Application of Quartz Crystal Microbalance as a Tool for Detergency Evaluation of Fatty Acid Contamination in Aqueous Systems

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Abstract: Removal process of a fatty acid from four substrates was monitored using a quartz crystal microbalance (QCM). Model substrates included carbon, silica, and gold sputtered electrodes and a polymer film prepared on a gold sputtered electrode. Stearic acid (SA), a model solid oily contaminant, was deposited on the substrates as an ultra-thin layer using the Langmuir–Blodgett (LB) technique. Cleaning tests of the SA-LB films were performed in aqueous solutions containing sodium chloride (NaCl), sodium hydroxide (NaOH), and/or sodium dodecyl sulfate (SDS). The removal efficiency was calculated from the QCM frequency vs. time curve obtained during the cleaning process. The neutralization by NaOH was effective for removing the SA-LB film from all substrates, although the reaction was slow. In the absence of NaOH, minor amounts of the SA-LB film was removed from the substrates, with the exception of silica, even in the SDS solution. To increase the removal efficiency of the SA-LB film in the absence of NaOH, the SA-LB film deposited on the substrates was exposed to atmospheric-pressure plasma before the cleaning process. This treatment promoted the removal of the film in the NaCl and/or SDS solutions, which we interpreted to be due to the hydrophilization of both the surfaces of the substrates and the SA-LB film.

Key words: quartz crystal microbalance, stearic acid, Langmuir-Blodgett method, atmospheric pressure plasma, detergency

1 INTRODUCTION

Due to the significant impact of contaminants on the quality and yield rate of products, it is often required that contaminants are completely removed during the industrial cleaning process. For example, the level of the read signal of a hard disk device for writing or reading data to/from the disk is strongly dependent on the flying-height of a magnetic head less than 10 nm above the surface of the disk. Therefore, the thickness of the contaminants on the hard disk substrate must be controlled at the nanometer-level.

Contaminants remaining on the products after a wet cleaning process are commonly removed by a subsequent etching or scraping process. However, these processes may cause mass loss of the material and change its surface morphology. To develop a precision cleaning method based only on a wet cleaning process, the detergency of trace-level contaminants should be improved. For this purpose, a well-defined detergent system is desirable, in which not only the type of substrate and contaminant but also the deposited mass and state of the contaminant on the substrate can be controlled. Simultaneously, an exact detergency evaluation technique is necessary.

In this study, for studying the removal of a trace-level contaminant from products, the Langmuir–Blodgett (LB) technique was applied to deposit a model contaminant onto a substrate. The LB technique can provide organized molecular assemblies with well-defined orientation and can therefore be utilized to deposit contaminants as an ultra-thin layer. For the detergency evaluation of trace-level contaminants on the nanogram scale, the quartz crystal microbalance (QCM) technique was used. In recent years, QCM frequency tracking in the aqueous phase has been commonly performed. Some researchers have reported the use of QCM frequency tracking for analyzing soil removal processes. We have also reported that the removal efficiency of fatty acid LB films from polymer surfaces was enhanced in aqueous solutions with the application of ultrasonic waves, and was dependent on the contaminant...
deposition state\textsuperscript{13}).

The model substrates used in the present system were the QCM electrodes of carbon, silica, gold, and a polymer prepared on the electrode as typical raw materials for industrial products. Stearic acid (SA), a model oily contaminant, was deposited onto the substrates as an extremely thin layer using the LB method. From the viewpoints of human health and environmental pollutants, water was chosen as a cleaning medium, as it is commonly used in industrial cleaning processes\textsuperscript{15}. The removal efficiency was determined by in situ monitoring of the QCM frequency during the cleaning of the SA-LB films in aqueous solutions.

2 EXPERIMENTAL

2.1 Materials

The AT-cut, 9 MHz QCMs with carbon (QA-A9M-C(M)), silica (QA-A9M-SIO2-S(M)), and gold (QA-A9M-AU(M)) sputtered electrodes were purchased from Seiko EG&G (Japan). The QCMs with silica and gold sputtered electrodes were ultrasonically cleaned in ethanol. The QCM with a carbon sputtered electrode was cleaned in ethanol without ultrasonic waves to avoid erosion. All of the QCMs were air-dried at 50°C for 20 min. Ultraviolet irradiation (172 nm) of the silica and gold electrodes was carried out to remove organic contaminants using a Xe\textsubscript{2} (noble gas dimers)/eximer vacuum UV apparatus (UER20-172, Ushio, Japan)\textsuperscript{13}. As a polymer substrate, a poly(ethylene terephthalate) (PET) film was prepared on the QCM with a gold electrode by spin-coating\textsuperscript{13}.

The long-chain fatty acid, SA (special grade 99%, MP Biomedicals, LLC, USA), was chosen as the model oily contaminant and was dissolved in chloroform (extra-pure grade, Wako Pure Chemical Industries, Ltd., Japan).

Sodium chloride (NaCl, analytical grade), sodium hydroxide (NaOH, analytical grade), and sodium dodecyl sulfate (C\textsubscript{12}H\textsubscript{25}OSO\textsubscript{3}Na, SDS, special grade) were used for preparing the aqueous detergent solutions and were purchased from Wako Pure Chemical Industries, Ltd., Japan. The critical micelle concentration of SDS in the presence of 1.0 mmol·dm\textsuperscript{-3} NaCl was determined to be 8.0 mmol·dm\textsuperscript{-3} at 20°C based on the surface tension measured by the pendant drop technique\textsuperscript{16}.

The water was purified using a Direct-Q UV apparatus (Millipore, USA).

2.2 Surface characterization of the substrates

To observe the substrate surface, scanning electron microscopy (SEM, SU1510, Hitachi, Japan) was used. Prior to the SEM observations, the substrates were sputter-coated with tungsten to make them electrically conductive. All SEM observations were performed at 5 kV.

The chemical compositions of the substrate surfaces were examined by X-ray photoelectron spectroscopy (XPS). For experimental convenience, the separation-type QCM (QA-A9M-AU (SEP), Seiko EG&G) was used for the XPS analysis of the gold substrate. The apparatus used was an Axis-Ultra DLD spectrometer (Kratos Analytical, Ltd., UK) with an Al K\textalpha monochromatic source at 1486.7 eV (75 W). Survey spectra and high-resolution spectra of C 1s and O 1s were acquired with pass energies of 80 and 20 eV and a slot aperture of 0.8 mm × 2.0 mm. Spectra were collected at a photoelectron take-off angle of 90°. The analytical chamber’s pressure was maintained at ~10\textsuperscript{-8} Pa. All spectra were corrected using the signal of C 1s at 284.8 eV as an internal reference.

2.3 Deposition of SA onto the substrates

In a liquid medium, the mass change calculated from the QCM frequencies before and after the SA-LB film deposition by the Sauerbrey equation\textsuperscript{18} is less than the actual deposited mass because of the missing mass effect\textsuperscript{18, 19}. Therefore, the QCM frequency was measured in aqueous solution prior to the deposition of the SA-LB film, and the QCM was then cleaned and dried.

The deposition of SA onto the QCM electrode was carried out by the LB method using a commercial apparatus (KSV Minitrough 2000, KSV NIMA, Finland). The poly(tetrafluoroethylene) (PTFE) trough (75 mm × 364 mm × 7 mm) was filled with 0.28 dm\textsuperscript{3} of ultrapure water as a subphase, and a 2.5 × 10\textsuperscript{-4} dm\textsuperscript{3} SA/chloroform solution (1.0 g·dm\textsuperscript{-3}) was spread onto the subphase using a microinjection syringe. After allowing 20 min for evaporation of the chloroform, the monolayer was compressed continuously with a barrier speed of 4.0 mm·min\textsuperscript{-1}.

The relation between the surface pressure and the occupied surface area per SA molecule was obtained using the same apparatus as previously reported\textsuperscript{20}. The surface pressure abruptly increased below 0.28 mN·m\textsuperscript{-1} and the membrane phase transition from liquid crystal to solid crystal occurred at 25 mN·m\textsuperscript{-1}. These results were in good agreement with the reference value\textsuperscript{21}. In the present study, the liquid crystal membranes were transferred onto the QCM electrode at surface pressures of 20 mN·m\textsuperscript{-1} by the vertical dipping method because of the difficulty in removing the solid crystal membrane from aqueous detergent systems\textsuperscript{11}.

After the LB film deposition, the QCM was stored in a room maintained at 20°C and 65% relative humidity for 24 h prior to cleaning.

2.4 Cleaning test

Cleaning tests of the SA-LB film were carried out according to previous studies\textsuperscript{11}. The experimental setup consisted of a well-type PTFE cell, a frequency counter (QCA922, Seiko EG&G, Japan), and Win QCM PS-P600.
frequency recording and analysis software (Seiko EG&G, Japan). After sealing both sides of the QCM electrode with silicone rubber O-rings, the QCM was fixed in a well-type cell. The QCM was then connected to a frequency counter, and the detergent solution was added to the cell. The detergent solutions used were NaCl ([NaCl] = 1.0 mmol·dm⁻³), NaOH solution ([NaCl] = 1.0 mmol·dm⁻³, [NaOH] = 1.0 mmol·dm⁻³), and SDS solution ([NaCl] = 1.0 mmol·dm⁻³, [SDS] = 8.0 mmol·dm⁻³). The QCM frequency was monitored for 30 min with stirring at 400 rpm using an agitator (EYELA ZZ-1000, Tokyo Rikakikai Co., Ltd., Japan). The cleaning test was carried out in a room maintained at 20°C and was repeated 4–8 times under the same conditions.

The removal efficiency was calculated from the frequency vs. time curve with the following equation:

\[ \text{Detergency(\%)} = \frac{F_0 - F_1}{F_0 - F_t} \times 100 \]

where \( F_0 \) is the frequency in the detergent solution before the contaminant deposition, \( F_1 \) is the minimum frequency immediately after the addition of the detergent solution, and \( F_t \) is the frequency at time \( t \) after cleaning.

2.5 Contact angle measurement

The contact angles were measured by the sessile drop technique using a video contact angle system with a CCD camera (VCA-2500, AST Products, USA). The contact angle was measured 1 s after placing a 2–3 μL water drop on the substrates with and without the SA-LB film. The measurements were repeated 6–10 times, and the standard deviations were within ±10%.

3 RESULTS AND DISCUSSION

3.1 Surface properties of the substrate

Figure 1 shows the SEM images of the carbon, silica, gold, and PET substrates. The surfaces of the QCM electrodes ((a), (b), and (c) in Fig. 1) were found to be smooth. However, surface roughness was observed for the PET film prepared on the gold electrode ((d) in Fig. 1).

Figure 2 shows the XPS survey spectra of the carbon, silica, gold, and PET substrates. The obtained atomic concentrations are summarized in Table 1. In the case of the carbon substrate, a peak attributed to O 1s was detected. The silica substrate had a peak attributed to C 1s and the gold substrate had C 1s and O 1s peaks due to residual impurities that could not be removed by ultrasonic cleaning in ethanol and UV irradiation in air. In the case of the PET, the F 1s peak, which was derived from the solvent, was detected. It was confirmed that the PET film completely covered the QCM gold electrode because the peaks owing to gold were not detected. The O:C atomic ratio was consistent with that reported for the commercially available PET film obtained in a previous work.

Fig. 1  SEM images of the (a) carbon, (b) silica, (c) gold, and (d) PET substrates.
3.2 Deposition of LB films onto substrates

Figure 3 shows the mass change ($\Delta m$) calculated from the QCM frequency change before and after the LB film deposition as a function of the number of dips. For the carbon, gold, and PET substrates, $\Delta m$ increased linearly with the number of dips, assuming that the monolayers on the water were transferred as a Y-type membrane. The transfer ratio of the SA monolayers onto the substrate, shown in Fig. 3, followed the sequence gold>PET>carbon. For the hydrophilic silica substrate, $\Delta m$ remained constant after two dips, suggesting that a single SA monolayer was transferred onto the silica substrate in contact with its hydrophilic part.

3.3 Removal of LB films from substrates

Typical QCM frequency vs. time curves during cleaning in the aqueous NaCl, NaOH, and SDS solutions are illustrated in Figs. 4, 5, and 6, respectively. The stability of the QCM frequency was within a few tens of Hertz in aqueous solution without agitation, and the QCM stability did not change due to agitation. In all cases, the frequency became almost constant after 30 min, and the removal efficiency at 30 min was determined to be the apparent equilibrium.
removal efficiency. The mean values and standard deviations of the repetitions are given in each figure.

In the NaCl solution (Fig. 4), the removal efficiencies were <10% for the carbon, gold, and PET substrates. In the case of the silica substrate, the removal efficiency was relatively large. It is well known that the penetration of the surfactant solution into the contact zone between the contaminant and the substrate may promote contaminant removal\(^1\). The removal of the SA-LB film from the silica surface can be caused by liquid penetration into the contact zone between the hydrophilic part of the SA-LB film (as mentioned in Section 3.2) and the silica substrate.

Fig. 4  Typical QCM frequency vs time curve for the removal process of stearic acid LB films from the carbon (a), silica (b), gold (c), and PET (d) substrates in the NaCl solution.

Fig. 5  Typical QCM frequency vs time curve for the removal process of stearic acid LB films from the carbon (a), silica (b), gold (c), and PET (d) substrates in the NaOH solution.
However, for the carbon, gold, and PET substrates, on which the SA-LB film was deposited in contact with their hydrophobic parts, the contribution of the liquid penetration to the removal of the SA-LB film may be small.

In the aqueous NaOH solution (Fig. 5), the SA-LB film was considerably removed from all substrates. It is considered that the neutralization of SA by alkali can contribute to the removal of an ultra-thin layer such as the SA-LB film.

In the SDS solution (Fig. 6), the removal efficiency of the
SA-LB film from the carbon, gold, and PET substrates was relatively small, as was that in the NaCl solution (see Fig. 4). It seems likely that the extremely thin SA-LB film deposited on the substrate in contact with its hydrophobic part is difficult to remove, even by the penetration of the surfactant solution.

From the experimental findings mentioned above, it is expected that the removal of the SA-LB film in the NaOH and SDS solutions is caused by neutralization and liquid penetration, respectively. Therefore, to compare the removal kinetics between neutralization and liquid penetration, the removal efficiencies from the silica and PET substrates in the initial stage vs. time were plotted, which were obtained from the QCM frequency vs. time curves shown in Figs. 5 and 6. The results are presented in Fig. 7. The removal of the SA-LB film from the PET substrate in the NaOH solution (Fig. 7a), which was caused only by neutralization, gradually increased with time. For the silica substrate, the SA-LB film was rapidly removed due to liquid penetration both in the NaOH (Fig. 7b) and SDS solutions (Fig. 7c). The neutralization is a slow reaction but can efficiently remove an ultra-thin oily contaminant from any substrate after a certain amount of time.

3.4 Effect of atmospheric pressure plasma exposure

The authors have reported that the atmospheric pressure plasma (APP) treatment of the polymer substrate after soiling promotes soil release by subsequent aqueous cleaning. To promote the removal in aqueous NaCl or SDS solution, the APP exposure to the QCM electrode with the SA-LB films was carried out using a commercial plasma pretreatment equipment (Plasmatreat GmbH, Germany) consisting of a plasma generator (FG1001), high-voltage transformer (HTR1001), and rotating nozzle jet (RD1004) under optimal conditions for obtaining high hydrophilicity without thermal damage. The QCM frequency reduction after APP exposure was within 10 ng and was much smaller than the deposition mass of the SA-LB film. The cleaning test was performed within 30 min of the APP exposure.

The effects of the APP treatment on the removal efficiencies of the SA-LB film in the aqueous NaCl and SDS solutions are shown in Fig. 8. The removal was drastically enhanced by the APP pretreatment in the cases of the carbon, gold, and PET substrates. Notably, the detergency for the carbon substrate was ~50% and is comparable to that in the NaOH solution (see Fig. 5). However, the APP effect was relatively small for the silica substrate.

Figure 9 shows the contact angles of water on the substrates and the SA-LB film deposited on each substrate. The contact angle on the carbon, gold, and PET substrates and the SA-LB films deposited on them was found to decrease markedly following the APP exposure. It is considered that such a wettability increase promotes liquid penetration and results in the enhanced soil removal, as shown in Fig. 8. However, in the case of the hydrophilic silica substrate, little change in wettability following the APP exposure was observed, which is consistent with the small in-

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**Fig. 8** Effect of plasma exposure on removal of stearic acid LB films from the four substrates in the NaCl (a) and SDS (b) solutions.

**Fig. 9** Effect of plasma exposure on contact angle of water on the substrates and stearic acid LB films.
crease in the removal efficiency.

4 CONCLUSIONS

The removal process of the trace-level contaminant of SA from carbon, silica, gold, and PET substrates was investigated using the QCM and LB deposition techniques. The removal efficiency was obtained from the QCM frequency change occurring during aqueous cleaning. It was found that the SA-LB film was considerably removed by neutralization in the NaOH solution, although the reaction was slow. The removal efficiency of the SA-LB film due to liquid penetration into the contact zone between the SA-LB film and the substrate was within ~10%, even in the presence of the surfactant. To increase the removal efficiency of the SA-LB film in the absence of NaOH, hydrophilization by APP exposure prior to aqueous cleaning was found to be effective.

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References

1) Kato, Y.; Umeda, H.; Fujimoto, H. Past and future developments of aluminum substrates for high density magnetic disks. KOBE STEEL ENGINEERING REPORTS 50-3, 50-53(2000).
2) Robert, G. G. Langmuir–Blodgett Films, Plenum, New York, pp. 17-92(1990).
3) Gotoh, K.; Nakata, Y. Detergency of oily contaminants as Assessed with a quartz crystal microbalance and the Langmuir-Blodgett method, J. Oleo. Sci. 53, 489-495(2004).
4) Gotoh, K. The role of liquid penetration in detergency of long-chain fatty acid. J. Surfact. Deterg. 8, 305-310 (2005).
5) Lu, C. S.; Lewis, O. Investigation of film-thickness determination by oscillating quartz resonators with large mass load. J. Appl. Phys. 43, 4385(1972).
6) Kanazawa, K. K.; Gordon II, J. G. Frequency of a quartz microbalance in contact with liquid crystal. Anal. Chem. 57, 1770-1771(1985).
7) Kanazawa, K. K. Mechanical behavior of films on the quartz microbalance. Faraday Discuss. 107, 77-90 (1997).
8) Weerawardena, A.; Drummond, C. J.; Caruso, F.; McCormick, M. Real time monitoring of the detergency process by using a quartz crystal microbalance. Langmuir 14, 575-577 (1998).
9) Shimomura, K.; Onozawa, H.; Komiyama, J. Protein soil release using protease as monitored with a quartz crystal microbalance. Textile Res. J. 67, 348-353 (1997).
10) Gotoh, K.; Tagawa, M. Detachment behavior of Langmuir–Blodgett films of arachidic acid from a gold surface studied by the quartz crystal microbalance method. Colloids Surf., A 196, 145-152 (2002).
11) Kanazaki, Y.; Kobayashi, Y.; Gotoh, K.; Dynamic analysis of the removal of fatty acid from a PET surface using a quartz crystal microbalance. J. Surfact. Deterg. 19, 627-636 (2016).
12) The commissioned research of Japanese Ministry of Economy, Trade, and Industry in FY 2008, http://www.meti.go.jp/policy/chemical_management/other/itaku/pdf/h20/houkukokusoho_senzai_h20.pdf, in Japanese, accessed in November, 2015.
13) Gotoh, K.; Tagawa, Y.; Tabata, I.; A quartz crystal microbalance simulation to examine the effect of ultraviolet light treatment on characteristics of polyethylene surface. J. Oleo Sci., 57, 495-501 (2008).
14) Nagai, Y.; Togawa, N.; Tagawa, Y.; Gotoh, K. Comparison of cleaning power between alcohol ethoxylates or methyl ester ethoxylates having different EO chain lengths and a common anionic surfactant. Tenside Surfact. Det. 51, 113-118 (2014).
15) Sauerbrey, G. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. Zeitschrift für Physik. 155, 206-222 (1959).
16) Furusawa, H.; Ozeki, T.; Morita, M.; Okahata, Y. Added mass effect on immobilizations of proteins on a 27 MHz quartz crystal microbalance in aqueous solution. Anal. Chem. 81, 2268-2273 (2009).
17) Ozeki, T.; Morita, M.; Yoshimine, H.; Furusawa, H.; Okahata, Y. Hydration and energy dissipation measurements of biomolecules on a piezoelectric quartz oscillator by admittance analyses. Anal. Chem. 79, 79-88 (2007).
18) Gotoh, K.; Kobayashi, Y.; Yasukawa A.; Ishigami, Y. Surface modification of PET films by atmospheric pressure plasma exposure with three reactive gas sources. Colloid Polym. Sci. 290, 1005-1014 (2012).
19) Rosen, M. J. Surfactants and Interfacial Phenomena. Wiley, Hoboken, pp. 353-378 (2004).
20) Gotoh, K.; Kanazaki, Y.; Uchimomaru, H. Introduction of atmospheric pressure plasma to aqueous detergent processes. J. Oleo Sci. 64, 817-824 (2015).