTFE [14–16]. In a previous paper, we have treated PTFE with H₂S plasma and found significant depletion of fluorine from the polymer surface, which was explained by photolysis, which appeared as a consequence of irradiation with VUV photons and simultaneous interaction with hydrogen atoms [17]. As shown by Skuratet et al., VUV photolysis of PTFE can cause the formation of free radicals [18]:



These free radicals can react with hydrogen atoms from plasma. However, it is still unclear whether solely individual species such as only VUV or only hydrogen atoms alone can cause significant surface modification, or whether a necessary condition to cause surface depletion of fluorine is a synergy between VUV and hydrogen atoms.

Tajima et al. [19] investigated the crosslinking of polyethylene (PE)

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surface exposed to ions, neutrals, and photons from inductively coupled Ar plasma. To de-convolute the effects of the various plasma species, Tajima used various optical windows with different transmissivities such as LiF, CaF₂, Al₂O₃, and SiO₂. The extent of surface crosslinking was determined by measuring the coefficient of friction. They found that surface modification occurred primarily because of the simultaneous effects of uncharged particles and VUV radiation, and secondarily due to ions and VUV radiation. Especially the VUV radiation at 137.7 nm was found to be important for chain-induced crosslinking.

Cho et al. investigated the modification of polyethylene terephthalate (PET) films exposed to the Ar–O₂ mixture [20] and to pure Ar plasma [3]. For both types of plasma, PET samples were either directly exposed to plasma or were covered with MgF₂ or quartz optical windows, transmitting only UV/VUV or UV radiation, respectively. They found that UV/VUV photons did not cause any changes in the surface roughness. Moreover, in the case of pure Ar plasma, UV/VUV photoirradiation did not cause any significant degradation of oxygen functionalities on the PET surface. However, degradation of C–O and O=C–O and consequential increase in C=O was observed for the sample exposed directly to Ar plasma. In the case of the Ar–O₂ mixture, they found the formation of the oxygen functionalities on the PET surface. Because of the elimination of ion etching, the formation of oxygen functionalities was enhanced for the sample covered with both optical windows in comparison to the sample that was directly exposed to Ar–O₂ plasma.

The same group also investigated the modification of PET polymer versus the dose of VUV photons emitted from O₂ or H₂ plasma [21]. They found that VUV irradiation caused the cleavage of C–O and O=C–O groups. Their concentration decreased and a carbonized layer that absorbs VUV photons was formed; therefore, reactions induced by VUV photons were limited to only several nanometers below the surface. They also found that VUV irradiation had only a minor effect on the surface roughness because only a slight increase in surface roughness was observed, and the surface remained smooth even after prolonged VUV irradiation. VUV irradiation also caused a decrease in the PET film thickness as a consequence of bond cleavage and formation of volatile products that desorb from the surface upon vacuum conditions [21]. They also proposed a model of modification by VUV photons and atoms from oxygen and hydrogen plasma. After the formation of dangling bonds during photolysis induced by VUV photons acting on C–O and O=C–O groups, hydrogen atoms from H₂ plasma terminated the dangling bonds. Whereas in the case of oxygen plasma, the dangling bonds acted as reaction sites for further reaction with oxygen atoms (either in the ground or metastable states) and molecules leading to an increase of the amount of C–O and O=C–O groups [21].

To further enlighten the role of various species and their synergy, we have investigated the mechanisms of PTFE modification in H₂ plasma and the role of various plasma species, especially the role of UV/VUV radiation and neutral hydrogen atoms.

2. Experimental

2.1. Plasma treatment

PTFE foils with a thickness of 0.5 mm were purchased from Goodfellow Ltd. The foils were cut to rectangular pieces with a size 5 × 5 mm² and placed to different positions in a plasma system shown in Fig. 1.

The discharge tube made from borosilicate glass was pumped with a rotary pump of a nominal pumping speed of 80 m³ h^{−1}, and the final pressure was approximately 1 Pa. Experiments were performed at the hydrogen pressure of 25 Pa (flow rate 85 sccm). Plasma was created using an RF discharge inside the discharge tube with a length of 80 cm and a diameter of 4 cm. A coil with six turns was mounted to the tube, as shown in Fig. 1. The coil was connected to an RF generator via a matching network. The RF generator operated at a frequency of

13.56 MHz, and its forward power was set to 500 W. At these conditions, highly luminous plasma was limited inside the coil, and discharge was sustained in the almost pure inductive mode (H-mode). The dissociation fraction was of the order of 10% and the radiation flux 10¹⁶ cm^{−2} s^{−1}. The power density was 25 W cm^{−3}.

PTFE samples were placed at three different positions: (1) in the middle of the coil, where the sample is subjected to various species including atoms, ions, and UV/VUV radiation; (2) to the early afterglow 2 cm away from the coils left edge, where the contribution of ions is negligible; and (3) in the late afterglow 55 cm from the coils left edge, where the sample is exposed to hydrogen atoms only. All three positions are marked in Fig. 1. Furthermore, for the cases of samples being placed in the glow and early afterglow regions, the samples were mounted onto holders with or without an additional top shielding using MgF₂, quartz or borosilicate optical windows to either transmit a specific type of radiation or eliminate the UV/VUV radiation, ions and/or atoms. When using a top-shield window, two configurations were applied; hereinafter called open or closed configuration. In a closed configuration, the sample was placed in a modular borosilicate glass chamber (holder) and covered by one of the above mentioned top-shield windows. In such a configuration, the contributions of atoms and ions were eliminated, and only photons with a particular wavelength were transmitted. Whereas in an open configuration, a 10 mm opening was made on the side of the glass chamber to allow hydrogen atoms enter the space inside the glass chamber by diffusion – in this case, the sample was exposed to atoms and radiation, but not to ions (plasma generation within the sample chamber was not possible due to the small size of the chamber). All three sample mounting configurations are shown in Fig. 2.

MgF₂ window (thickness 2 mm) was purchased from Crystal GmbH. The quartz glass windows of thickness 1.1 mm were purchased from Jinzhou City Success Quartz Glass Factory and the borosilicate windows of thickness 1.1 mm from Deltalab. In Table 1, the characteristics of the top-shield windows are shown. MgF₂ window is transparent for UV and VUV radiation, i.e., wavelengths longer than 115 nm. Quartz window is transparent for UV radiation, i.e., wavelengths longer than 155 nm, whereas borosilicate window effectively absorbs both VUV and a part of UV radiation because it is transparent for wavelengths above ~ 300 nm.

Exposure times of the samples ranged from 1 to 7 s for the experiments where samples were exposed directly to plasma and for experiments with the MgF₂ window. Experiments with quartz and borosilicate windows were performed only at exposure times of 5 s.

2.2. Plasma characterization

Plasma was characterized by optical emission spectroscopy (OES) and catalytic probes (to determine the density of hydrogen atoms). OES measurements were performed using a 16-bit Avantes AvaSpec 3648 fiber optic spectrometer, with a nominal spectral resolution of 0.5 nm in the range of 200 to 1100 nm. The integration time ranged from 0.1 ms to 60 s. A typical OES spectrum is shown in Fig. 3. Here, the H_α, H_β, and H_γ lines were left to saturation to make the Fulcher band of hydrogen molecules clearly distinguishable. The OES spectra were measured along the tube to get a distribution of radiation. Because of the linear response of the sensor, normalization to the lowest integration time was done. The results are shown in Fig. 4.

Hydrogen atom density along the tube was measured with a catalytic probe described elsewhere [22]. The results are shown in Fig. 5.

2.3. Surface characterization

For surface characterization of PTFE samples after various treatments, we used an XPS instrument TFA–XPS from Physical Electronics (Munich, Germany). The samples were excited with monochromatic Al K_{α1,2} radiation at 1486.6 eV over an area of 400 μm². Photoelectrons were detected with a hemispherical analyser positioned at an angle of

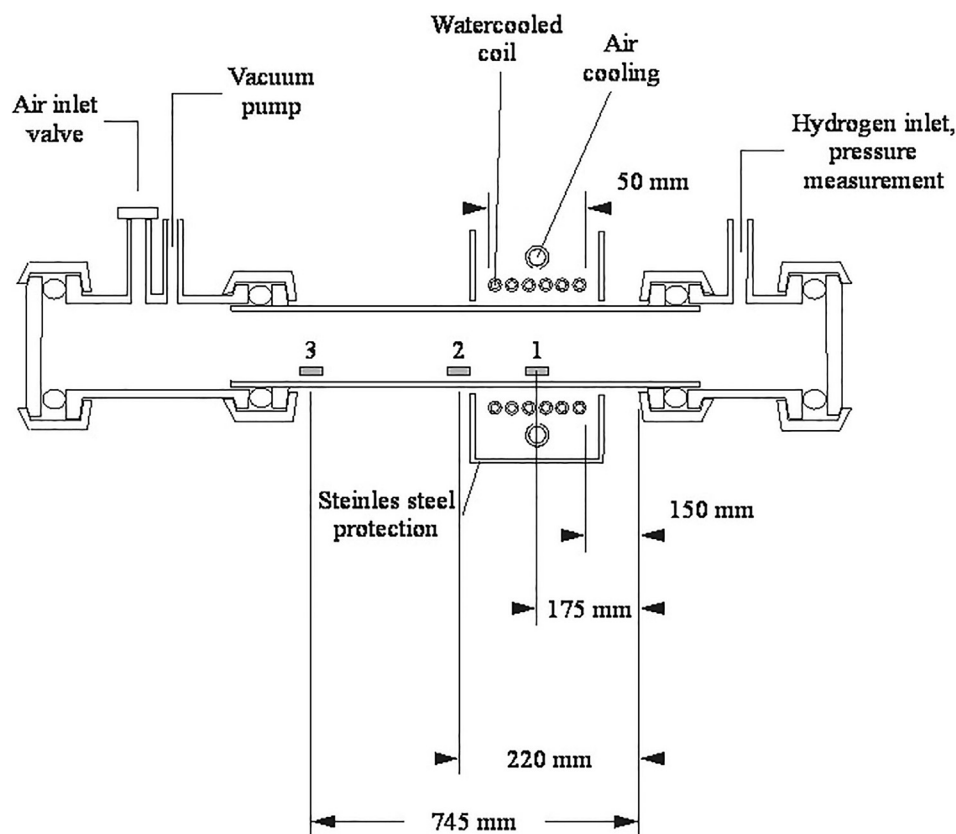


Fig. 1. Experimental plasma system.

45° with respect to the normal of the sample surface. XPS survey spectra were measured at a pass energy of 187 eV using an energy step of 0.4 eV. High-resolution C1s peaks were measured at a pass energy of 29.35 eV using an energy step of 0.125 eV. Individual survey and high-resolution spectra of the samples can be found in [Supplementary information](#). An additional electron gun was used for surface neutralization during XPS measurements. Spectra were calibrated by using adventitious carbon C-C that was assigned a value of 284.8 eV. The measured spectra were analysed using MultiPak v8.1c software (supplied by Physical Electronics, Munich Germany).

3. Results and discussion

Samples were treated in the highly luminous plasma when placed at position 1, as marked in [Fig. 1](#). The time evolution of PTFE surface atomic composition for the case of direct plasma treatment (configuration A in [Fig. 2](#)), as deduced from XPS survey spectra, is shown in [Fig. 6](#). Individual XPS survey spectra can be found in [Supplementary \(Fig. S1\)](#). As expected, the surface of the untreated PTFE contains only carbon and fluorine. The fluorine concentration is ~ 69 at. %, which is close enough to the theoretical value (i.e., ~ 67 at. %). Even a second of exposure to luminous hydrogen plasma causes a dramatic decrease in the fluorine content, which is also reflected in the shape of C1s peaks showing degradation of CF₂ groups (see [Fig. S2](#) in [Supplementary](#)). The original F/C ratio of 2.2 drops to approximately 0.4. Simultaneously, some oxygen appears on the surface. The decrease of the F/C ratio is explained by a bond scission because of VUV radiation, as shown in [Eq. \(1\)](#). The appearance of oxygen may or may not be due to the residual atmosphere in the plasma system. Dangling bonds formed upon treatment of the PTFE may interact with oxygen upon breaking vacuum conditions and before mounting the sample into the XPS instrument. The concentration of oxygen is rather low at up to a few at. %, thus the surface of the sample treated directly with hydrogen plasma is far from

being completely oxidized.

Such a quick modification of the PTFE surface, as shown in [Fig. 6](#), and in [Supplemental \(Figs. S1, S2\)](#), is explained by extensive radiation in the UV and VUV range of the OES spectrum. Our spectrometer does not allow measuring the hard UV part of the spectrum, but the intensive Balmer series suggest even more intensive Lyman series of hydrogen atoms. The Balmer series reveal transitions to the first excited state, whereas the Lyman series reveal transitions to the ground state; therefore, the latter is always more intensive. According to Fantz et al. [\[23\]](#) the intensity of Lyman series is over an order of magnitude larger than the Balmer series in the inductively coupled plasma (ICP) in the H-mode sustained in a practically identical reactor as ours. Furthermore, Fantz also measured the molecular bands (both Lyman and Werner) and found their intensity comparable to the Lyman H_α. In fact, they found that the total VUV flux onto a surface facing hydrogen ICP plasma is few times 10²⁰ photons m⁻² s⁻¹ and the radiant power in the VUV range is approximately 100 W at the forward RF power of 600 W. Such a huge flux of VUV radiation causes significant bond scission in the thin surface film as the penetration depth is only of the order of 10 nm.

The F/C ratio in [Fig. 6](#) does not decrease further for treatment times more than a second. In fact, the opposite effect is clearly visible in [Fig. 6](#): there is a minimum in the F curve. The minimum has been already observed for other plasma/polymer systems and explained by thermal effects [\[24\]](#). The PTFE sample exposed directly to hydrogen plasma is heated predominantly by surface neutralization of hydrogen ions, absorption of photons, and surface recombination of hydrogen atoms to parent molecules. Furthermore, the ions bombard the surface because they are accelerated in the sheath next to the surface. In our case, the samples were kept at a floating potential; therefore, the kinetic energy of ions is approximately 20 eV. The contribution of different mechanisms for heating the material cannot be calculated because of uncertainties in coefficients, but they can be estimated. The density of plasma sustained in the H-mode at the pressure of a few 10 Pa is often

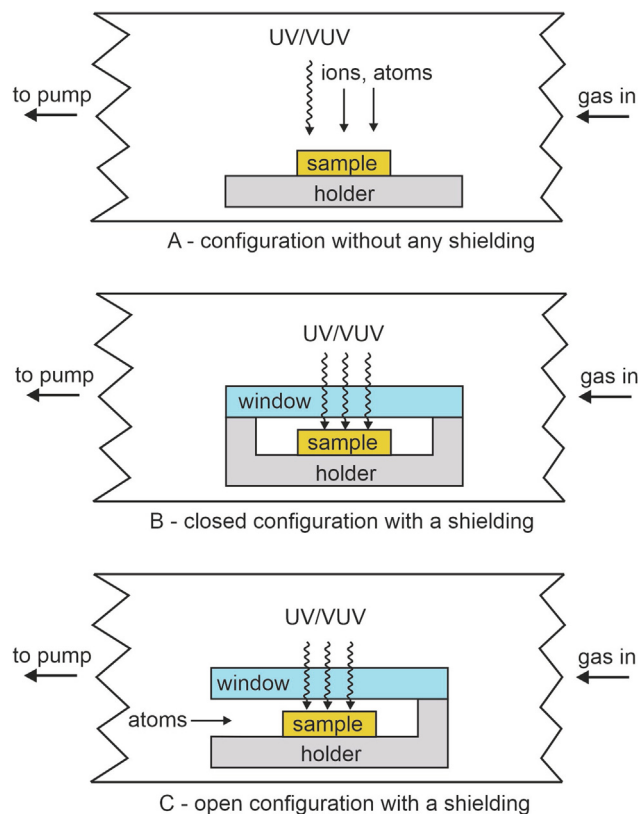


Fig. 2. The sample holders. A) the sample is placed on a microscope slide, B) the sample in modular borosilicate glass sample holder is covered with a window to prevent any interaction with ions or atoms, C) same as B) but there is an opening in the side-wall of the sample holder to allow H-atoms interacting with the sample.

Table 1

Characteristics of different top window shields used in the experiments.

Top windowshield	Transparent for wavelengthslonger than	Cutoff wavelength**	Radiation
MgF ₂	115 nm*		VUV + UV
Quartz	155 nm*	164.4 nm	UV
borosilicate	> 300 nm***	330 nm	Above UV

*as measured by OES [3,20].

**corresponding to 20% transmittance [19].

*** measured with our OES.

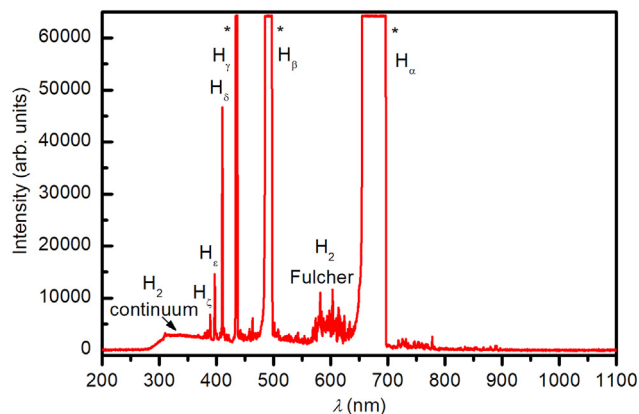


Fig. 3. A typical OES spectrum of hydrogen plasma inside the coil.

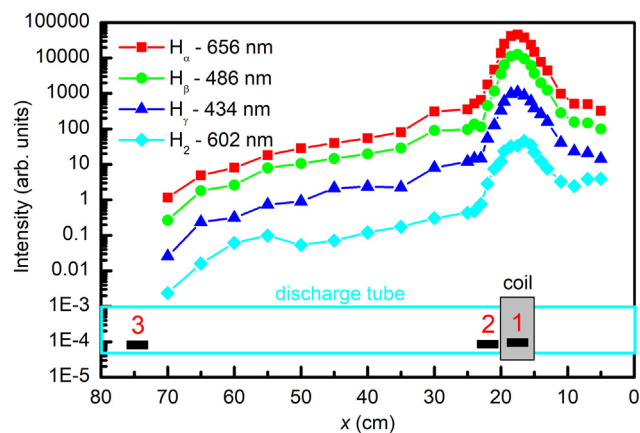


Fig. 4. Variation of the intensity of typical spectral features along the discharge tube. Rectangle indicates the position of the coil. Various positions of the samples are shown with numbers: (1) in glow region, (2) early afterglow, and (3) late afterglow.

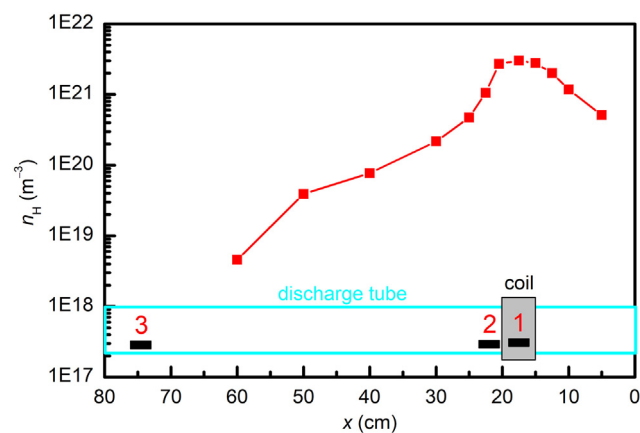


Fig. 5. Variation of the H-atom density along the discharge tube.

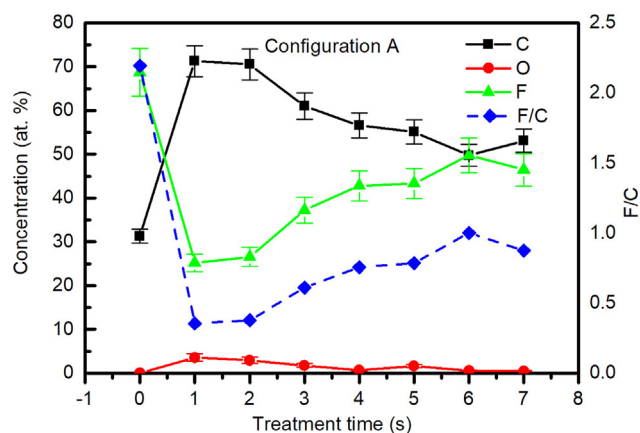


Fig. 6. The time evolution of the surface composition for a direct exposure of PTFE to hydrogen plasma (configuration A in Fig. 2).

few times 10^{18} m^{-3} . The flux of ions onto the surface of a plasma-facing material is a product of an ion density and the Bohm velocity [25], i.e., $4 \times 10^4 \text{ W m}^{-2}$ at the ion density of 10^{18} m^{-3} . The power dissipated on the polymer surface by heterogeneous recombination of H atoms to parent molecules can be estimated from a known H-atom density (Fig. 5) and its recombination coefficient (i.e. $(8 \pm 3) \times 10^{-4}$ [26]). At the H-atom density of 3×10^{21} (see Fig. 5) and the average random velocity of H atoms of 3000 m/s, the power dissipated on the PTFE

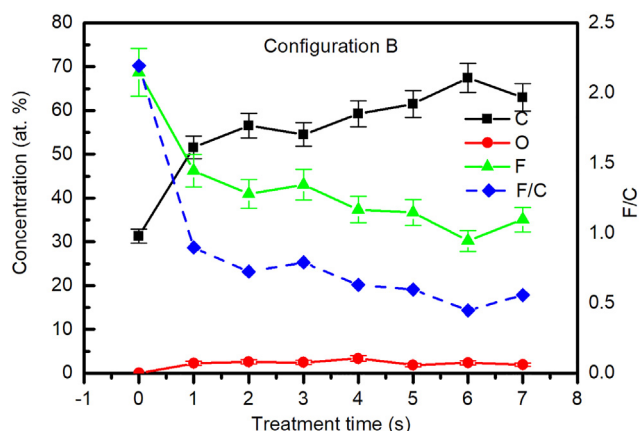


Fig. 7. The time evolution of the surface composition for exposure of PTFE to VUV radiation from hydrogen plasma only (configuration B in Fig. 2).

surface because of heterogeneous recombination of H atoms is just below 10^3 W m^{-2} . This is at least an order of magnitude smaller than the power dissipated due to surface neutralization of charged particles and bombardment by ions because of the fact, that the foil was always at the floating potential. The power dissipated by absorption of UV and VUV radiation with the flux $10^{20} \text{ m}^{-2} \text{ s}^{-1}$ [23] is roughly 160 W m^{-2} . There are other heating methods such as accommodation of gaseous molecules and atoms, but their energy is marginal as compared to the potential and kinetic energy of ions. The polymer temperature, therefore, increases rapidly upon direct treatment with gaseous plasma (configuration A in Fig. 2), and much slower in the case of indirect treatments (configurations B and C in Fig. 2). Melting was observed with a naked eye after approximately 10 s of the direct plasma treatment. The increased temperature causes photochemical etching of the PTFE, and thus a loss of F-depleted material. That is why a minimum is observed in the F curve of Fig. 6.

The evolution of surface composition with treatment time is different when the sample is covered with a window (see also Fig. S3 in Supplemental). Fig. 7 reveals the atom concentration on the PTFE surface as deduced from XPS survey spectra for the case of a closed configuration B as shown in Fig. 2. In this configuration, the sample is exposed to the radiation only, because the MgF_2 window prevents ions or atoms to interact with the PTFE surface. Interestingly enough, the F/C ratio decreases significantly even after a second of treatment, but not as much as in the case of direct exposure to hydrogen plasma. The result shown in Fig. 7 indicates that the F/C ratio drops to approximately 0.9 after a second of treatment with the radiation only and keeps decreasing until it becomes approximately 0.5, i.e., close to the value observed in Fig. 6 for 1 s treatment. Evidently, the radiation alone can cause the desired modification; however, the required treatment time to obtain a very low F/C ratio is longer. In this case, the thermal effects are less pronounced than in the case of direct exposure to plasma but not negligible taking into account intensive radiation, at least for treatment times up to 7 s. Therefore, no degradation of the F-depleted layer is observed and the CF_2 peak in high-resolution spectra (see Fig. S4 in Supplemental) keeps decreasing with increasing treatment time.

Because the F/C ratio does not increase for prolonged treatment, and the CF_2 peak does not partially recover as in the case of the configuration A, it is feasible to conclude that the heating is not extensive enough to cause significant desorption of F-depleted material. As already estimated, the major heating mechanism of any plasma-facing material is surface neutralization and bombardment with ions. Because the sample in the configuration B (Fig. 2) is exposed to VUV radiation only, the heating is moderate at about 160 W m^{-2} . Such a power density will cause heating at the rate of the order of 1 K/s providing the thermal capacity of the shield from Fig. 2B is large.

Similar results as in the configuration B of Fig. 2 are also observed in

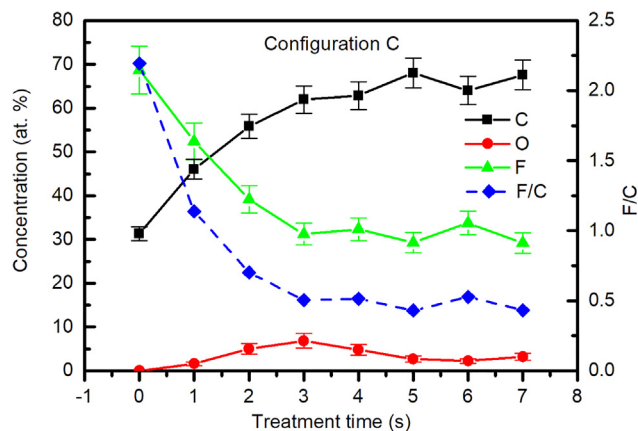


Fig. 8. The time evolution of the surface composition for exposure of PTFE to VUV radiation from hydrogen plasma and H-atoms (configuration C in Fig. 2).

the configuration C. In this case, the PTFE samples were allowed to interact with atomic hydrogen as well as with radiation. The time evolution of the surface composition for configuration C (Fig. 2) at position 1 (Fig. 1) is shown in Fig. 8. Corresponding XPS survey and high-resolution spectra are shown in Figs. S5 and S6 in Supplemental. The curves in Fig. 8 are rather smooth and indicate the asymptotic approach of the surface composition to the value observed for the case of direct exposure to the hydrogen plasma for 1 s. The thermal effects in configuration C should be similar to that of the configuration B, because the H-atom density within the shield should be much smaller than in the unperturbed plasma (Fig. 5).

For comparison, the time evolution of the most important result (i.e., F/C ratio as deduced from XPS survey spectra) for all three configurations is shown in Fig. 9. The measured data points are somewhat scattered, but the trend is obvious: for the case of direct exposure to hydrogen plasma (configuration A) a minimum is observed, whereas for the other two cases (configurations B, C) a gradual approach of the F/C ratio to the value of approximately 0.5 is observed. As mentioned earlier, the minimum in the curve obtained for the case of direct exposure is attributed to thermal effects that in turn cause significant desorption of light C-rich fragments. There is a slight difference between configurations B and C, but it is hardly relevant, taking into account the accuracy of XPS.

In another set of experiments, the MgF_2 window was replaced with quartz glass or a borosilicate glass window using the configuration B (Fig. 2). The experiments were only performed for the treatment time of 5 s where the results presented in Fig. 9 show already good depletion of

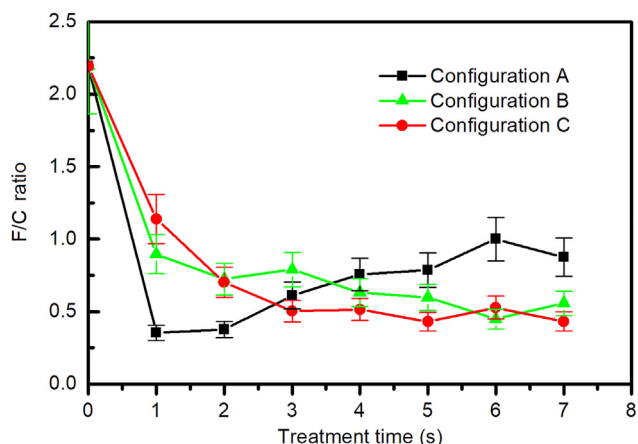


Fig. 9. Variation of the F/C signal versus treatment time for PTFE sample with or without shielding with MgF_2 window.

Table 2

Surface chemical composition of PTFE samples placed in a glow region (position 1) after treatment with various plasma species for 5 s.

Sample position	Configuration – treatment conditions	C (at. %)	O (at. %)	F (at. %)	F/C	Plasma species
1 - H ₂ glow	untreated	31.1	0.4	68.5	2.2	
	A - without window	55.1	1.6	43.3	0.8	H, H ⁺ , UV, VUV
	B - MgF ₂ closed	61.5	1.8	36.7	0.6	UV, VUV
	C - MgF ₂ open	68.0	2.7	29.3	0.4	H, UV, VUV
	B - Quartz closed	39.2	2.4	58.4	1.5	UV
	B - borosilicate closed	32.1	0.6	67.3	2.1	/

F for the configurations B and C. The F/C ratio for all configurations when the samples are treated in the middle of the coil (position 1 of Fig. 1) are summarized in Table 2. The F/C ratio for the case of the sample covered with a quartz window is 1.5. This value is definitely below the value typical for the untreated PTFE, but much higher than for the case of a sample covered with MgF₂ window. As mentioned earlier in this paper, the quartz glass is transparent for UV, but absorbs VUV radiation. The result of Table 2 clearly shows that the UV radiation causes depletion of F from the surface, but the effect is far less pronounced than for VUV radiation. According to Fantz et al. [23], the UV radiation from ICP hydrogen plasma in the H-mode arises partially from the Lyman B – X band as well as the continuum (transition a – b) of neutral hydrogen molecules. The radiation in the range above 155 nm (the cut-off, see Table 1) is comparable to the radiation in the VUV range, but the depletion of the surface (Table 2) is much less efficient, especially when considering the behaviour of curves presented in Figs. 7 and 8. The UV radiation definitely causes bond scission in the surface of PTFE and thus F depletion, but the lower efficiency as compared to VUV could be explained by a larger penetration depth of such radiation in polymers. The penetration depth increases with increasing wavelength in the UV-VUV range so fewer photons are absorbed in the surface film (as probed by XPS); therefore, the depletion of F is much lower in the case of UV than VUV radiation. Still, it is not negligible, as deduced from the result shown in Table 2.

Table 2 also shows the surface composition as measured by XPS in the case when the sample is in configuration B of Fig. 2, but the window is made from borosilicate glass. The F/C ratio for this case is practically the same as for the untreated sample. As shown in Table 1, this material is neither transparent for VUV nor UV, thus the result is highly expected.

The treatment of the PTFE samples in all three configurations (A, B, and C) was also performed away from the region of extensive luminosity. Fig. 4 reveals that the radiation at position 2 is roughly two orders of magnitude less intensive than within the coil. This position is referred to as “early afterglow”. At position 2, the radiation and the flux of ions on the PTFE surface are much less intensive than at position 1 (in the centre of the coil), but the H-atom density is almost comparable, as shown in Fig. 5. The results of XPS characterization using different configurations for the case of exposure to the early afterglow of hydrogen plasma for 5 s are shown in Table 3. The F/C ratio for the case A of direct exposure of PTFE to an early afterglow for 5 s is rather low at 0.6. This value is somehow larger than for the optimal treatments in the glowing plasma itself, but the difference is not significant. Radiation effects cannot explain the result because of the huge differences, as shown in Fig. 4. Furthermore, the density of charged particles at

position 2 is negligible as compared to glowing plasma inside the coil. The rather complete depletion of the F in the case of direct exposure to the early afterglow is therefore explained by extensive interaction of PTFE surface with atomic hydrogen. The thermal effects in the early afterglow are considered to be of minor importance for the 5 s treatment; therefore, one can conclude that a large flux of atoms (similar to that in the centre of the coil) together with weak irradiation causes surface modification. This conclusion is supported by the F/C ratio for the samples covered with MgF₂ window (configuration B, C), which is also presented in Table 3. For the case of a covered sample, the F/C ratio hardly differs from the value of an untreated sample. The huge difference in the F/C ratios between the uncovered (marked as “A - without window” in Table 3) and the sample covered with MgF₂ window (marked “B - MgF₂ closed” in Table 3) therefore confirms the key role of atomic hydrogen. Poor depletion in the case of PTFE exposure to the early afterglow was also observed for the case of borosilicate glass and MgF₂ windows in the configuration C of Fig. 2. In the case of borosilicate glass, the measured F/C is even somehow larger than for untreated samples but within the limits of an experimental error.

Few samples were also treated in the late afterglow, at position 3, as marked in Fig. 1. Based on the results summarized in Tables 2 and 3, only direct exposures were performed (configuration A in Fig. 2). As shown in Fig. 4, the radiation in the late afterglow is further reduced and is 4–5 orders of magnitude weaker than inside the coil. Also, the H-atom density is close to the detection limit of the catalytic probe (see Fig. 5). The F/C ratio of a sample exposed to the late afterglow is added to Table 3. It is the same as for the untreated sample indicating a little effect of such treatment on the surface chemistry. Obviously, both the H-atom density and the radiation are too weak at the position 3 of Fig. 1 to cause any measurable effect after 5 s.

The results summarized in Tables 2 and 3, therefore, indicate the synergy between the UV and/or VUV radiation and H atoms. The difference in the F/C ratio for the direct treatment and treatment with the MgF₂ window (Table 3) is significant (0.6 versus about 2). It is not feasible to measure the H-atom flux onto the surface of the PTFE sample in the configuration C, but it is definitely much smaller than in the configuration A. The reason is surface recombination of H atoms within the shield covered with the MgF₂ window. The loss of atoms should be replaced by diffusion of H atoms from the surrounding atmosphere as shown with an arrow in Fig. 2C. The diffusion is a slow process for particle transport, so the H-atom density within the shield of Fig. 2C is much smaller than in the configuration of Fig. 2A. The F/C ratio for the “closed” and “open” configurations in Tables 2 and 3 is similar, and so is in configurations B and C in Fig. 9. This observation indicates that

Table 3

Surface chemical composition of PTFE samples placed in the early or late afterglow (position 2, 3) after treatment with various plasma species for 5 s.

Sample position	Configuration – treatment conditions	C (at. %)	O (at. %)	F (at. %)	F/C	Plasma species
2 - Early afterglow	A - without window	58.5	4.6	36.9	0.6	H, UV, VUV
	B - MgF ₂ closed	33.7	0.9	65.5	1.9	UV, VUV
	C - MgF ₂ open	32.0	0.5	67.5	2.1	H, UV, VUV
	C - borosilicate open	29.5	0.7	69.8	2.4	H
	A - without window	31.3	0.8	67.9	2.2	H

the required flux of H atoms to benefit from the synergy with VUV radiation is rather small, definitely much smaller than the available H-atom flux in the configuration without the MgF₂ window.

A feasible explanation of the synergy between the H atoms and radiation is as follows: The VUV and even UV radiation causes bond scission. The VUV photons' energies exceed the C-F binding energy, which is approximately 6 eV [27]. The H atoms (if present) terminate the dangling bonds and also interact with F-atoms to form more stable HF molecules. The flux of H atoms on the surface of a sample directly exposed to plasma in the H-mode or in the early afterglow is large. Fig. 5 reveals H-atom densities between approximately 6 and $30 \times 10^{20} \text{ m}^{-3}$, which corresponds to the flux of H atoms onto the surface of between 6 and $30 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ at the neutral gas kinetic temperature of 700 K. This is orders of magnitude larger than the flux of photons (approximately $1 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$). The available flux upon direct exposure is more than enough to terminate the dangling bonds and thus prevent the termination by F atoms. If the flux of H atoms is insufficient, the depletion of the surface layer is a much slower process as revealed from the comparison between the direct and indirect treatment in the early afterglow (Table 3).

4. Conclusions

The experimental results presented in this paper show the rapid depletion of fluorine from the PTFE surface, providing the fluence of VUV radiation is rather significant. Because the penetration depth of VUV in organic material is low, the extensive absorption of such photons causes significant bond scission in the surface layer of PTFE. According to the results summarized in Figs. 7–9, the required VUV fluence for the optimal depletion of fluorine from the PTFE surface is close to 10^{17} cm^{-2} . The atom surface density in solid materials is of the order of 10^{15} cm^{-2} ; therefore, the efficiency of VUV radiation is far from 100%, which can be explained by a finite penetration depth of such photons in the PTFE material. The efficiency is further increased by synergistic effects of hydrogen atoms. In the case of direct exposure of PTFE to hydrogen plasma in the H-mode, the required VUV fluence for the optimal depletion is a few times lower than for the case of VUV radiation alone. Nevertheless, the required fluence is not so significantly lower; therefore, it can be concluded that in most practical cases, the exposure of PTFE to VUV radiation alone is effective enough. The direct exposure to plasma causes pronounced heating of the polymer; therefore, the optimal conditions are within a very limited range of treatment times. This effect makes direct exposure less attractive for practical applications where depletion of fluorine from the PTFE surface is desired, i.e., for improved wettability before deposition of the desired coating. The UV radiation itself (without VUV contribution) causes weak depletion of the PTFE surface which is explained by the fact that the photons in the high-energy part of the deep UV radiation have the energy larger than the C-F binding energy, but the penetration depth in organic material for UV is larger than for VUV, so the surface effects are less pronounced. The H atoms alone (without hard UV or VUV radiation) do not cause measurable effects on the surface composition of PTFE.

The work presented in this paper was performed using small samples placed in the experimental plasma device separately. In any practical application, however, the materials to be depleted from fluorine should move through the discharge zone at speed optimized to achieve the appropriate fluences of reactive plasma species and radiation.

CRediT authorship contribution statement

Dane Lojen: Visualization, Investigation, Formal analysis. **Rok Zaplotnik:** Conceptualization, Methodology. **Gregor Primc:** Validation, Data curation. **Miran Mozetič:** Writing - review & editing, Funding acquisition. **Alenka Vesel:** Supervision, Project

administration, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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