

AFM Study of Discrete Surface Functional Group Fabricated by Langmuir-Blodgett Technique

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We have studied the Langmuir-Blodgett (LB) films formed with the mixture of stearic acid (SA) and stearyl mercaptan (SM) which have approximately the same lengths but different head groups. It was confirmed with atomic force microscopy (AFM) that flat and tight bilayer films were obtained with the mixtures which contain less than 10% of SM. AFM images showed that the surfaces contained a number of protrusions exhibiting higher frictional force. The density of the protrusions was nearly proportional to the concentration of SM. The histogram of the topographic height for the high-friction spots clearly exhibited two peaks at around 1.7 and 2.6 Å, which can be explained by the models where the -SH shifts outward for one and two -(CH₂)- units, respectively. These results imply that some part of the -SH groups protrude from the surface. Such protruded -SH groups could be chemically active sites. The distribution of the maximum friction had only single peak in contrast to the height distribution.

Key words: Langmuir-Blodgett film, stearic acid, stearyl mercaptan, AFM, FFM, chemical identification

1. INTRODUCTION

Obtaining a flat surface that contains discrete functional groups with aimed density is doubtless valuable for nanometer scale science and technology. The functional groups can be used as nucleation sites for vacuum deposition or as adsorption sites for biomolecules. Furthermore, such a surface can be used as a test structure for scanning probe microscopy (SPM) in terms of chemical identification. For this purpose, we have studied the Langmuir-Blodgett (LB) films [1] formed with the mixture of stearic acid (SA) and stearyl mercaptan (SM) on atomically flat silicon substrates. Mixed LB films have been extensively studied with SPM such as atomic force microscopy (AFM) and frictional force microscopy (FFM) [2-7]. Most of the mixed materials used in those works are immiscible and are separated to the domains with the size ranging from hundreds of angstroms to micrometers. However, two molecules used in this work have approximately the same shapes and lengths, and the only difference is in their head groups. SM has a sulfhydryl (-SH) group instead of a carboxyl (-COOH) group, as shown in Fig. 1. In this case, relatively higher concentration of SM is expected to be miscible in the SA monolayer. Moreover, part of the SM molecules will be incorporated upside down due to the weaker hydrophilicity of the -SH groups than that of -COOH groups. It is also expected that some part of them protrude from the surface and become the active sites.

In this paper, the morphology and the distribution of the frictional force of obtained films have been studied with AFM and FFM. The evidence of the formation of such active sites will be shown. Some interesting

behavior of the active sites with frictional force will be discussed.

2. EXPERIMENTAL DETAILS

A Si(111) wafer with 0.5° off-angle was used as the substrate. The wafer was thermally oxidized to form a 5000 Å thick oxide film. It was, then, cut into small pieces and cleaned by dipping into boiling aqueous Na₂S₂O₈. A flat substrate was prepared by removing the surface oxide with 1% HF followed by anisotropic etching with 40% aqueous NH₄F for 15 min. This substrate surface is known to be atomically flat consisting of well-ordered atomic steps [8] and to be hydrophobic.

LB films were deposited using rectangular trough (Lauda). It was confirmed by gas chromatography that SA (Nacalai Tesque) and SM (Tokyo Kasei) contain no significant impurity that has a longer alkyl chain. Two solutions of SA and SM, 0.5 mg/ml in chloroform for each material, were used to form a mixture of specific ratio, and the mixture was spread over the surface of

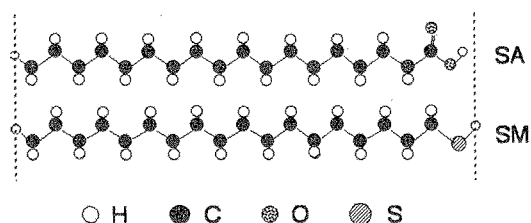


Fig.1 Molecular structures of stearic acid (SA) and stearyl mercaptan (SM).

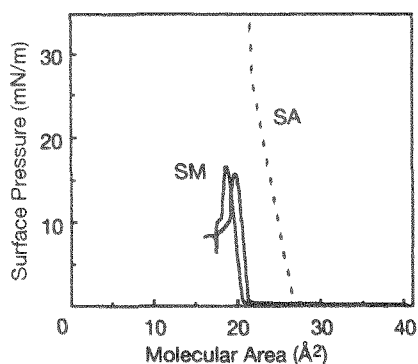


Fig.2 π -A isotherms of SA (a dashed line) and SM (solid lines) at a temperature of 22°C.

semiconductor grade ultra-pure water filled in the trough. The monolayer films on the water subphase were compressed to a surface pressure of 35 mN/m and were then transferred onto substrates with a vertical immersion speed of 15 cm/min. All films were deposited by single complete cycle of the substrate motion, which resulted in bilayer films having hydrophobic surfaces.

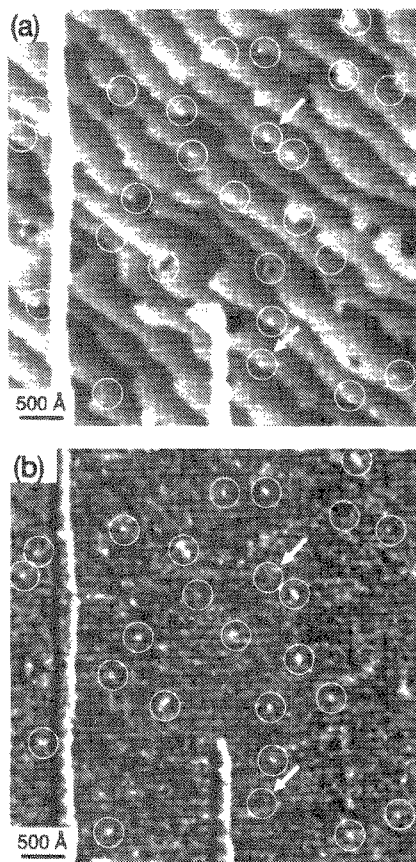


Fig.3 AFM images of a mixture LB film (SA:SM = 98:2): (a) a topographic image and (b) a frictional force image. White circles denote high-friction spots seen in the frictional force image and corresponding protrusions in the topographic image, however those with arrows do not exhibit higher friction.

AFM and FFM (Digital Instruments, NanoScope IIIa) measurements were carried out simultaneously in nitrogen atmosphere using triangular-shape silicon nitride cantilevers with the stiffness of 0.12 N/m. The images were obtained using variable height mode where the force load was set weak enough so that the tip traces the surface steadily.

3. RESULTS AND DISCUSSION

Prior to the film transfer, a surface pressure-area (π -A) isotherm of each component was measured. Figure 2 shows the π -A isotherms of SA (a dashed line) and SM (solid lines) measured at a temperature of 22°C. To show the reproducibility of unstable character of SM, two isotherms obtained with different experimental runs are plotted in the figure. SA shows a typical liquid condensed-solid transition and is durable against high surface pressure, but SM directly changes from gas to solid and collapses at 15 mN/m. These isotherms show that SM is not a suitable molecule to obtain a good Langmuir monolayer on water surface compared to SA. The π -A isotherms of the mixture of SA and SM were also measured. The only difference from that of SA was a slight decrease of the liquid-solid transition pressure as the SM concentration raised from 2 to 20%. This suggests that the interaction with surrounding SA molecules has stabilized the small amount of SM molecules in the closely packed SA monolayers.

AFM observations of the macroscopic shapes of the LB films showed that the surfaces were rough and unstable when the concentration of SM exceeds 10%, but flat and stable to clearly exhibit substrate atomic steps through the films at the concentration range of 2-10%. Therefore, we observed the surfaces of the films of two representative compositions, SA:SM = 98:2 and 90:10, more precisely for the detection of functional groups.

Figure 3 shows typical (a) topographic and (b) frictional force images obtained on a mixture LB film of SA:SM = 98:2. The AFM tip was scanned from right to left to suppress frictional signals due to substrate steps. Two belt-like protrusions in this area are a kind of defect which is frequently observed on fatty acid LB films [9].

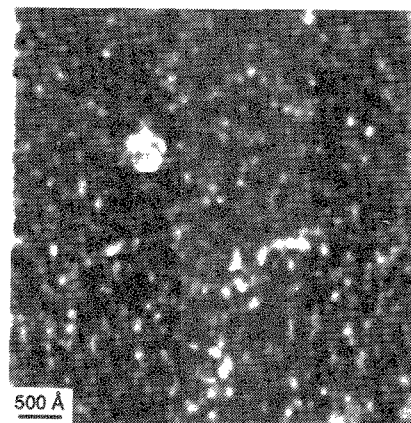


Fig.4 A frictional force image of a mixture LB film (SA:SM = 90:10).

Table 1. Densities of high-friction spots and their ratio to SM densities.

concentration of SM (%)	density of SM molecules, σ_{SM} (cm ⁻²)	density of high-friction spots, σ_{hf} (cm ⁻²)	$\sigma_{hf} / \sigma_{SM}$
2	9.1×10^{12}	1×10^{10}	1.1×10^{-3}
10	4.5×10^{13}	6×10^{10}	1.3×10^{-3}

Existence of this defect implies that this area is certainly covered with the LB film. In these images, we can see a number of protrusions exhibiting higher frictional force, which are marked with white circles. The appearances of the protrusions and higher frictional spots were reproducible for many different places on the sample even when the imaging parameters were moderately changed. As far as we observed on this film, the high-friction spots always appeared with corresponding protrusions, but protrusions did not always appear with high-friction spots. For example, two protrusions marked by arrows in Fig. 3 are not accompanied with high-friction spots. These imply that the protrusions are classified into at least two types of structures having different chemical natures: one causes high-friction and the other does not. The latter may be due to impurity molecules having longer alkyl chains.

In a similar way, topographic and frictional force images were taken on a mixture LB film of SA:SM = 90:10, one of the frictional force images is shown in Fig. 4. The images of the films containing higher concentration of SM always appeared more noisy than those containing less SM, probably because the molecular packing became loose by increasing SM. However, there is no doubt that the density of the high-friction spots is increased with the SM concentration.

Densities of high-friction spots and their ratio to SM area densities on these two films are summarized in Table 1. The density of SM molecules, σ_{SM} was estimated according to the concentration of SM in the raw material and a typical molecular area of SA in LB films, 22 Å². When the density of high-friction spots, σ_{hf} , was calculated from the number of the spots in Figs. 3(b) and 4, a distorted spot of which size was larger than others was counted redundantly. It is because such a large and distorted spot is considered to consist of two or three adjacent spots which are connected due to the spatial resolution of the measurement. From these

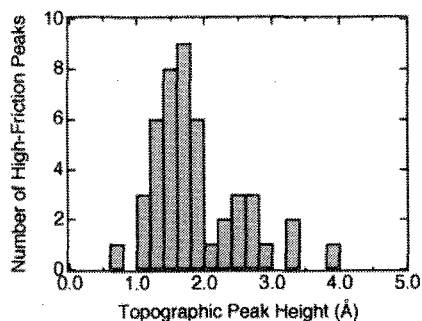


Fig.5 A histogram of topographic peak height of the protrusions on the mixture LB films which exhibit higher friction.

results, σ_{hf} is considered nearly proportional to σ_{SM} , and the ratio is around 1/1000. In these LB films, the fraction of protruded -SH group against all SM molecules, namely the activation ratio, is written as: $f_i \times f_p$, where f_i is the probability that a SM is configured upside down in a molecular layer and f_p is the probability that the SM is shifted outward from the layer surface. The f_i is supposed to be small because a -SH group is hydrophilic although the hydrophilicity is not strong as that of a -COOH group. Hence, 1/1000 is not a surprising value for D_{hf}/D_{SM} .

The diameter of the high-friction spots observed in this work was more than a few tens angstroms. However, it increased with continuous image acquisitions and was recovered when a new tip was used. Therefore, the size and the shape are considered to depend on the tip apex, which means that the original structure causing the higher friction is smaller than the observed size. Assuming the interaction between a sphere of 100 Å radius and a protrusion of approximately 1.5 Å heights, this model for the protrusion will be discussed later in Fig. 6, the original structure is possibly a single molecule.

From many images including Figs. 3(b) and 4, we chose many isolated high-friction spots which have clear shape and are apart from substrate steps. A histogram of their topographic peak height is shown in Fig. 5. The total number of the sampled spots is 46. The histogram obviously exhibits two peaks at around 1.7 and 2.6 Å. The shape of the peaks has a longer tail on the lower side. This asymmetric shape is regarded as a result of elastic deformation when the protrusions are pressed by the AFM tips.

Here, we consider a model of the mixture film where the molecules are closely packed and are nearly perpendicular to the substrate. This model is consistent with the fact that molecular images showing centered rectangular lattice were observed with AFM, and that thicknesses of the films measured with ellipsometry were within the range of 45-50 Å. A SM molecule

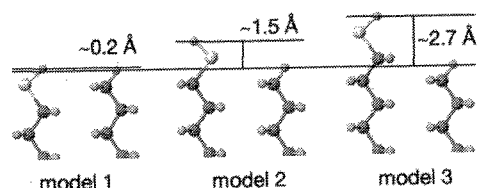


Fig.6 A schematic models of the protrusions exhibiting higher friction in the mixture LB films. The SM molecules are configured at the same height as (model 1), a -(CH₂)- unit higher (model 2) and two -(CH₂)- units higher (model 3) than the neighboring SA molecules.

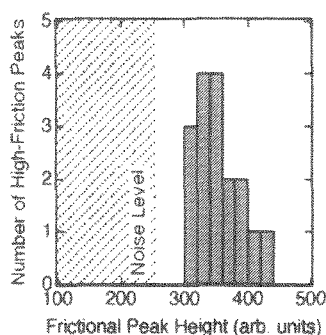


Fig.7 A histogram of frictional peak height of the high-friction spots on the mixture LB film.

included upside-down in a SA monolayer will take the states shown schematically in Fig. 6 since the packing is restricted by the shape of the alkyl chains. In these models, the SM molecules are configured at the same level as (model 1), a $-(CH_2)-$ unit higher (model 2) and two $-(CH_2)-$ units higher (model 3) than the neighboring SA molecules. A SM is 0.2 Å higher than its neighbors even in the model 1 because the length of C-S-H structure is longer than that of C-C-H, and is 1.5 or 2.7 Å higher in the model 2 or 3, respectively. On the other hand, the heights of the corresponding structures become 0, 1.3 and 2.5 Å, respectively, if the -SH group is replaced with a $-CH_3$ group. Consequently, the original structures of the height distribution shown in Fig. 5 is more likely to be the protruding -SH rather than the protruding $-CH_3$.

Considering these results, it is concluded that the flat surfaces which contain discrete functional groups were obtained as initially expected. The only doubt remained is whether the high-friction spot contains a single -SH group or more. The clearly appeared peaks in the height distribution is, however, an encouraging fact which implies that the spot consists of a single -SH group.

An interesting point is that the distribution of the maximum friction at these spots has only single peak in contrast to the height distribution. Figure 7 shows a histogram of frictional peak height of the high-friction spots. In this case, the sampled spots were chosen from one frictional force image, because not only the size, but also the maximum friction was varied with tip conditions. Therefore, the total number of the sampled spots is 17, which is much smaller than Fig. 5. Although the background noise level is not sufficiently low, the high-friction spots chosen for Fig. 5 also exhibited higher friction than the noise level. Besides, the topographic height of the spots sampled for Fig. 7 also distributed similarly to Fig. 5. Accordingly, the maximum friction surely has narrower dispersion than the topographic height does. This suggests that the friction depends dominantly on the chemical uniqueness of the functional group, but not on how much it protrudes from the film surface. However, if the -SH group is hindered by neighboring molecules such as the model 1 structure in Fig. 6, it is considered to be inactive for the tip scan, since no high-friction spot without corresponding protrusion was found in this work.

4. SUMMARY

LB films formed with the mixture of SA and SM, which have approximately the same lengths but different head groups, were studied with a view to prepare a test structure for AFM detection of discrete functional groups. It was confirmed that flat and tight films were obtained with the mixtures which contain less than 10% of SM. The surfaces contained number of protrusions exhibiting higher frictional force. Their density was nearly proportional to and was around 1/1000 of the SM area density. The distribution of the topographic height of these spots clearly exhibited two peaks around 1.7 and 2.6 Å, which can be well explained by the models where the -SH group shifts outward for one and two $-(CH_2)-$ units of an alkyl chain. These results imply that the expected surface was successfully obtained. It was, then, found that the distribution of the maximum friction at these spots had only single peak in contrast to the height distribution. While FFM is well known to be sensitive to the surface chemical composition [4], these results suggest that even an isolated functional group produces greater effect on frictional force than the height difference of the group.

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