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LB Deposition of a Stearic Acid Multilayer without Heavy Metals

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LB films consisting of stearic acid (SA) multilayers and silicon substrates without heavy metal were prepared using a computer-controlled LB film deposition apparatus. Using dimethyldioctadecylammonium bromide as the first (or first and second) monolayer(s), up to 70 layers were deposited, and the interference color was expressed. This indicated that the surface charge of the substrate needed to be canceled in order to successfully deposit a multilayer. Moreover, it was demonstrated that LB multilayers of fatty acid could be prepared using a computer-controlled apparatus even without using a heavy metal salt.

The Langmuir–Blodgett (LB) technique is an advanced method for preparing flat and ordered organic multilayers, and is expected to lead to the creation of novel nano-device systems.[1–5] This method was first published by Blodgett, who transferred more than 200 layers of fatty acid monolayers onto plates made of glass or metal.[1] Today, this method is presented in many textbooks on interface chemistry, and is well-known as a method to form LB multilayers.[3] However, many textbooks suggest adding a heavy metal salt, like cadmium chloride, to the aqueous subphase as did Blodgett, and even recent papers follow this suggestion.[6,7] One problem of demonstrating LB deposition by this method is the need to dispose of a large quantity of waste solution containing heavy metal after the experiment.

Shiozawa and Fukuda examined the deposition of a long-chain fatty acid monolayer on the surface of pure water onto a hydrophobic surface, and succeeded in building a perfect Y-type film.[8] The deposition ratio was 1 in both the up and down modes at 29.5 mN/m. However, it is very difficult to keep the surface pressure of the monolayer of a fatty acid, such as stearic acid (SA), at 29.5 mN/m when using most of the computer-controlled LB film deposition apparatus[9] on the market. The reason for this is that a computer makes the barrier open or close when it detects any deviation of the surface pressure from the provided range. Because the change in the surface pressure of the fatty acid monolayer is very fast, nearly 30 mN/m, as shown in Fig. 1, the movement of the barrier becomes very unstable.

The details are as follows. The surface pressure was 24.0 mN/m at the transfer point (A = 0.200 nm^2) of the SA monolayer. On the other hand, the surface pressure was 52.0 mN/m at the collapse point (A = 0.186 nm^2). Between these two points, the surface pressure rose 28 mN/m when 7% of the SA monolayer was compressed. Generally, the deposition pressure must be kept at ±0.5 mN/m to stabilize the monolayer. In this case, however, the surface pressure exceeds this error range when the monolayer is compressed by only 0.25%. For example, in the case of our trough, the length of which is only 180 mm, if the barrier is in the 100 mm position when the deposition is started, the change of the surface pressure soon exceeds the error range by a mere 0.25 mm movement of the barrier. When this occurs, the stability of the monolayer is limited. This means that the computer-controlled apparatus must be operated at a surface pressure lower than the transfer pressure (24 mN/m in the case of stearic acid) of the monolayer.

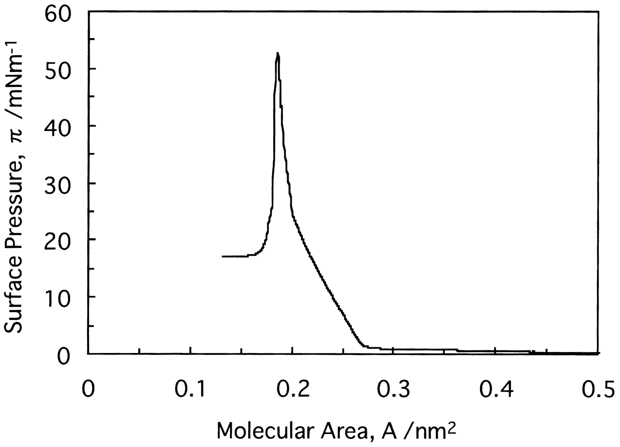

Fig. 1. Surface pressure–molecular area isotherm of stearic acid monolayer at 20 °C.

By the way, we have attempted to prepare several LB films using various materials to develop a novel display system[10] using structural color.[11] In this work, we also at first used stearic acid with a silicone substrate as materials of LB films, though we wanted to avoid using heavy metals. This resulted in the successful building of a perfect Y-type deposition film of organic layers without any heavy metals at a lower deposition pressure. This study proved a process and method for making depositions.

Experimental

Stearic acid (SA) was purchased from Tokyo Kasei Kogyo. Dimethyldioctadecylammonium bromide (DDOA) was purchased from Wako Pure Chemicals Industries. The spreading solvents for monolayers were of spectrograde from Nakalai Tesque. All commercial reagents were used without further purification. Water was distilled and deionized by a Milli-Q system (Millipore).

Silicon wafers (n-type (100) wafers) were purchased from Shin-Etsu Chemical. Substrates (15×20–25 mm) were cut from a wafer, washed with acetone, and cleaned by exposure for 20 min in air to vacuum ultraviolet light generated from an excimer lamp (Ushio electric, UER20-172V, λ = 172 nm and 10 mW cm^{-2}).[12] Due to this cleaning, a thin oxide (SiO_2) layer of ca. 2 nm in thickness was formed on the samples.

A surface pressure (π) - molecular area (A) measurement and LB deposition was performed using a “Bio-trough” NL-BIO40-MWCT (Nippon Laser & Electronics Lab.).

Results and Discussion

Direct Deposition of Surfactants. First, we simply tried to deposit a monolayer of SA onto a substrate of silicon at 22 mN/m. The substrate was soaked in aqueous subphase before spreading the monolayer because the SiO_2 surface was hydrophilic. After spreading and compressing, deposition was performed. The dipping rate was 10 mm/min. Fig. 2 shows the change in the deposition ratio with the dipping numbers. One dipping number means one movement of the dipper in the up or down mode. The deposition ratio was almost 1 in the first step, but returned to almost 0 in the next down mode. This indicated that the monolayer on the substrate had come off and returned to the aqueous surface. The isoelectric point of SiO_2 is about 2.[13,14] The charge of the SiO_2 surface in pure water is negative and SA also has a negative charge. This suggests that the SA monolayer has little affinity to the silicon surface in the aqueous subphase.

Although many textbooks suggest drying the substrate after the first deposition,[1] or using iron(III) stearate as the first layer[2] to render the first layer stable, this study only used the LB apparatus. Because it was assumed that positive surfactants might be stable on a negative surface, the deposition of DDOA monolayers was attempted. The deposition pressure was 35 mN/m. As a result, although the deposition succeeded to the third layer, the transferred layer came off in the next down mode (Fig. 2). This was probably due to the structure in which ammonium groups of the second and third layers face each other and become unstable in the aqueous subphase because the dissociation degree of ammonium groups is high. However, this indicated that the first DDOA monolayer was fixed stably on the silicone surface, even in the aqueous subphase.

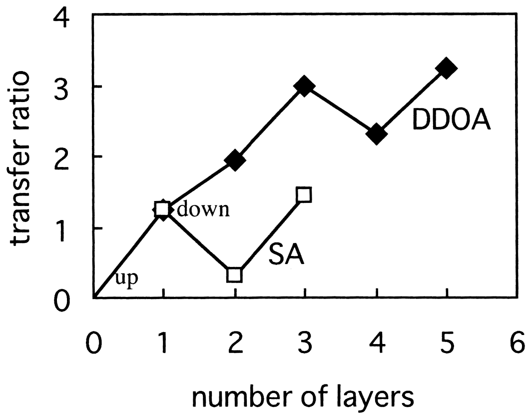

Fig. 2. Transfer ratio of stearic acid (open square) and DDOA (close diamond) monolayers onto silicon substrate. Dipping rate was 10 mm/min.

Deposition of SA Layers onto DDOA LB Film. Since in DDOA the first layer deposited in the up mode did not come off in the next down mode, the deposition of an SA monolayer was attempted onto the DDOA deposited surface. After one monolayer of DDOA had been deposited in the up mode onto the bare silicon substrate, the DDOA monolayer on the aqueous surface was sucked away, an SA monolayer was re-spread, and then deposited onto the DDOA deposited surface. From Fig. 3, it can be seen that reproducibility was not achieved in the results of three repetitions of this experiment under the same condition. However, deposition in the down mode occurred on every occasion.

Even when the deposition did not occur in the up mode, the barrier was always observed to be temporarily closed at the moment that the dipper began to move upward. The same experiment was then repeated with an increased dipping rate in the up mode to 50 mm/min, because the barrier speed would also be higher and the force that pressed the monolayer against the substrate would increase. This succeeded and a Y-type film was prepared, as shown in Fig. 4. In this study, 70 layers of SA were deposited onto a DDOA layer. Beyond 30 layers, the substrate showed interference colors (Fig. 5): yellow at 31 layers, red at 37, red purple at 43, blue purple at 49, blue at 57, and light blue at 71 layers (including DDOA layers).

Preparation of More Stable Film. Although the experi-

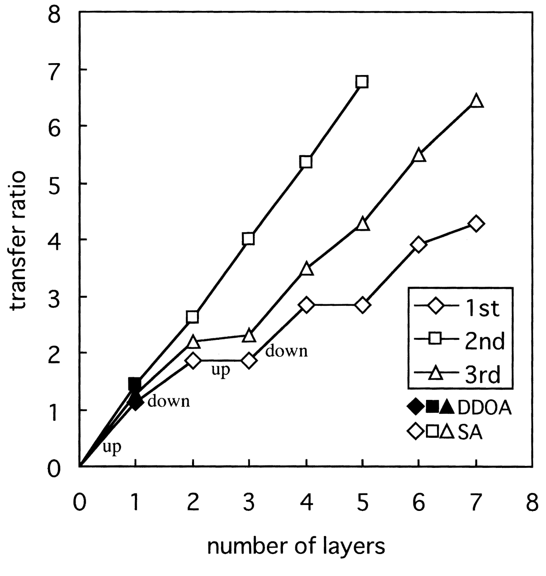

Fig. 3. Transfer ratio of one DDOA monolayer (close) and stearic acid monolayers (open) onto silicon substrate. Plots of various shapes (diamond, square, and triangle) show reproducibility. Dipping rate was 10 mm/min.

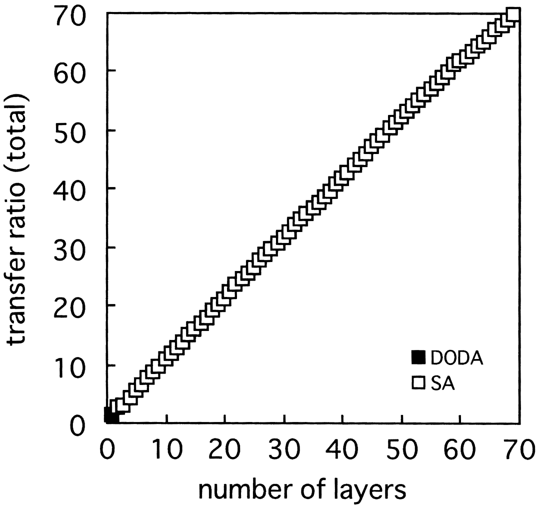

Fig. 4. Transfer ratio of one DDOA monolayer (close) and stearic acid monolayers (open) onto silicon substrate. Dipping rate was 10 mm/min (in up mode for DDOA and down mode for SA) or 50 mm/min (in up mode for SA).

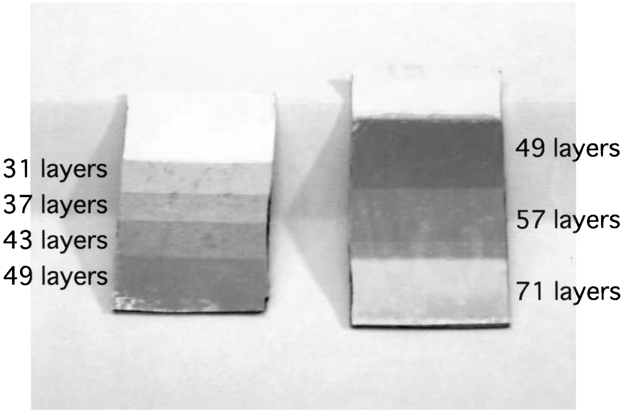

Fig. 5. Digital camera image of the interference colored substrates. The right and left ones were prepared in the case of Figs. 4 and 6, respectively. Different colors on a substrate show difference of the number of layers by changing the dipping length. The scratches at the bottom of the left substrate are putted accidentally after experiment.

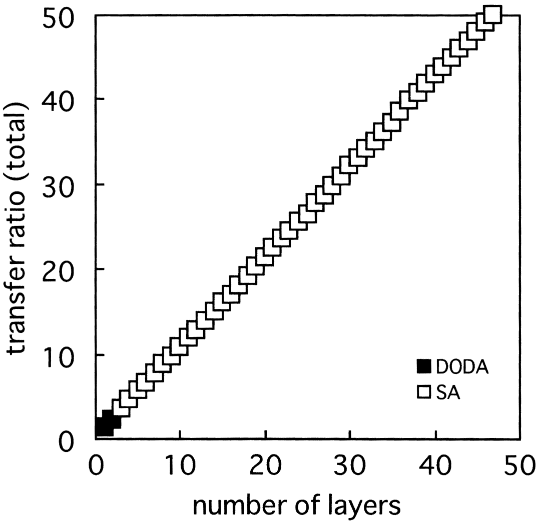

Fig. 6. Transfer ratios of two DDOA monolayers (close) and stearic acid monolayers (open) onto silicon substrate. Dipping rate was 10 mm/min.

ment succeeded, such a high dipping rate increases the chance of incomplete deposition. The above experiments indicated that the deposition of a multilayer always succeeded when the deposition of the third layer succeeded (see Figs. 3 and 4). Next, the DDOA layer was used in the first and second layers because it was expected that deposition on the third layer of SA (which had a negative charge) onto the DDOA dilayer (which had positive surface) would be stable. After two layers of DDOA were deposited in the up and down modes, the DDOA monolayer on the aqueous surface was sucked away, and the SA monolayer was re-spread and deposited onto the substrate. Because the substrate was soaked in an aqueous subphase when two DDOA layers had been deposited, re-spreading of the SA monolayer was performed while trying not to change the aqueous subphase level. The dipping rate was 10 mm/min in both the up and down modes. As a result, a perfect Y-type deposition film was successfully prepared, even in the example shown in Fig. 6. In this study, 49 layers were deposited including DDOA layers. This substrate also showed interference colors (Fig. 5) in a similar manner to that mentioned above.

Confirmation of Interference Color. The incident light with a certain incident angle (α) is emphasized or enfeebled at the surface, which depends on the wavelengths (λ) of light. The λ values of the emphasized or enfeebled light are expressed as follows:[15]

$$\lambda = \frac{2dl}{m}\sqrt{n^2 - \sin^2\alpha} \quad (emphasized), \tag{1}$$

$$\lambda = \frac{4dl}{2m-1}\sqrt{n^2 - \sin^2\alpha} \quad (enfeebled), \tag{2}$$

where d is the thickness of one layer of the SA or DDOA, l is the number of layers, n is the refractive index of the layer, and m is a natural number ($m = 1, 2, \ldots$). The d value corresponds to the length of one SA (or DDOA) molecule, calculated to be 2.2–2.3 nm by CPK model. We could thus see light having a particular wavelength (particular color) from such a surface.

Using above equations (with the values of $\alpha = 0$, $n = 1.5$ and $d = 2.2$ nm), we can expect the colors of the substrates. Table 1 shows the expected wavelength of the emphasized or enfeebled light and its color along with the actual color of the front view of the prepared substrate. The expected and actual colors almost correspond, which shows that these colors are interference colors.

Conclusion

The deposition of SA was disrupted by a negative charge on the surface of a silicon substrate. By using a positive surfactant (DDOA in this study), the negative charge on the silicon surface was cancelled, and it became possible to deposit an SA monolayer. Thus, this study has shown that an LB film of fatty

Table 1. Calculated λ Values and Expected and Actual Colors of Prepared Substrates

Number of layers, n	Calculated λ value[a)] /nm	Expected color	Actual color
31	409	yellow	dark yellow
37	488	orange	brown (dark orange)
43	568	purple	red purple
49	647	blue	blue purple
57	752	cyan	blue
71	469	blue	light blue

a) Calculated by Eq. 2 except for the case of $n = 71$ which is calculated by Eq. 1.

acid can be easily prepared with a computer-controlled LB apparatus without using a heavy metal salt, while the interference colors were adequately expressed using a silicone substrate and organic molecules.

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