Title:

Effect of humidity conditions on active oxygen species generated under ultraviolet light irradiation and etching characteristics of fluorocarbon polymer

Kei Oya*, Ryota Watanabe, Yuta Soga, Yuki Ikeda, Takaharu Nakamura, and Satoru Iwamori

*Department of Mechanical Engineering, School of Engineering, Tokai University, 4-1-1
Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan*

* Corresponding author. Phone: +81 463 58 1211 (ex: 4362) FAX: +81 463 59 2207

E-mail address: k.oya@tokai-u.jp

All e-mail address

Kei Oya: k.oya@tokai-u.jp

Ryota Watanabe: 4bmkm074@mail.tokai-u.jp

Yuta Soga: fudou1230@gmail.com

Yuki Ikeda: ikeda0yuki@gmail.com

Takaharu Nakamura: 1bem2233@mail.tokai-u.jp

Satoru Iwamori: iwamori@tokai-u.jp

Abstract

For efficient industrial application, it is necessary to understand the formation mechanisms of active oxygen species under ultraviolet (UV) light irradiation. In this study, active oxygen was generated by UV lamps (providing wavelengths of 185 and 254 nm) at two different humidity levels. The generation of excited singlet oxygen [$O(^1D)$] and hydroxyl radicals (OH^*) in the atmosphere were detected using the electron spin resonance (ESR) method, while ozone (O_3) was detected using a gas tube. The concentrations of $O(^1D)$ and O_3 generated under low humidity conditions were much higher than those generated at high humidity. On the other hand, the concentration of OH^* generated under high humidity condition were much higher than that generated at low humidity. The amount of $O(^1D)$ increased linearly with irradiation time, while the increase of O_3 concentration was observed to be suppressed after 5 min. Fluorocarbon thin films r.f.-sputtered onto quartz crystal oscillators were used to investigate the etching behavior of generated active oxygen species. The etching rates were found to be higher at high humidity, which is believed to be due to the contribution of OH^* whose concentration was higher in the presence of larger amounts of water in the atmosphere.

Keywords: Active oxygen; UV light irradiation; Humidity; Electron spin resonance; Fluorocarbon thin film; X-ray photoelectron spectroscopy.

1. Introduction

Because of its extremely strong oxidative abilities, active oxygen is extensively used in industrial processes, *e.g.* for surface cleaning, modification, and sterilization. In such processes, it is important to control the density of the active oxygen precisely. Measurement of active oxygen species in ambient atmosphere requires specialized and high-cost equipment typically incorporating an optical laser system [1] or a vacuum ultraviolet (UV) light source [2,3]. A simple method for real-time sensing such species using reasonably priced equipment is not currently available. We have previously reported the [sensing](#) of active oxygen using the quartz crystal oscillator of a quartz crystal microbalance (QCM) coated with a fluorocarbon thin film [4,5]. The adhesion properties and effect of atomic oxygen exposure on the surface of the fluorocarbon thin films were also studied [4,5].

Although many species of active oxygen are known, those with long lifetime or high oxidation abilities such as excited singlet oxygen [atom](#) [$O(^1D)$], ozone (O_3), hydroxyl radicals (OH^*), and hydrogen peroxide (H_2O_2), are of special interest [6-14]. Such species were proposed to form as follows [9-14]. [Firstly, being irradiated with UV light with the wavelength of 185 nm, a ground-state oxygen molecule \(\$^3O_2\$ \) decomposes into two ground-state oxygen atoms \[\$O\(^3P\)\$ \]. Then, \$O_3\$ is formed when \$O\(^3P\)\$ binds with another \$^3O_2\$. An \$O\(^1D\)\$ and an excited singlet oxygen molecule \(\$^1O_2\$ \) are generated when \$O_3\$ is decomposed by irradiation of UV light with 254 nm. Finally \$OH^*\$ species come to being when \$O_3\$ are decomposed and bind with hydrogen atoms. The \$OH^*\$ radicals are also generated through the exposure of water molecules to UV light with the wavelength of 185 nm.](#)

Because the above reactions are based on the decomposition of oxygen and water molecules, it is necessary to control the environmental humidity when generating active oxygen species. However, while for industrial applications understanding the formation

mechanisms of all active oxygen species is important, their generation behavior has not been described in detail thus far. The electron spin resonance (ESR) spectroscopy is one of the most efficient methods to detect radicals with short lifetime, such as $O(^1D)$ and OH^* [15,16]. In this method, stable radicals are first generated via reaction with a spin-trapping agent and then detected by an ESR apparatus. However, there are no reports on detection of active oxygen species in the atmosphere. In this study, qualitative and quantitative analyses of active oxygen species generated by means of UV lamps (with 185/254 nm) were carried at both low and high humidity.

The oxidation and etching abilities of active oxygen species are expected to be applied surface modification process for polymeric materials. As described above, the fluorocarbon thin film deposited onto the quartz crystal oscillator of a QCM is sensitive to active oxygen species [4,5]. In the present study, to investigate the effect of the generated species on the oxidation and etching of organic materials, the films r.f.-sputtered onto quartz crystal oscillators were prepared, and their etching and surface modification characteristics were evaluated. Fluorocarbon films prepared via r.f. sputtering have been already reported to be etched by atomic oxygen inhomogeneously, although the etching has been observed to proceed linearly with exposure time [4]. In this paper, we study the effect of humidity on the etching behavior of such films in the presence of active oxygen species.

2. Materials and methods

2.1. Generation and detection of active oxygen species

An active oxygen sterilization (AOS) system (Active-Dry, Iwasaki Electric Co., Ltd., Japan) equipped with three UV lamps was used for the generation of active oxygen species.

The combined power of the lamps was 16 W, comprising of two 6 W lamps and one 4 W lamp. The active oxygen species were generated at low and high humidity. The wavelengths of the UV light were 185 and 254 nm. The temperature in the system was kept at 30°C by introducing warm air continuously. For low humidity (< 20%RH), prior to being introduced into the AOS system, dry air was pumped through a bottle with silica gel which was kept at 30°C. For high humidity (> 90%RH), air passed through a water bottle also kept at 30°C. The air pumping was stopped when the exposure of active oxygen was performed.

Generated $O(^1D)$ species were detected through their reaction with a spin-trapping agent, 2,2,6,6-tetramethyl-1,4-piperidone (TEMP; Sigma-Aldrich Co., LLC., USA), which resulted in stable molecules of 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPOL). The UV lamps were used to irradiate a 5 mM TEMP solution for 30 min under low- or high-humidity conditions. The active oxygen species were also generated in a 100 mM TEMP solution for 3, 5, 8, 10, and 15 min at 25°C and at atmospheric humidity about 40%RH. The concentration of produced TEMPOL was detected using an ESR apparatus (JES-FA200, Jeol Ltd., Japan). The generated $O(^1D)$ was detected by measuring the height of the main central peak. A calibration curve was prepared using a TEMPOL solution.

The concentration of generated O_3 (both at low and high humidity) was monitored using gas detector tubes (No.18M, Gastec Corporation, Japan) after UV irradiation for 5, 10, and 15 min. In addition, the amount of O_3 generated at atmospheric humidity after UV irradiation for 5 min was also measured. The detectable concentration range of the used tubes is 4 to 400 ppm.

The generated OH^* were also detected by the spin trapping method. OH^* reacts with 5-(2,2-dimethyl-1,3-propoxycyclo-phosphoryl)-5-methyl-1-pyrroline *n*-oxide (CYPMPO; Sigma-Aldrich) producing stable molecules normally referred to as CYPMPO-OH. CYPMPO was dissolved in *N,N*-dimethylformamide, and the final concentration of the solution was 4

mM. The solution was placed into the AOS system for 5 min and at low, atmospheric, or high humidity. The generated CYPMPO-OH molecules were also detected using ESR. The amount of OH* generated at each humidity was detected by measuring the height of the 5th peak from low magnetic flux density excluding the leftmost Mn peak.

2.2. Preparation of fluorocarbon thin film

Poly(tetrafluoroethylene) (PTFE; Hakudo Co., Ltd., Japan) was deposited using an r.f. sputtering apparatus (RFS-200, Ulvac Inc., Japan) onto quartz crystal oscillators (QA-A9M-AU, Seiko EG&G Co., Ltd., Japan). The oscillators were attached onto a dedicated folder at the anode in the sputtering chamber while the PTFE target was held at the cathode. Plasma discharge was generated by applying voltage after the introduction of Ar gas into the chamber. The r.f. sputtering conditions used are summarized in Table 1.

2.3. Etching behavior of fluorocarbon thin film

The etching behavior of the fluorocarbon thin films exposed to active oxygen species either at low or high humidity were monitored using the QCM method. The specimens were subjected to active oxygen species in the AOS system for 30, 60, 90 and 120 min. The amount of film material etched out was evaluated by monitoring the frequency changes demonstrated by the quartz crystal unit.

2.4. Surface analysis of fluorocarbon thin film

The fluorocarbon thin film were exposed to active oxygen species generated via UV

lamps for 120 min at low and high humidity, and the resulting surface topographies were observed by a laser microscope (VK-X200, Keyence Corporation, Japan). The same analysis was carried out on an unexposed film as a control. The analyzed area was $100 \times 140.8 \mu\text{m}^2$. The surface roughness parameters, such as arithmetic mean roughness (R_a), maximum peak height (R_p), and maximum valley depth (R_v), were also determined.

The changes in the surface chemical composition caused by etching were analyzed by X-ray photoelectron spectroscopy (XPS; Quantum 2000, Ulvac-phi Inc., Japan). The same analysis was carried out on an unexposed film as a control. The elemental composition of carbon (C1s), nitrogen (N1s), oxygen (O1s), and fluorine (F1s) at the film surfaces was analyzed. Then, the amount of O1s and F1s in each film surface was normalized using the area of each C1s XPS spectrum. The peak of the obtained XPS O1s spectrum could be deconvoluted three separate peaks, such as O^2 , OH, and H_2O [17,18]. The spectra were fitted by a mixed symmetrical Gaussian/Lorentzian function. The full width at half maximum of each peak was 1.75. The peak area ratio of O^2 and OH on each film was calculated.

2.5. Statistical analysis

All data are presented as mean $\pm$ standard deviation (SD) and were analyzed using student's two-tailed t -test with the significance level set at $P < 0.05$. In addition, multiple comparison by the Bonferroni-Holm method was performed using the t -test values when the number of experimental groups was more than three.

3. Results

3.1. Generation behavior of active oxygen species

Because of constant UV irradiation, temperature in the AOS system was slightly elevated. For instance, during irradiation experiments carried out for 120 min it was observed to be about $33 \pm 3^\circ\text{C}$. The humidity referred to as low, atmospheric, and high was kept at 6 ± 1 , 40 ± 3 , and $99 \pm 0\%\text{RH}$, respectively.

ESR spectra obtained after the reaction of active oxygen species with TEMP for 30 min at low and high humidity are shown in Fig. 1. Each $\text{O}(^1D)$ concentration calculated using the TEMPOL calibration curve is summarized in Fig. 2. The concentration of $\text{O}(^1D)$ generated at low humidity was about three times higher than that generated at high humidity. In addition, the amount of generated $\text{O}(^1D)$ increased exponentially during the first 5 min, after which it was essentially constant, as shown in Fig. 3.

The changes in O_3 concentration with time observed at low and high humidity are summarized in Fig. 4. In addition, the O_3 concentration achieved after UV irradiation for 5 min as a function of environment humidity is presented in Fig. 5. The concentration observed at low humidity is seen to be about five times larger for all UV irradiation times when compared to that obtained at high humidity. A similar trend was observed for $\text{O}(^1D)$ species. The concentration of O_3 generated at atmospheric humidity was larger than observed at high humidity, being smaller than that at low humidity. In addition, the O_3 concentration was found to be saturated after 5 min irrespective of humidity level used.

The ESR spectra obtained after the reaction of active oxygen species with CYPMPO at low, atmospheric, and high humidity are shown in Fig. 6. In addition, all peak height values of absorption intensity at the 5th peak from low magnetic flux density are presented in Fig. 7. The sample processed at high humidity demonstrates the highest peak. It is also seen in Fig. 7 that the samples processed at atmospheric and high humidity exhibit significantly larger peaks compared to that of the sample treated at low humidity.

3.2. Etching behavior of fluorocarbon thin film

The frequency change of the fluorocarbon thin film after the exposure of active oxygen species in the AOS system for 120 min is shown in Fig. 8. The frequency is seen to change approximately linearly with exposure time, irrespective of humidity conditions during etching. However, the frequency change was faster for the sample etched in highly humid environment (see Fig. 8). As a result, after etching for as long as 90 and 120 min, the sample etched in highly humid atmosphere demonstrated its vibration frequency about 2.5 times larger than its counterpart treated under low humidity conditions.

3.3. Surface morphology of fluorocarbon thin film

The surface topography of the fluorocarbon thin films before and after exposure to active oxygen species are shown in Figs. 9(a-c). In addition, various surface roughness parameters, R_a , R_p , and R_v , for the same samples are presented in Figs. 10(a-c). Both R_a values of the films exposed to active oxygen species are seen to be significantly higher than that of the untreated sample. The value of the film treated at low humidity was significantly higher compared to that of the sample processed at high humidity. Although there was no significant difference in the R_p values of the films exposed at low and high humidity (see Fig. 10(b)), the R_v values of the exposed films (irrespective of humidity during exposure) were significantly higher than that of the untreated counterpart. Interestingly, the R_v value of the film processed at low humidity was significantly higher than that of the film processed at high humidity. These results indicate that the exposure to active oxygen species under UV light irradiation affect the film surface roughness. Moreover, the effect seems to be stronger in low

humidity environment.

3.4. Surface chemical compositions of fluorocarbon thin film

The surface chemical composition of fluorocarbon thin films before and after exposure to the active oxygen species under different humidity conditions was analyzed by XPS, the results being summarized in Table 2. The oxygen content was slightly larger in the surface of exposed films, although no clear effect of humidity was observed. On the other hand, a smaller amount of fluorine was found in the film processed at low humidity, if compared to its counterpart treated at high humidity. Interestingly, no obvious difference was observed between the films before and after exposure at high humidity. The peak areas and ratios of the O^{2-} and OH obtained from O1s spectra of each fluorocarbon thin film were summarized in Table 3. The amount of OH in the surface processed at high humidity was 5% larger than that at low humidity. These results suggest that the fluorocarbon thin films were oxidized and defluorinated during the exposure to the active oxygen species. In addition, the humidity level seems to influence on the degrees of oxidation and defluorination processes.

4. Discussion

In this study, it was demonstrated that the active oxygen species, *i.e.*, $O(^1D)$, O_3 , and OH^* , are generated by exposing air (containing oxygen and water molecules) to UV light irradiation (with wavelengths of 185 and 254 nm). We also present quantitative data on the amount of each species generated under UV irradiation over time. The experimental values

for $O(^1D)$ and OH^* species are integrated values, but those for O_3 are momentary values. It was demonstrated that the amount of generated O_3 was saturated within 5 min after exposure to UV light. On the other hand, the amount of generated $O(^1D)$ increased exponentially during the first 5 min, after which it was essentially constant. O_3 is known to be the first active oxygen species generated from molecular oxygen. After its appearance, O_3 gives rise to other active oxygen species such as $O(^1D)$ and OH^* . Although the detection methods for all these species are different, the obtained data indicate that O_3 is generated actively within the first 5 min of UV irradiation. At the same time, the amount of generated $O(^1D)$ increases exponentially with the increase in O_3 amount, after which $O(^1D)$ is produced at a constant level.

The difference in the amount of OH^* generated at low, atmospheric, and high humidity was revealed by the ESR measurements performed in this study. It is known that CYPMPO reacts specifically with OH^* and oxy- radicals [19,20]. It is also known that each radical can be recognized from each ESR spectrum because each spectrum reacted is different [21]. The spectra obtained in this study are specific to CYPMPO-OH, and the 4th and 5th peaks counted from low magnetic flux density in the ESR spectrum indicate specific CYPMPO-OH peaks. Therefore, the peak height of the 5th peak was measured in this study. The amount of OH^* generated at high humidity was larger than that at low humidity, whereas the amounts of $O(^1D)$ and O_3 species generated at low humidity were larger than those at high humidity. H_2O molecules are essential for OH^* generation by means of UV light. On the other hand, O_2 molecules are essential for the production of $O(^1D)$ and O_3 species. In this study, it was demonstrated that the humidity influences significantly the generation of active oxygen species as their concentrations. Therefore, the amount of $O(^1D)$ generated at low humidity will be larger than that at atmospheric humidity. The peak height of OH^* generated at high humidity exhibits no significant difference compared to that at atmospheric humidity.

It is known that the moisture weakens the illumination intensity of UV light. We have also obtained a data that the illumination intensity of UV light with the wavelength of 254 nm for 30 min irradiation at low humidity was $0.7 \pm 0.09 \text{ mW cm}^{-2}$, whereas that at high humidity was $0.5 \pm 0.03 \text{ mW cm}^{-2}$. Therefore, it considered that the generation efficiency of OH* under UV light irradiation at high humidity was lower than that at atmospheric humidity. In this experiment, no significant difference exhibited between high and atmospheric humidity, although the amount of H₂O molecules in the AOS system at high humidity was larger than that at atmospheric humidity.

From the results of QCM measurements, the fluorocarbon thin film was etched by the active oxygen species generated via UV irradiation at each tested humidity. The mass loss was larger at high humidity. As described above, the presence of water molecules could facilitate the production of OH*, while the latter radicals are believed to contribute significantly to the film etching (their oxidizing properties are well-known to be much stronger than of the other active oxygen species). In this study, the UV light was also exposed to the fluorocarbon thin film. The UV light also etches the polymeric film surfaces. As described above, the illumination intensity of UV light at low humidity was higher than that at the high humidity. The difference in the etching amount of the film was also affected by UV light irradiation.

The results of XPS analysis revealed that the films were oxidized upon exposure to active oxygen species generated via UV light irradiation. The films were defluorinated when exposed at low humidity. On the other hand, the content of OH* at the film surface exposed at high humidity was 5% larger than that at low humidity, although difference of the oxidization amounts cannot be recognized at both humidity conditions. They were also roughened as a result of etching with active oxygen species and UV light. The etching was found to affect the film surface in depth direction. In addition, the surface roughness of the film processed at low

humidity was larger than that processed at high humidity. As described above, the distribution of generated active oxygen species depends on the environment humidity. It is believed that the active oxygen species generated from oxygen molecules relate strongly to defluorination and roughening of the film surface compared to the species generated from water molecules. However, the etched amount of the film processed at high humidity was significantly higher than that processed at low humidity. The difference of the illumination intensity also influences on the etching amount of the film. The quantum energy of UV light can be calculated using the following equation:

$$E = h\nu = h \frac{c}{\lambda} \quad (1)$$

where, E , h , ν , c , and λ are the quantum energy, Planck's constant, frequency, light speed, and wavelength, respectively. The energies of the UV lights, whose wavelengths are 185 and 254 nm, are thus calculated to be 650 kJ mol⁻¹ and 473 kJ mol⁻¹, respectively. On the other hand, the binding energies of the C-C and C-F bonds are 357 kJ mol⁻¹ and 489 kJ mol⁻¹, respectively. Therefore, the C-C bond is easily cloven compared to the C-F bond by irradiation of the two wavelengths of UV light. It is considered that fluorocarbon compounds, which are etching products, react with O(¹D), and polymerize and form ether compounds at the surface of the fluorocarbon thin film. On the other hand, the etching products can also react with OH*, and form alcohol compounds, however they cannot polymerize at the surface. The ether compounds suggest that a part of the etching products still remain at the surface of the fluorocarbon thin films. On the other hand, the alcohol compounds suggest that almost all of the etching products are etched and removed from the surface of the fluorocarbon thin films. Therefore, one can conclude that the active oxygen species generated at high humidity etch the film, while the species generated at low humidity do not etch the film apparently. On the other hand, the roughened surface generally weakens the intensity of the emitted XPS

signal. Therefore, the oxygen content of the film processed at low humidity might be larger than that of the film etched at high humidity. In accordance with the difference in oxygen content, the difference in the amount of fluorine between the samples processed at low and high humidity may thus become quite small. Further analysis, such as measurements of defluorination and production of fluoride, may be required.

Another major technique to produce active oxygen species is plasma irradiation. However, the use of plasmas, such as atmospheric pressure pulsed corona discharge and glow discharge, generates various nitrogen oxides, which poses pollution risks to environment [22,23]. As described above, the energy of UV light, with the wavelength of 185 and 254 nm, are 650 kJ mol^{-1} (6.7 eV) and 473 kJ mol^{-1} (4.9 eV), respectively. The binding energy of the triple bond in N_2 molecule ($\text{N}\equiv\text{N}$) is 945 kJ mol^{-1} (9.8 eV) [24]. The energy of the used UV light is thus smaller than that of the N_2 triple bond. Therefore, nitrogen oxides are not generated from N_2 molecules using the UV lamps used in this work. The active oxygen species produced by means of UV light can be applied for green surface modification and etching process.

5. Conclusions

Active oxygen species, $\text{O}(^1D)$, O_3 , and OH^* , were generated via UV light irradiation (with the wavelengths of 185 and 254 nm). The generated $\text{O}(^1D)$ and OH^* were detected using the electron spin resonance method. The amounts of $\text{O}(^1D)$ and O_3 generated at low humidity were much larger than those at high humidity. On the other hand, the concentration of OH^* generated under high humidity condition were much higher than that generated at low humidity. In addition, the generation behavior of each active oxygen species was found to be time dependent. Although the amount of generated $\text{O}(^1D)$ increased linearly with time, the

increase in O_3 concentration was suppressed after 5 min of exposure to UV light. Fluorocarbon films were etched by the produced active oxygen species faster at high humidity, while their surface became rougher upon etching at low humidity. The elemental composition of the film surfaces exposed to the active oxygen species at low and high humidity was slightly different. Therefore, atmospheric humidity is shown to influence on both the generation and oxidation properties of active oxygen species.

Acknowledgements

This work was financially supported by a Grant-in-Aid for A-STEP (No. AS2414101P) from the Japan Science and Technology Agency (JST).

References

- [1] R. Ono, Y. Yamashita, K. Takezawa, T. Oda, J. Phys. D: Appl. Phys. 38 (2005) 2812.
- [2] S. Takashima, M. Hori, T. Goto, A. Kono, M. Ito, K. Yoneda, Appl. Phys. Lett. 75 (1999) 3929.
- [3] H. Nagai, M. Hiramatsu, M. Hori, T. Goto, Rev. Sci. Instrum. 74 (2003) 3453.
- [4] S. Iwamori, K. Yoshino, H. Matsumoto, K. Noda, I. Nishiyama, Sens. Actuat. B: Chem. 171-172 (2012) 769.
- [5] K. Yoshino, H. Matsumoto, T. Iwasaki, S. Kinoshita, K. Noda, S. Iwamori, Vacuum 93 (2013) 84.
- [6] J. P. Burrows, R. A. Cox, R. G. Derwent, J. Photochem. 16 (1981) 147.
- [7] M. Salvermoser, D. E. Murnick, U. Kogelschatz, Ozone Sci. Eng. 30 (2008) 228.
- [8] K. Yoshihara, Y. Takatori, K. Miyazaki, Y. Kajii, Proc. Jpn. Acad. Ser. B 83 (2007) 320.
- [9] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, Atoms. Chem. Phys. 4 (2004) 1461.
- [10] L. T. Molina, M. J. Molina, J. Geophys. Res. 91 (1986) 14501.
- [11] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe, J. Phys. Chem. Ref. Data 21 (1992) 1125.
- [12] D. S. Stafford, M. J. Kushner, J. Appl. Phys. 96 (2004) 2451.
- [13] J. A. Manion, R. E. Huie, R. D. Levin, D. R. Burgess Jr., V. L. Orkin, W. Tsang, W. S. McGivern, J. W. Hudgens, V. D. Knyazev, D. B. Atkinson, E. Chai, A. M. Tereza, C-Y. Lin, T. C. Allison, W. G. Mallard, F. Westley, J. T. Herron, R. F. Hampson, D. H. Frizzell, *NIST Chemical Kinetics Database* (National Institute of Standards and Technology, Gaithersburg, U. S., 2008) NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.4.3, Data version 2008.12.

- [14] D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, J. Warnatz, *J. Phys. Chem. Ref. Data* 34 (2005) 757.
- [15] S. K. Han, T. M. Hwang, Y. Yoon, J. W. Kang, *Chemosphere* 84 (2011) 1095.
- [16] G. Liu, J. Zhao, H. Hidaka, *J. Photochem. Photobiol. A: Chem.* 133 (2000) 83.
- [17] K. Asami, S. C. Chen, H. Hamazaki, K. Hashimoto, *Corros. Sci.* 35 (1993) 43.
- [18] K. Asami, K. Hashimoto, *Corros. Sci.* 17 (1997) 559.
- [19] M. Kamibayashi, S. Oowada, H. Kameda, T. Okada, O. Inanami, S. Ohta, T. Ozawa, K. Makino, Y. Kotake, *Free Radic. Res.* 40 (2006) 1166.
- [20] N. Endo, S. Oowada, Y. Sueishi, M. Shimmei, K. Makino, H. Fujii, Y. Kotake, *J. Clin. Biochem. Nutr.* 45 (2009) 193.
- [21] S. Oowada, N. Endo, H. Kameya, M. Shimmei, Y. Kotake, *J. Clin. Biochem. Nutr.* 51 (2012) 117.
- [22] Y. Teramoto, R. Ono, T. Oda, *Jpn. J. Appl. Phys.* 111 (2012) 113302.
- [23] S. F. Adams, C. A. DeJoseph Jr., C. C. Carter, T. A. Miller, J. M. Williamson, *J. Phys. Chem. A* 105 (2001) 5977.
- [24] M. T. Nguyen, *Coord. Chem. Rev.* 244 (2003) 93.

Figure Captions

Fig. 1. ESR spectra of TEMP after reaction with $O(^1D)$ at (a) low and (b) high humidity.

Fig. 2. Concentration of $O(^1D)$ generated at low and high humidity after 30 min of exposure to UV light. The data are presented as the mean $\pm$ SD; $n=4$; $*P < 0.05$.

Fig. 3. Concentration of $O(^1D)$ generated over time at atmospheric humidity.

Fig. 4. Concentration of O_3 generated over time at low and high humidity. The data are the mean $\pm$ SD; $n=4$.

Fig. 5. Concentration of O_3 generated at different humidity values after 5 min of exposure to UV light. The data are the mean $\pm$ SD; $n=3$.

Fig. 6. ESR spectra of CYPMPO reacting with OH^* at (a) low, (b) atmospheric, and (c) high humidity after 5 min of exposure to UV light.

Fig. 7. Concentration of OH^* generated at different humidity values after 5 min of irradiation with UV light. The data are the mean $\pm$ SD; $n=5$. $*P < 0.05$ vs low humidity condition.

Fig. 8. Frequency changes of quartz oscillators coated with fluorocarbon thin films as a function of etching time with active oxygen species at low and high humidity. The data are the mean $\pm$ SD; $n=3$; $*P < 0.05$ vs low humidity condition at the same UV light irradiation time.

Fig. 9. Surface topography of fluorocarbon thin films (a) before processing and after processing in (b) low- and (c) high- humidity atmosphere.

Fig. 10. Surface roughness parameters of fluorocarbon thin films after exposure to active oxygen species at different humidity: (a) R_a , (b) R_p , and (c) R_v . The data are the mean $\pm$ SD; $n=5$; $*P < 0.05$. The dotted line indicates a value of the untreated film. “†” indicates a significant difference vs the value of the untreated film. All data were statistically analyzed by means of Student’s two-tailed t -test ($P < 0.05$) with Bonferroni-Holm correction.

Table 1. Conditions applied during film preparation

Evacuation pressure	1×10^{-2} Pa
Applied voltage	50 W
Ar gas flow rate	4.0 sccm
Operating pressure	3.5 Pa
Operation time	20 min

Table 2. Ratio of chemical elements of each fluorocarbon thin film normalized to peak area of carbon

	O/C	F/C
Untreated	0.03	1.34
$6 \pm 1\%RH$ (Low humidity)	0.06	1.28
$99 \pm 0\%RH$ (High humidity)	0.06	1.35

Table 3. Peak areas and ratios of the O^2 and OH obtained from $O1s$ spectra of each fluorocarbon thin film

	O^2	OH
Untreated	37% (127)	63% (212)
$6 \pm 1\%RH$ (Low humidity)	30% (143)	70% (338)
$99 \pm 0\%RH$ (High humidity)	25% (133)	75% (390)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9(a)

Figure 9(b)

Figure 9(c)

Figure 10(a)

Figure 10(b)

Figure 10(c)

Graphical abstract

*Active oxygen species were generated
In low/high humidity conditions
via 185/254nm UV light irradiation*