Spreading Properties of Monolayer Lubricant Films: Effect of Bonded Molecules

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Monolayer lubricant films applied to head–disk interface of hard disk drives consist of bonded and mobile molecules. We measured the diffusion coefficient of mobile molecules that spread through the spaces not covered with bonded molecules and revealed its dependence on the coverage fraction. The diffusion coefficient gradually decreased with increasing coverage from 0.2 to 0.8, and its trend was well represented by reptation theory. However, the diffusion coefficient significantly decreased at a coverage higher than 0.8, in contrast to the prediction of reptation theory. The reason for this decrease is thought to be the disappearance of minimum spaces required for mobile molecules to spread through.

Index Terms—Head–disk interface, monolayer lubricant film, perfluoropolyether, spreading.

I. INTRODUCTION

MONOLAYER lubricant films with thicknesses of 1–2 nm are used to lubricate the head–disk interface (HDI) of hard disk drives. A monolayer lubricant film must have good retention and replenishment characteristics. Retention is important for avoiding direct contact between the magnetic head and the disk. Replenishment is essential to repair lubricant films ruptured by contact with the head. To secure both retention and replenishment, lubricant films consist of two different types of molecules: bonded molecules, which chemically bond to the disk surface, and mobile molecules, which weakly adsorb to the disk and can move diffusively. The bonded molecules are mainly responsible for retention, whereas the mobile molecules confer replenishment properties through their diffusive motion. Pit and Marchon determined the diffusion coefficient of the monolayer lubricant film by monitoring the temporal decay of a lubricant film thickness with well-controlled initial sinusoidal thickness modulation [1]. However, lubricant films they used were mainly composed of nonbonded molecules. When the lubricant film is a monolayer, the mobile molecules exist in the same plane as the bonded molecules, and they must spread through the spaces that are not covered by the bonded molecules to accomplish replenishment. Our previous research revealed that the diffusion coefficient of mobile molecules decreased with increasing coverage of bonded molecules on the disk surface. This spreading property could be explained by the modified reptation model and could be reproduced in a molecular dynamics simulation [2], [3]. However, the diffusion coefficient measurement in the previous study did not have enough accuracy to reveal the detailed mechanism of the dependence of the spreading properties on the coverage of bonded molecules. In this paper, we refine the experimental procedure and reveal the details of the spreading phenomenon of mobile molecules. We also study the relation between the
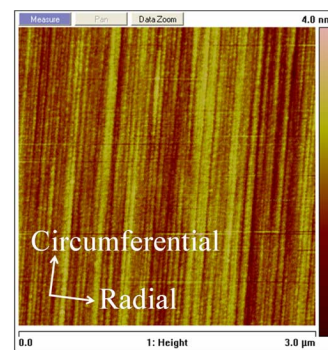
Fig. 1. Surface topography of sample disk without lubricants measured by AFM. Bright area represents higher region. Surface texture was observed in the circumferential direction.

distribution and conformation of the bonded molecules and the spreading of mobile molecules.

II. SAMPLE PREPARATION

A perfluoropolyether (PFPE) lubricant, Fomblin Zdol4000, was used as a sample lubricant. Zdol4000 has a linear chain structure and hydroxyl end groups on both sides of the chain. Due to the flexibility of the chain, Zdol4000 molecules usually have a random coiled structure with a gyration diameter of around 3 nm. The monolayer thickness of Zdol4000 was determined from the height of "terraced profiles" at the film boundary, and it was 2.3 nm. These "terraced profiles" are described in [4].

As a substrate, we used a magnetic disk with a diamond-like carbon overcoat. The surface topography of the disk without the lubricant was measured by atomic force microscopy (AFM). As shown in Fig. 1, the disks were textured in the circumferential direction. The root-mean-square surface roughness was around 0.4 nm.

Lubricant films were applied to the disks by using the dip-coating method. The film thickness was kept around 2 nm by adjusting the solution concentration and lifting speed of the dip-coating. It was measured by using a scanning ellipsometer. The spot size of the scanning ellipsometer was 35 μm in diameter. Only some of the lubricant molecules applied to the disk

surface became bonded molecules through chemical bonding between the hydroxyl end groups and adsorption site on the disk. Lubricant molecules that did not chemically bond to the surface became mobile. To accelerate the chemical bonding, in other words, to control the amount of bonded molecules, annealing or an ultraviolet-ray treatment is usually used. In the study described in this paper, we used annealing. The annealing temperature was 120 or 150 °C. By increasing the annealing time (from 15 min to 12 h), the amount and coverage of bonded molecules could be increased. We covered many disks with different amounts of bonded molecules. After the annealing treatment, these disks were rinsed in solvent (HFE), and all mobile molecules were removed from the surface. Eventually, we prepared many disks covered only with bonded molecules and had coverages ranging from 0.2 to 0.9. The minimum coverage of 0.2 was the saturated value that can be achieved at room temperature. Section III-A describes how we measured the coverage of bonded molecules.

III. CHARACTERIZATION OF BONDED MOLECULES

Bonded molecules were characterized by their coverage, molecular height, and distribution on the disk surface. Coverage was determined by measuring the contact angle. The molecular height was estimated from the coverage and the average thickness measured by the scanning ellipsometer. AFM was used to observe the distribution of bonded molecules. We also tried to measure the molecular height directly in order to compare it with the estimated results. These characterizations are described below.

A. Coverage of Bonded Molecules

The coverage C was obtained by measuring the surface energy of the disks covered by the bonded molecules and applying Cassie–Baxter's law

$$C = (\sqrt{\gamma} - \sqrt{\gamma_s})/(\sqrt{\gamma_l} - \sqrt{\gamma_s}) \qquad (1)$$

where γ is the measured surface energy. γ_s and γ_l represent the surface energies of a disk without any lubricant and one fully covered with lubricant, respectively [5]. The surface energies were determined by measuring the contact angle with hexadecane as a test liquid.

B. Estimation of Molecular Height

We measured the thicknesses of the bonded molecules on the disk by using an ellipsometer. In the ellipsometric measurement, the thickness was calculated from the measured changes in the polarization state of light reflected from the sample surface on the basis of an optical model of a disk fully covered by lubricant film of uniform thickness. Therefore, the measured thicknesses of our samples must be less than the monolayer thickness of 2.3 nm since our samples were only partially covered by bonded molecules. Thicknesses less than a monolayer represent the average thickness of the areas with and without lubricant molecules covering them. In other words, the values should represent the thicknesses of a hypothetical lubricant film whose bonded molecules are flattened to cover the disk surface fully
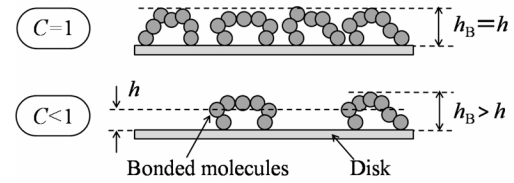

Fig. 2. Schematic diagram that explains the difference between molecular height h_B and thickness h measured by the scanning ellipsometer. If the lubricant film is a monolayer ($C = 1$), h_B is equal to h. If the disk is partially covered by lubricant molecules, i.e., a submonolayer ($C < 1$), h_B is larger than h.
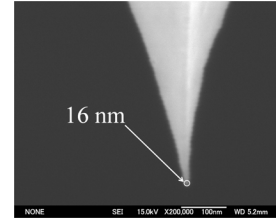

Fig. 3. SEM inspection image of the fluorinated tip of the cantilever probe.

and uniformly. Therefore, as schematically shown in Fig. 2, the height of the bonded molecule from the disk surface was larger than the thickness measured by the ellipsometer. Assuming that the volume of molecules is conserved, the height of the bonded molecules can be estimated as

$$h_B = h/C. \qquad (2)$$

Here, h_B and h represent the height of the bonded molecules and thickness measured by the ellipsometer, respectively.

C. Direct Observation of Molecular Distribution and Height

Tani measured the topography of the lubricated disk surface by using an AFM with a fluorinated cantilever probe and determined the height of adsorbed lubricant molecules [6]. The fluorinated probe enabled measurement of the deformable lubricated surface because it does not interact much with lubricant molecules. In the same manner as Tani's experiments, we measured the surface topography of the disk covered by bonded molecules by using an AFM with a fluorinated cantilever probe. The scanning electron microscope (SEM) inspection image of the fluorinated probe's tip is shown in Fig. 3. The diameter of the tip was around 16 nm. We observed the distributions of bonded molecules on the disk surface and determined their height, and we compared them with the estimated results.

IV. MEASUREMENT OF DIFFUSION COEFFICIENT

The diffusion coefficient of mobile molecules spreading through spaces between bonded molecules was measured by the following procedure. Sample disks with various coverages of bonded molecules were prepared as described in Section II. Using the dip-coating method, mobile molecules (Zdol4000) were again applied to the half-plane of those disks. Since the coverage of the bonded molecules was saturated at room temperature, the mobile molecules added afterward did not turn

into bonded ones during the spreading. The total thickness of the region of mobile and bonded molecules was kept at around 2 nm by adjusting the amount of mobile molecules. Since the monolayer thickness was around 2.3 nm, the lubricant films were monolayer to submonolayer. When the total thickness was larger than the monolayer, diffusion of mobile molecules became much faster than those in the monolayer (see Appendix). Therefore, the total thickness was controlled carefully not to over the monolayer thickness.

After the dip-coating, the samples were left for 24 h. During this time, mobile molecules spread to the other half of the disk surface. The thickness profile around the boundary was measured with the scanning ellipsometer. Since the diffusion coefficient of the monolayer and submonolayer film does not depend on the thickness, the boundary profile at position x and time t can be obtained by solving the diffusion equation [7]

$$\frac{\partial h(x,t)}{\partial t} = D\frac{\partial^2 h(x,t)}{\partial x^2}. \tag{3}$$

Here, $h(x,t)$ and D represent the thickness profile at the boundary and the diffusion coefficient of mobile molecules. The solution is

$$h(x,t) = \frac{1}{2}h_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{x/2\sqrt{Dt}} e^{-\xi^2}d\xi\right) \tag{4}$$

where h_0 is the initial thickness of added mobile molecules. The diffusion coefficient D was obtained by fitting (4) to the boundary profiles measured after 24 h of spreading.

To improve the accuracy of determining the diffusion coefficient, we made two modifications to the experimental procedure of the previous study. One was an environmental control during the 24 h of spreading. Samples were enclosed in a sealed dessicator with gas ports. Humidity was kept at 20% by a continuous flow of dry air. Temperature was kept constant at 22 °C. The other modification was to compensate for the difference in the initial boundary profile between our experiments and diffusion theory. In diffusion theory, the initial boundary profile, which is the boundary profile at $t = 0$, should be a right-angled step geometry. However, the measured initial profiles were usually curved steps, as shown in Fig. 4. In addition, these curved steps were slightly different from sample to sample. The elapsed time between the dip-coating of mobile molecules and the profile measurement was a few minutes, and it was negligibly small considering that the diffusion coefficient was on the order of 10^{-12} m²/s. Therefore, this curved step was mainly due to uncontrollable conditions in the dip-coating and not due to the elapsed time for the initial profile measurement.

Differences in the initial profiles between experiment and theory, and also between samples, caused the errors and variations in the diffusion coefficient. To correct these errors and variations, we assumed that the initial boundary profiles obtained in the experiment were those attained after a certain spreading time, which was the hypothetical spreading time. Moreover, the time t in (4) was divided into two terms as follows:
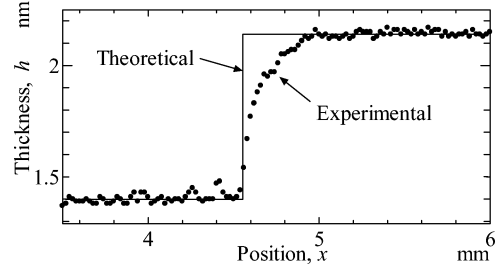
$$t = t' + \Delta t. \tag{5}$$

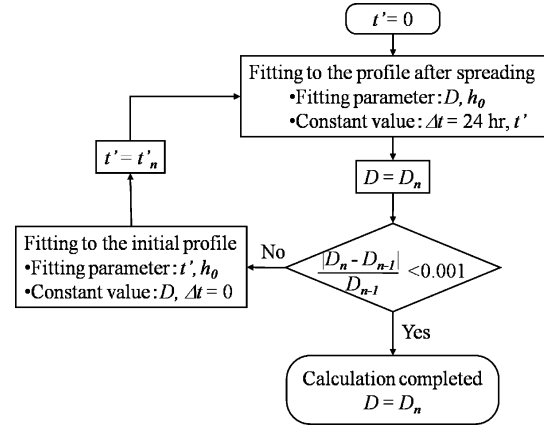Fig. 4. Difference in the initial boundary profiles given by diffusion theory and in the experiment.

Fig. 5. Flowchart of the fitting calculation to determine the diffusion coefficient D and the hypothetical spreading time t'.

The first term t' represents the hypothetical spreading time at which the initial profiles in the experiment were reached. The second term Δt is the actual spreading time, i.e., 24 h. Both t' and D were determined by the fitting calculation. Since t' and D were in the same term, as shown in (4), they cannot be determined from a single fitting calculation. Therefore, the fitting calculation followed the flowchart shown in Fig. 5. The boundary profiles were measured twice, i.e., immediately after the dip-coating and 24 h later. The former was named the initial profile and the latter the profile after spreading. First, the profile after spreading was fitted by using the least squares method with the fitting parameters of D and h_0 and with constant values of $\Delta t = 8.64 \times 10^4$ s (24 h) and $t' = 0$. The value of D determined in the first fitting calculation was named D_1. Next, the initial profile was fitted using the fitting parameters of t' and h_0 at the constant values of $D = D_1$ and $\Delta t = 0$. As a result of the second fitting, t' was determined as t'_1. Again, the profile after spreading was fitted using the fitting parameters of D and h_0 at constant values of $\Delta t = 8.64 \times 10^4$ s and $t' = t'_1$. After this third calculation, we obtained a more accurate value of D, i.e., D_2. We alternately continued these fitting calculations until the condition of $|D_n - D_{n-1}|/D_{n-1} < 0.001$ was satisfied. The subscript n is the repeat count of the fitting calculation. The determined hypothetical spreading time t' differed between samples and ranged from 3000 to 7000 s. These values correspond to 3–8% of the total spreading time of 24 h. Therefore, the fitting calculation described above is essential for accurate determination of the diffusion coefficient.
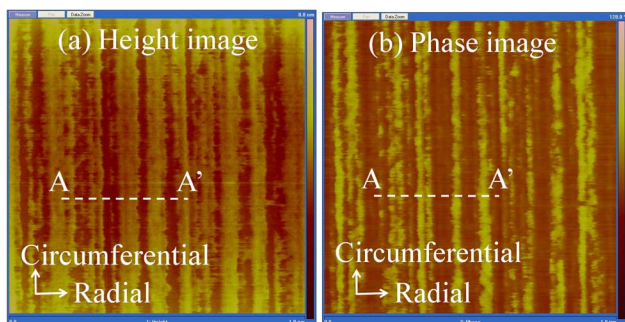
Fig. 6. Surface topography measured by AFM with fluorinated cantilever probe: (a) height image and (b) phase image.

Fig. 7. Cross-sectional view at $A-A'$ boundary in Fig. 6(a) and (b). A step-like profile can be observed in both the (a) height and (b) phase shift.

Fig. 8. Relationship between coverage of bonded molecules and their molecular height. Filled triangles are molecular heights measured by AFM; open circles are those estimated by (2).

V. EXPERIMENTAL RESULTS

A. Distribution and Molecular Height of Bonded Molecules

Height and phase images obtained by the AFM measurement are shown in Fig. 6(a) and (b). The coverage of the disk was 0.9. As shown in Fig. 6(a), the distinct ridged profile conformed to the surface texture. Please note that, in the phase image of Fig. 6(b), the darker area represents the retardation in the phase, which can be caused by the viscous interaction between the probe tip and the bonded molecules. Fig. 7(a) and (b) shows the cross-sectional view at $A-A'$ boundary in Fig. 6(a) and (b), respectively. As shown in the cross-sectional views, a step-like profile was observed in both the height and phase images. By comparing these, the higher areas showed the larger phase retardation caused by the viscous damping of bonded molecules. On the other hand, the phase shift was negligibly small in the lower areas. As a result, it is considered that the higher areas in the height image represent the formation of the bonded molecules along the surface texture, and the amount of bonded molecules in the lower area was quite small. Therefore, height differences between the lower areas and higher areas should give the molecular height. Since the width of the lower area was 50–100 nm, the fluorinated probe tip with the diameter of around 16 nm (Fig. 3) was small enough to measure the molecular height. We selected multiple points where the step-like topography could be observed in the height image and averaged their molecular heights. We measured the molecular heights of samples with different coverages.

The relationship between the coverage C and the molecular height of bonded molecules is shown in Fig. 8. The filled triangles in the figure are the molecular heights obtained by the AFM measurement. The blank circles represent those estimated by using (2). The molecular heights measured by AFM agreed well with the estimated ones. Therefore, the estimation using (2) provided valid results. As shown in Fig. 8, molecular heights increased with increasing C, and they showed a large increase especially at $C > 0.8$. This result indicates that, for coverages higher than 0.8, the main chains of bonded molecules might be raised upward from the disk surface due to the interaction between densely packed neighboring molecules.

There was significant difference between the estimated molecular heights and those measured by AFM at the lowest coverage of 0.3. The possible reason to explain this difference is that the flexible main chains of the lubricant molecules could
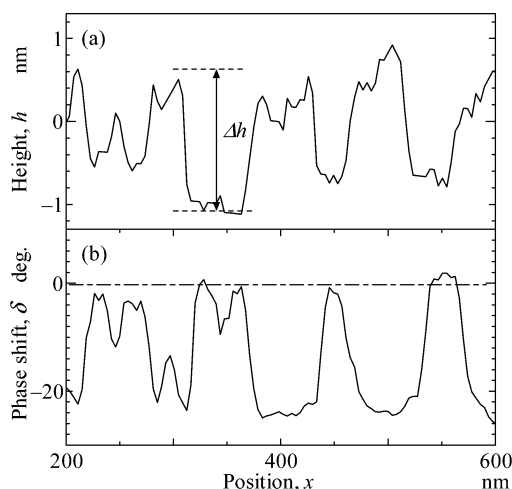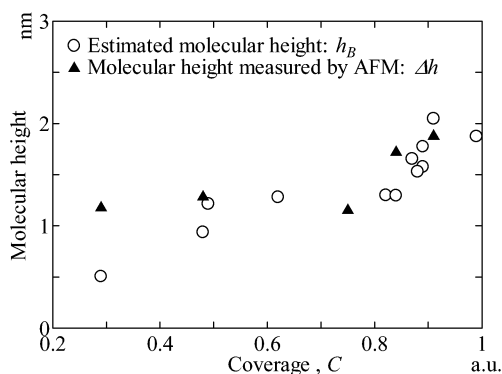
be raised upward by the intermolecular attractive force of the probe tip. Although the probe tip was fluorinated and the interaction between the tip and the lubricant was reduced, there still exists the weak intermolecular attractive force such as van der Waals interaction. According to the estimated molecular height, it is considered that the main chains should lie flat on the disk surface at the coverage of 0.3. However, during the AFM measurement with tapping mode, the probe tip might have pulled up the lying main chains, and the higher molecular height could be measured. At the higher coverage, movement of the main chains must be restricted due to the densely packed neighboring molecules, and changes of the molecular conformation might not occur during the AFM measurement. This might lead to good agreement between the estimated results and the measured ones at the higher coverages.

B. Dependence of Diffusion Coefficient of Mobile Molecules on the Coverage of Bonded Molecules

The measured diffusion coefficients are plotted against coverage C in Fig. 9. The AFM measurements indicate that the bonded molecules conformed to the surface texture. To verify the effect of the distribution of bonded molecules on the mobile molecules' diffusion, we measured the diffusion coefficient in
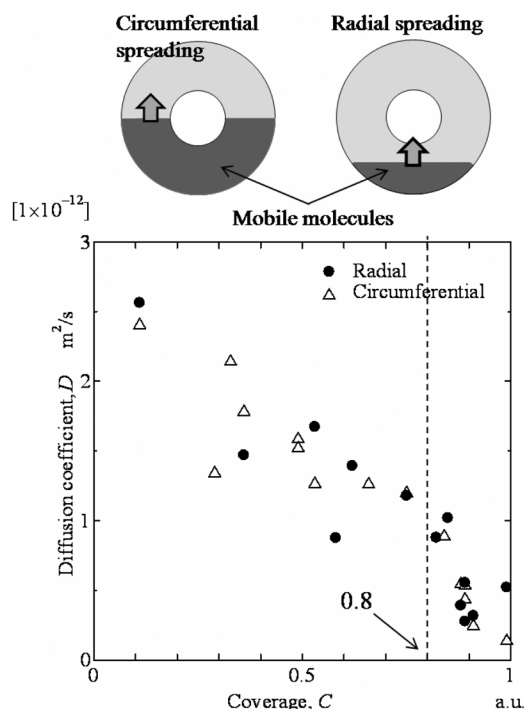
Fig. 9. Relationship between coverage and diffusion coefficient of mobile molecules measured in radial (filled circles) and circumferential (open triangles) directions.

Fig. 10. Diffusion coefficient in the experiment compared with those predicted by reptation theory and the molecular dynamics simulation.

the radial and circumferential directions. The former is vertical and the latter is parallel to the surface texture.

In Fig. 9, the filled circles represent diffusion coefficients in the radial direction. The open triangles are those in the circumferential direction. These diffusion coefficients decreased with increasing C because of the reduced space between bonded molecules. There was no significant difference in the spreading direction. The decrease in the diffusion coefficient roughly matches the results of the previous study. A new finding in the study described in this paper is that the diffusion coefficient D showed large decrease at coverages higher than 0.8.

VI. DISCUSSION

As shown in Fig. 10, the diffusion coefficients measured in the experiment were compared to those obtained by molecular dynamics (MD) simulations and reptation theory. The experimental and MD results were normalized with their average values. Based on reptation theory assuming that the area covered by the bonded molecules was a square of side a, the relationship between the coverage C and the diffusion coefficient D can be expressed by the following equation [2]:

$$D = \frac{D_0}{\frac{l}{a}\sqrt{C}+1}. \tag{6}$$

In the above equation, D_0 and l are the diffusion coefficient at zero coverage and the chain length of mobile molecules. Equation (6) was fitted to the experimental results. The filled circles and crosses in Fig. 10 are the results of the experiment and MD simulation, respectively. The experimental and MD simulation results matched well. The fitting curve well
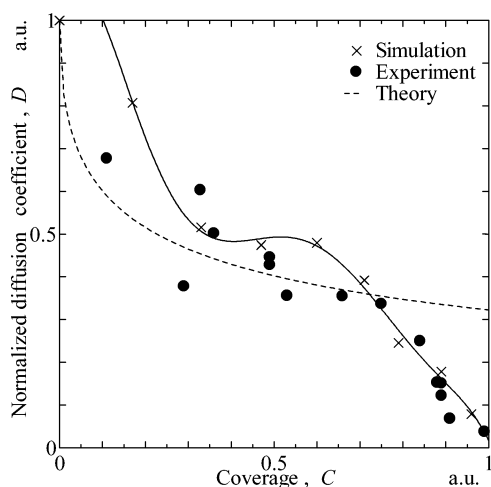
represents the experimental results for coverages of less than 0.8. However, for coverages higher than 0.8, the experimental results showed a prominent decrease in comparison with the fitting curve. The reason for this discrepancy is the neglected volume of the mobile molecules in the theoretical treatment. In reptation theory, the volumes of mobile molecules are neglected, although their lengths are considered. Therefore, the mobile molecules can spread through any tiny space between bonded molecules in reptation theory. In contrast, actual mobile molecules and also those in the MD simulation require a certain minimum space to spread because they have finite volumes. Remember the sudden increase in molecular height at $C > 0.8$ described in the previous section. This may be due to the raised conformation of main chains caused by the interaction between densely packed bonded molecules. From a different point of view, the sudden increase in molecular height suggests that bonded molecules get close enough to interact with each other. In other words, the space between bonded molecules could be less than a single molecular space at $C > 0.8$ and might not allow mobile molecules to spread through. Consequently, we believe that the remarkable decrease in D at $C > 0.8$ is caused by the lack of single molecular space or lack of space required for mobile molecules to spread through.

The mechanism that suppresses mobile molecules' spreading with increasing of coverage can be summarized as follows. The diffusion coefficient decreases at coverages from 0.2 to 0.8 as the width of the spaces between bonded molecules gets smaller; this trend is well represented by reptation theory. The large decrease at coverages higher than 0.8 can be caused by the lack of essential space for mobile molecules to spread through.

Zhang *et al.* measured the spreading characteristics of monolayer lubricant films that had the stripe-patterned distribution of bonded molecules [8]. The stripe-pattern was made by ultraviolet light irradiation onto the lubricated disk via photomasks with the desired patterns. Their results indicated that a part of mobile molecules diffused faster in a direction parallel to the stripe pattern compared with the diffusion in the perpendicular direction. In our study, although the bonded molecules showed anisotropic distribution along with the disk texture, there was

no significant difference in the diffusion coefficients between the radial direction and circumferential direction, as shown in Fig. 9. In our case, since the bonded molecules were formed by annealing process, the anisotropic distribution became prominent with increasing coverage. When the distinct pattern was formed, the amount of mobile molecules that diffused at the area with less bonded molecules, which may diffuse faster, can be smaller. Therefore, those contributions to the thickness profile were expected to be small. As a result, we considered that the differences in the spreading properties caused by the spreading direction might not be measured because of the lack of accuracy in the determination of the diffusion coefficient in our study.

VII. SUMMARY

We measured spreading properties of mobile molecules coexisting with bonded molecules in monolayer lubricant films. Our results are summarized as follows.

- Bonded molecules were formed along the surface texture on the disk surface.
- Molecular heights of bonded molecules were estimated from the coverages and the average thicknesses measured by the scanning ellipsometer. We revealed that bonded molecules had raised conformation at coverages higher than 0.8. The validity of the estimation was confirmed by the direct measurement of molecular heights using AFM.
- Diffusion coefficient of mobile molecules decreased with increasing coverages of bonded molecules.
- Diffusion of mobile molecules reduced drastically at coverages higher than 0.8. This may be caused by the lack of space required for mobile molecules to spread through, which were indirectly confirmed by the relationship between the coverage and the height of bonded molecules.

APPENDIX

The relationship between total thicknesses of lubricant films and diffusion coefficients of the mobile molecules is shown in Fig. 11. At $h > 2.3$ nm, i.e., thicker than the monolayer thickness, diffusion coefficients were larger than those at $h < 2.3$ nm. This could be caused by the mobile molecules that diffuse on the monolayer film, which means the diffusion in the second layer. Since there is no disturbance of bonded molecules, mobile molecules in the second layer should have faster diffusion coefficient compared to those in the monolayer.
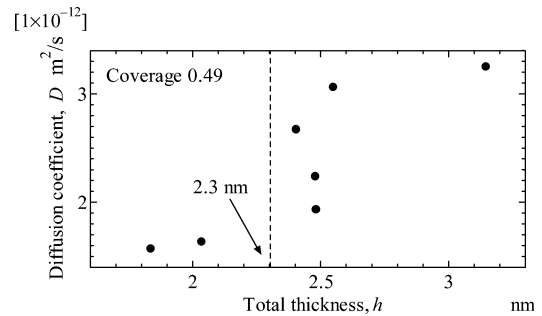

Fig. 11. Relationship between total thicknesses of lubricant films and diffusion coefficients of the mobile molecules. Coverage of the bonded molecules was 0.49.

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