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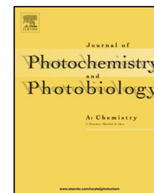

Effect of humidity conditions on active oxygen species generated under ultraviolet light irradiation and etching characteristics of fluorocarbon polymer

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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.

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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 oxidization 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,

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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.

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 [17,18]. 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 (N≡N) is 945 kJ mol^{-1} (9.8 eV) [19]. 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.

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-l,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.18 M, 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 4–400 ppm.

The generated OH^* were also detected by the spin trapping method. OH^* reacts with 5-(2,2-dimethy-1,3-propoxycyclo-phosphoryl)-5-methyl-1-pryoline 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 $100 \times 140.8\ \mu m^2$. 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 [20,21]. The spectra were fitted by a mixed symmetrical Gaussian/Lorentzian function. The full width at half

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

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