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Monitoring of Surface Treatment Effects on Sputter-coated Organic Film under Atomic Oxygen and Ultraviolet Irradiation

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We have been investigating the monitoring of surface treatment under ultraviolet lamp processing utilizing a quartz crystal microbalance (QCM) with organic thin film. In this study, the behavior of surface modification on sputter-coated organic thin film was successfully measured by QCM. The film erosion mechanism is discussed here based on the results of surface analyses by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

The surface modification of engineering polymers such as poly(ethylene terephthalate) (PET), poly(methyl methacrylate) (PMMA), and polyimide (PI) is a crucial factor to ensure adhesion for metal deposition and/or gluing to other materials in microelectronics technology. Various methods are employed for surface treatment. In particular, surface modification utilizing ultraviolet irradiation has been attracting attention.[1–3] However, it is difficult to immediately grasp the effects of treatment in such processing. An in situ method of monitoring the effects of treatment is, therefore, desired for practical application. We have been investigating the properties of organic thin films prepared by sputtering as candidates for new functional polymer materials. In this study, we investigated the mechanism of surface treatment utilizing a sputter-coated organic film on quartz crystal to gain a fundamental understanding of surface modification in polymers.

In the present study, we used a low-pressure mercury UV lamp (QGL90U-31, Iwasaki Electric) as an ultraviolet source. It is known that ozone (O_3) and excited atomic oxygen ($O(^1D)$) are generated under UV radiation (185/254 nm) as active oxygen species via photochemical reactions. In particular, $O(^1D)$ is the predominant oxidant for surface treatment because of its extraordinary rate constant (10^5–$10^6\,L\,mol^{-1}\,s^{-1}$). Organic thin film was prepared by RF (13.56 MHz) sputtering with a polyimide target (Upilex-S, Ube Industries)[4] on a quartz crystal substrate (SC-101, Maxtek Inc.) that had a resonant frequency of 6 MHz. Deposition was carried out under an argon gas pressure of 0.5 Pa and with RF power of 150 W. The obtained film thickness was ca. 100 nm. A quartz crystal microbalance (QCM) with sputter-coated organic film was mounted in a metal sensor head and set under the UV lamp in various positions. It is considered that the surface temperature of the films depends on the intensity of the UV light and can influence the etch rate of the films. Therefore, the sensor head temperature was maintained at a constant 20 °C by circulating water. The QCM was connected to an oscillator (Q-pod, Sigma Instruments), and the frequency shift induced by UV irradiation was recorded. To clarify the effect of UV irradiation on the organic film, UV-filtering glass was inserted between the UV lamp and sensor head to allow light of less than 200 nm wavelength to be cut if necessary. The respective integrated UV light volumes of 185- and 254-nm irradiation at the 20 mm position were 2.9 and 16.2 $mW\,cm^{-2}$ in the absence of UV-filtering glass, and 0.9 and 15.4 $mW\,cm^{-2}$ in the presence of UV-filtering glass. The concentration of ozone generated in the lamp box was a constant 200 ppm, and the quantity of $O(^1D)$ acting on the polymer surface was assumed to be roughly equivalent under both experimental conditions.

Figure 1 shows images obtained by atomic force microscopy (AFM) (SPA-300, Seiko Instruments) of the polymer–QCM surface before and after irradiation (15 min exposure at 20 mm). The AFM images were taken at a scan frequency of 2 Hz with a scan area of 1000 nm. The surface before exposure exhibits fine protuberances with an arithmetic mean roughness (R_a) of ca. 0.19 nm (Figure 1a). On the other hand, the protuberances are not so pronounced on the irradiated surfaces (Figures 1b and 1c), with an R_a value of 0.05 and 0.18 nm for irradiations at 185/254 and 254 nm, respectively.

Table 1 shows the atomic concentration ratio of the specimens before and after irradiation, analyzed by X-ray photoelectron spectroscopy (XPS) (Axis Ultra, Kratos). The analysis of each element was performed in 0.1 eV steps using Al Kα X-rays (10 kV, 10 mA). It was confirmed that the C1s ratio was reduced and the O1s ratio was increased after irradiation. In particular, the increase in the O1s ratio was slightly larger in the case of irradiation at 185/254 nm than at 254 nm.

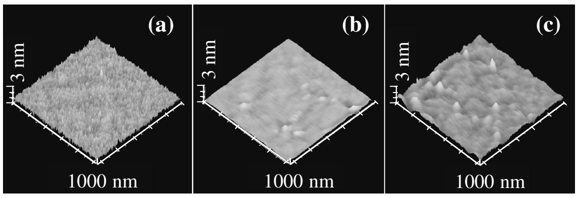

Figure 1. AFM images of polymer–QCM: (a) before irradiation and after irradiation at (b) 185/254 nm and (c) 254 nm.

Table 1. XPS atomic concentration ratio of sputter-coated organic films: (a) before irradiation and after irradiation at (b) 185/254 nm and (c) 254 nm

	Atomic concentration ratio/%		
	C1s	N1s	O1s
(a) Before	87.7	4.3	8.0
(b) 185/254 nm	82.5	4.0	13.5
(c) 254 nm	84.0	3.7	12.4

Table 2. XPS peak deconvolution results of sputter-coated organic films: (a) before irradiation and after irradiation at (b) 185/254 nm and (c) 254 nm

	Relative content/%					
	PDA 285.0 eV	BPDA 286.0 eV	C–O–C 286.6 eV	C=O 287.7 eV	C–O–N 288.9 eV	CO–OH 289.6 eV
(a)	67.0	17.1	6.0	5.9	2.8	1.2
(b)	61.1	14.4	9.1	8.1	4.8	2.8
(c)	59.6	12.4	10.6	8.4	5.7	3.4

Table 2 shows typical XPS peak deconvolution results for the C1s spectrum of the specimens before and after irradiation. The C1s spectrum was calibrated with the hydrocarbon photoelectron peak at 285.0 eV. Peak synthesis was performed at full-width half maximum (FWHM) fixed at 1.4 eV. An increase in the relative content of all the oxidative functional groups—C–O–C (286.6 eV), C=O (287.7 eV), C–O–N (288.9 eV), and CO–OH (289.6 eV)—was observed for both irradiated surfaces. Peak reductions in PDA (285.0 eV) and BPDA (286.0 eV) were also confirmed. From these results, it was verified that there was a slight increase in the formation of oxidative functional groups on the surface irradiated at 254 nm compared with that irradiated at 185/254 nm.

Pei and Wang reported the formation of "nodule" and "floccule" morphologies on copolymerized polyimide films after UV irradiation, arising from the photostability of the polymer.[5] Moreover, they concluded that the difference in these topologies originates from the degree of oxidation, with floccules being a more oxidized form than nodules. On the other hand, the formation of nodules was only seen in the 254-nm-irradiated surface in the present study. We, therefore, believe that the nodules disappeared as a result of further oxidation and bond scission of oxidative functional groups due to 185-nm UV irradiation, as shown in Figure 1b. We also believe this to be due to a difference in the polymer characteristics of bulk films and those of the film we used, which was prepared by RF sputtering. In fact, it has already been confirmed that when etched by atomic oxygen irradiation our sputter-coated organic film remains atomically flat under inductively coupled oxygen plasma.[6]

Figure 2 shows the typical frequency change characteristics of the polymer–QCM. For 185/254-nm irradiation at 20 mm, the frequency linearly increased up to 60 Hz at an elapsed time of 15 min. This frequency increase indicates a decrease in the mass of organic film on the QCM. Since the frequency shift of 1 Hz was converted into a mass change of ca. 16 ng on the QCM, whose detection area of 8 mm dia., used in this study from the Sauerbrey equation, a 60 Hz increase corresponds to a mass loss of ca. 0.96 µg.

The frequency shift for 254-nm irradiation was less than that for 185/254-nm irradiation. The tendency of this result is in good agreement with the results obtained for the surface morphologies (AFM) and chemical bonding states (XPS) described above. In other words, the flat surface shown in Figure 1b was the result of oxidation and subsequent weight loss. This is because 185-nm UV irradiation promotes the surface oxidation of organic film, so the erosion rate progressed more rapidly than in the case of 254-nm irradiation alone.

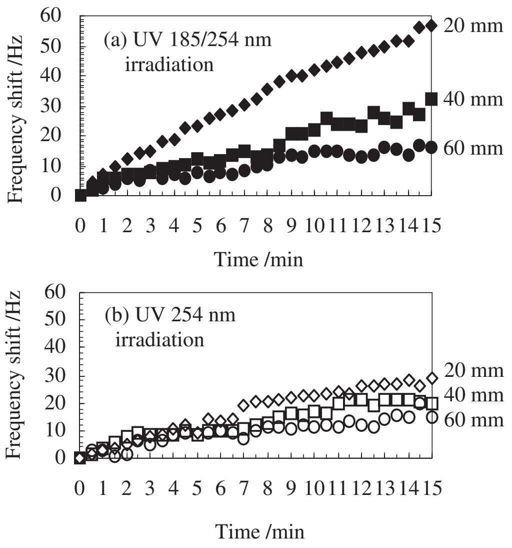

Figure 2. Typical frequency change of polymer–QCM.

From these results, the mechanism of organic film erosion is considered to be as follows: First, the surface reacts with atomic oxygen, and oxidative functional groups are then generated. Subsequently, UV light breaks the chemical bonds. Oxidation and erosion gradually progress through the repetition of this process. Since 185-nm light has sufficient activation energy (>6.7 eV) to promote surface oxidation and break the various chemical bonds, this might also promote the erosion and suppression of nodule-like morphology formation.

We have investigated the effects of UV and atomic oxygen irradiation on surfaces utilizing a sputter-coated organic thin film on QCM. The results confirm that surface erosion can be succesfully monitored in real time by QCM. The role of 185-nm irradiation was also revealed in this study.

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