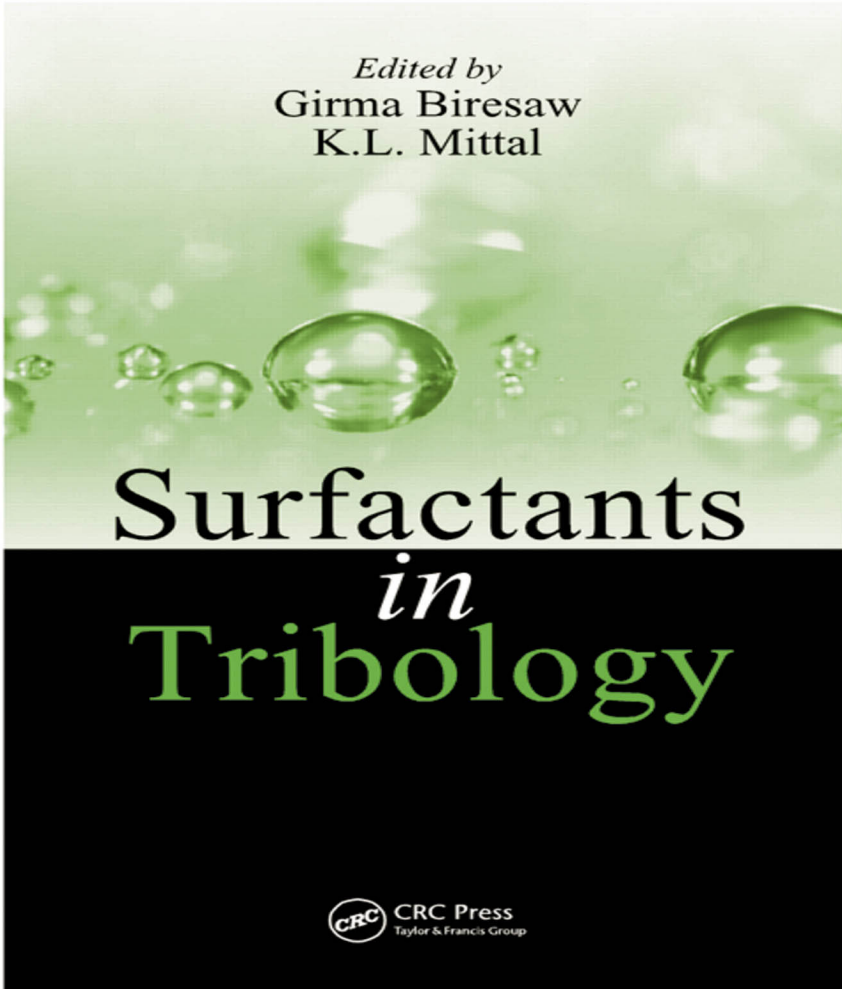


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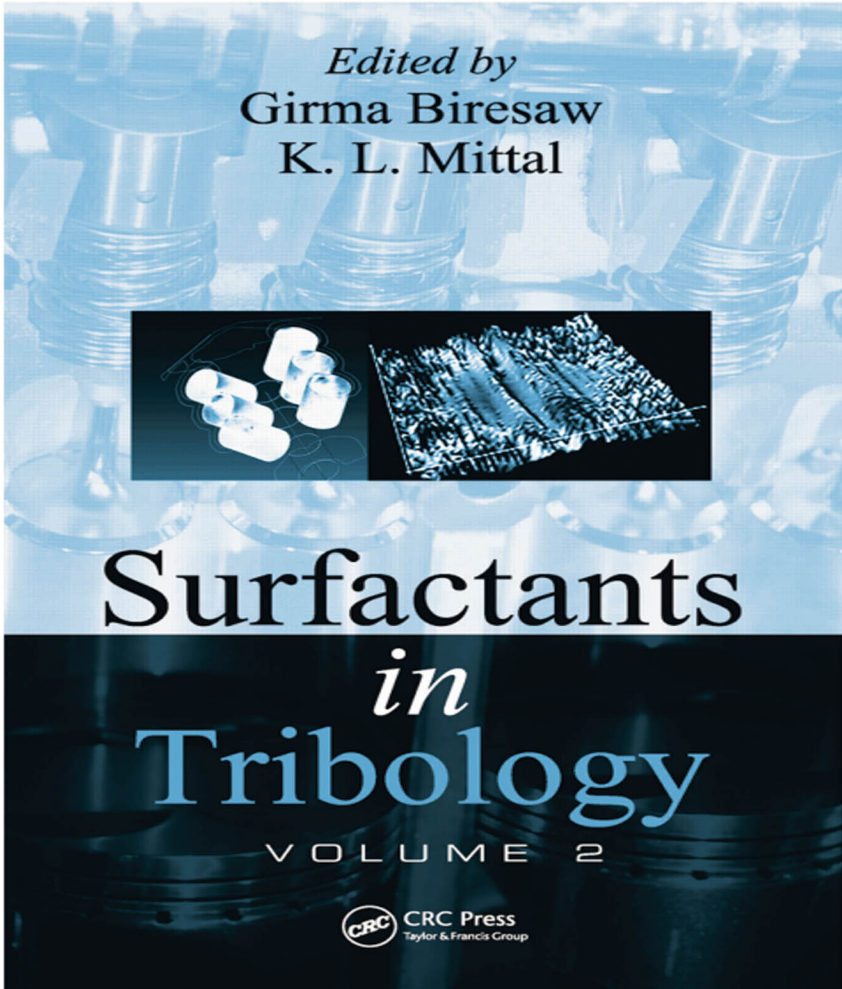
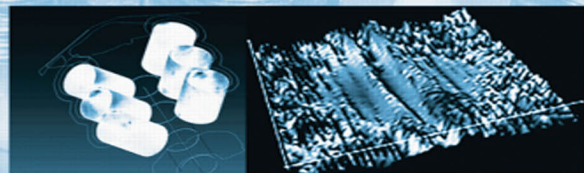
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Surfactants *in* Tribology

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Surfactants *in* Tribology

VOLUME 2

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Preface

This book presents recent developments and research activities that highlight the importance of surfactants in tribological phenomena. Even a cursory look at the literature will evince the high tempo of research in both fields: tribology and surfactants.

In light of these research trends, we organized a symposium on the topic of “The Role of Surfactants in Tribology” as a part of the 16th International Symposium on Surfactants in Solution (SIS) in Seoul, Korea, June 4–9, 2006. The SIS series is a biennial event started in 1976. Since then, these meetings have been held in many corners of the globe, attended by a “who’s who” list of members of the surfactant community. These meetings are widely recognized as the premier forum for discussing the latest research findings on surfactants in solution.

In keeping with the SIS tradition, the leading researchers in the fields of surfactants and tribology were invited to present their latest findings at the SIS event in 2006. In essence, this symposium represented a nexus between the research arenas of surfactants and tribology. The participants were invited to submit chapters to this book based on their presentations. In addition, we solicited and obtained chapters from other leading researchers who were not able to participate in the 2006 symposium. Thus this book represents the cumulative wisdom of many active and renowned scientists and technologists engaged in the study of surfactants in varied tribological phenomena.

Surfactants play a variety of critical roles in tribology, which subsumes the phenomena of three processes: friction, wear, and lubrication. The most widely recognized role of surfactants deals with their ability to control friction and wear. Surfactants also allow for control of a wide range of properties of lubricants, such as emulsification/demulsification, bioresistance, oxidation resistance, rust/corrosion prevention, etc. This book is a compendium of recent advances dealing with the role of surfactants in all three subjects within the purview of tribology. The book comprises chapters dealing with theoretical, experimental, and technological advances. Topics covered in the book include the role of surfactants in the tribological aspects of self-assembled monolayers (SAMs), microelectromechanical systems (MEMS), and nanoelectromechanical systems (NEMS). The book also addresses recent advances in fundamental tribological issues such as friction, wear, adsorption, tribochemical reactions, and surface/interfacial interactions.

The chapters in this book are grouped into five parts, each comprising chapters with a common theme. Part I consists of a single chapter dealing with the fundamentals of surfactants. Part II contains three chapters dealing with tribological aspects of micro- and nanodevices. Topics covered in Part II include tribological aspects of micropatterns of two-dimensional asperity arrays, MEMS, NEMS, and magnetic recording devices. Part III has six chapters dealing with self-assembled monolayers and ultrathin films relevant to tribological phenomena. Topics covered in Part III include tribological aspects of organosilane monolayers, ultrathin self-assembled films, superhydrophobic films, MoDTC/ZDDP tribofilms, and surfactant-coated

copper nanoparticles. Part IV has five chapters dealing with polymeric and biobased surfactants. Topics dealt with in Part IV include various tribological aspects related to polymeric gels, elastomers sliding against hydrophilic and hydrophobic surfaces, agriculture-based amphiphiles, vegetable oils, and biobased greases. Part V contains six chapters dealing with surfactant adsorption and aggregation relevant to tribological phenomena. Topics covered in Part V include the design of surfactants for lubrication, aqueous nonionic surfactant-based lubricants, adsorption and aggregation kinetics, surfactant and polymer nanostructures, and engine oils.

This book is the first to comprehensively treat the relevance of surfactants in tribology and brings together researchers from both the tribology and surfactants arenas. Consequently, this book is a valuable repository of information for a wide range of individuals engaged in research, development, and manufacturing. Tribological phenomena play a crucial role in the performance of a legion of consumer, industrial, and high-tech products, including MEMS, NEMS, magnetic recording media, metalworking, cars, aircraft, etc. Surfactants can be beneficially used to reduce wear and friction, with significant economic implications.

We sincerely hope that the bountiful information in this book will be a valuable resource for chemists, chemical engineers, petroleum engineers, automotive engineers, lubricant formulators, materials scientists, and tribologists. Indeed, the book should be of special interest to those engaged in the study of MEMS, NEMS, and biodevices or, more broadly, to anyone who seeks to understand and solve tribological issues.

Girma Biresaw, Ph.D.
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Editors

Girma Biresaw received a Ph.D. in physical-organic chemistry from the University of California–Davis and spent 4 years as a postdoctoral research fellow at the University of California–Santa Barbara, investigating reaction kinetics and products in surfactant-based organized assemblies. Biresaw then joined the Aluminum Company of America as a scientist and conducted research in tribology, surface/colloid science, and adhesion for 12 years. Biresaw joined the Agricultural Research Service of the U.S. Department of Agriculture in Peoria, IL, in 1998 as a research chemist, and became a lead scientist in 2002. To date, Biresaw has authored/coauthored more than 150 scientific publications, including more than 40 peer-reviewed manuscripts, 6 patents, more than 25 proceedings and book chapters, and more than 80 scientific abstracts.

Kashmiri Lal Mittal received his Ph.D. degree from the University of Southern California in 1970 and was associated with the IBM Corp. from 1972 to 1993. He is currently teaching and consulting worldwide in the areas of adhesion and surface cleaning. He is the editor of 89 published books, as well as others that are in the process of publication, within the realms of surface and colloid science and of adhesion. He has received many awards and honors and is listed in many biographical reference works. Mittal is a founding editor of the international *Journal of Adhesion Science and Technology* and has served on the editorial boards of a number of scientific and technical journals. Mittal was recognized for his contributions and accomplishments by the worldwide adhesion community by organizing on his 50th birthday, the First International Congress on Adhesion Science and Technology in Amsterdam in 1995. In 2002 he was honored by the global surfactant community, which inaugurated the Kash Mittal Award in the surfactant field in his honor. In 2003 he was honored by the Maria Curie-Skłodowska University, Lublin, Poland, which awarded him the title of doctor *honoris causa*.



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Part I

General



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1 Introduction to Surfactants

Michael L. Free

ABSTRACT

Surfactants play an important role in tribological applications. They have properties and characteristics that make them ideal in many lubrication applications. This chapter discusses the general properties and characteristics of surfactants that form the foundation for their role in tribological applications.

1.1 INTRODUCTION

Surfactants are important to many technologically important areas that vary from detergency and cleaning to manufacturing of metal parts and, of course, tribology. Details regarding their general properties are found in a variety of fundamental literature [1–7]. More specific information regarding their application can be found in the fundamental literature as well as in literature that is more specifically related to tribology [8–14].

Surfactants are molecules that have both hydrophilic and hydrophobic sections that impart partial affinity toward both polar and nonpolar surfaces. The hydrophobic section of surfactant molecules consists of nonpolar moieties such as repeating carbon-hydrogen (CH_2) units or carbon-fluorine (CF_2) units. The hydrophilic sections of surfactant molecules contain ionic functional groups such as ammonium (NH_4^+) or carboxylate (CO_2^-), or they consist of nonionic polar groups such as the hydroxyl portion of alcohol molecules. Thus, surfactants are at least partially soluble in polar liquids such as water as well as nonpolar media such as hexane.

The surfactant affinity toward both polar and nonpolar media makes surfactants more likely to be found at boundaries as well as to associate with other surfactant molecules. Consequently, surfactant molecules are particularly active at interfacial boundaries between solids and liquids, liquids and liquids, and liquids and gasses. The word “surfactant” is a contraction of the words “surface active agent.” An example of a common surfactant, sodium dodecyl sulfate, is shown in fig. 1.1.

1.2 TYPES OF SURFACTANTS

The three main types of surfactants are ionic, zwitterionic, and nonionic. Zwitterionic surfactants have anionic and cationic constituents. Examples of zwitterionic surfactants include betaines and dimethyl amine oxides. Ionic surfactants are generally classified as cationic if they are positively charged or anionic if they are negatively

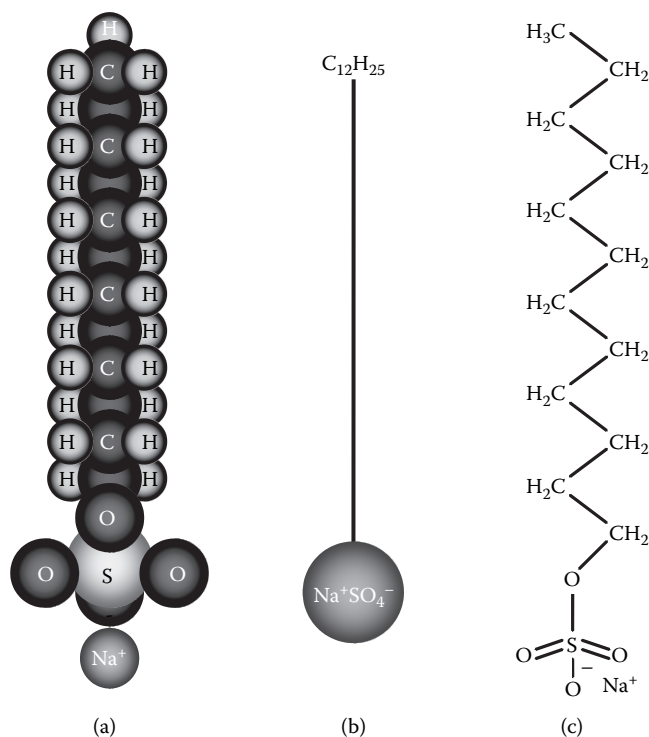


FIGURE 1.1 (See color insert following page 80.) Comparison of (a) space-filling atomic, (b) simplified, and (c) simplified atomic views of sodium dodecyl sulfate. The letters represent the atomic symbols. These views represent the lowest energy state. However, due to molecular vibrations, the actual shape varies with time, and the average shape is not a straight chain as shown. Note that the angle for these views does not reveal the fact that the repeating carbon-hydrogen section of adsorbed sodium dodecyl sulfate is not perpendicular to the surface.

charged when dissolved in aqueous media from a neutral salt form. Most common cationic surfactants are made with amine salts such as cetyl trimethyl ammonium bromide and cetyl pyridinium chloride. Anionic surfactant examples include carboxylate, sulfonate, and sulfate functional groups in salt forms such as sodium oleate, sodium dodecyl benzene sulfonate, and sodium dodecyl sulfate. Nonionic surfactants are not ionic and are, therefore, not found in salt forms. Nonionic surfactants generally consist of alcohols, polyglucosides, and poly(ethylene oxide)s that have attached hydrocarbon chains.

Nearly all surfactants contain between 4 and 18 carbon atoms that are connected in a continuous sequence as shown for sodium dodecyl sulfate in fig. 1.1. In some cases, hydrocarbon sections form branches from a central hydrocarbon chain. In other cases, the hydrophobic portion of the surfactant may contain an aromatic ring structure. Most common surfactants are near the middle of this range (10–14) for the number of carbon atoms in the central chain, which generally determines the molecular length.

The length of the hydrocarbon chain is the primary factor that determines the surfactant solubility. Long-chain surfactant molecules have very low solubility in aqueous media. In contrast, long-chain surfactant molecules have high solubility in nonpolar media such as oils. Structural features such as double bonds or aromatic structures also alter their solubilities.

1.3 ASSOCIATION AND AGGREGATION

The dual nature or amphiphilicity of surfactant molecules provides a thermodynamic driving force for adsorption and aggregation of surfactant molecules. In aqueous media the hydrophobic sections of surfactant molecules are attracted to the hydrophobic section of adjacent surfactant molecules. The association of adjacent hydrophobic sections of surfactant molecules reduces the less favorable interactions between water molecules and individual hydrophobic sections of surfactant, thereby reducing system free energy. The effects of association between adjacent hydrophobic sections of surfactant molecules are enhanced in aggregate structures such as adsorbed layers of surfactant and solution micelles.

Micelles are spherical aggregates of surfactant molecules that can be represented by fig. 1.2a. The concentration at which micelles form in solution is known as the critical micelle concentration (CMC). The concentration at which surfactants aggregate at surfaces to form monolayer-level surface coverage (see fig. 1.2b) is referred to as the surface aggregation concentration (SAC). The SAC is usually very similar to the CMC, although the SAC is usually lower due to interactions with immobile lattice atoms. Other aggregate structures such as bilayers and cylindrical micelles can also form above the CMC or SAC.

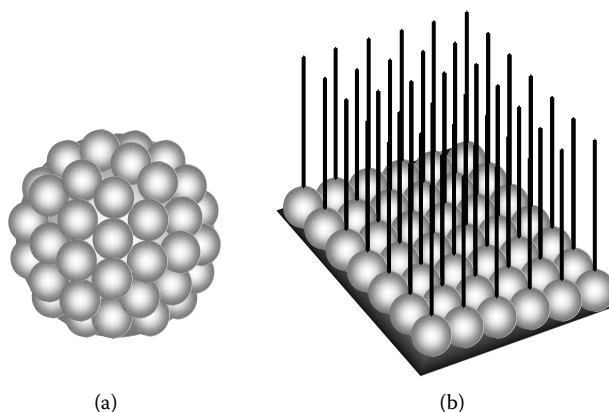


FIGURE 1.2 (a) Illustration of the outer portion of a spherical micelle in which the spheres represent the hydrophilic functional group of surfactant molecules; (b) illustration of surfactant molecules adsorbed at a surface at the monolayer coverage level in which the spheres represent the hydrophilic functional group of surfactant molecules and the lines represent the hydrocarbon chain.

1.3.1 FACTORS AFFECTING AGGREGATION

The aggregation process is a strong function of the length of the hydrophobic section of the surfactant molecule. Longer hydrocarbon chains lead to a greater tendency for aggregation. Other factors that affect aggregation strongly include ionic strength, which is indicative of the dissolved charge concentration, and temperature. The effect of these factors is mathematically considered in the following equation [15]:

$$\text{CMC} \equiv \text{SAC} \equiv \exp\left(\frac{1}{RT}[(L-x)\Delta G_{\text{c.l.}} + k(L-x)RT \ln(\alpha)]\right) \quad (1.1)$$

in which R is the gas constant (J/mole-K), T is the absolute temperature (K), L is the total number of consecutive CH_2 units in the surfactant molecule, $\Delta G_{\text{c.l.}}$ is the free energy increment for each CH_2 unit of chain length as denoted by the subscript “c.l.” (J/mole), x is the number of CH_2 units needed to initiate aggregation, k is a solvent polarity factor, and α is the traditional ion activity coefficient that characterizes the interaction between hydrocarbon chains and the polar aqueous media based on a single-charged ion. Although the equation accounts for temperature effects, the Krafft point, which is the temperature above which surfactant solubility rises sharply, must also be considered. Surfactants are generally used at or above the Krafft point.

Aggregate structures such as micelles can be used to deliver organic or aqueous media. Micelles can easily accommodate oils in their interior. As the micelles swell with oil in their interior volume, they form emulsions. Micelles can also be inverted in organic solvents (hydrophobic portions forming the outer perimeter) to form reverse micelles that can accommodate small droplets of water to form oil-based emulsions. Many products containing water and oil are produced in emulsified form.

1.4 ADSORPTION

Interfaces between one solid phase and another phase, such as between solids and liquids, often provide an ideal location for adsorption of surfactant. The solid substrate can provide specific sites at which the hydrophilic head group of a surfactant molecule may bond chemically or physically. Chemical bonding or chemisorption involves a chemical reaction at the surface between the surfactant and the substrate that produces a chemical bond. Physical bonding may involve electrostatic and van der Waals forces between the surfactant and the substrate as well as between surfactant molecules. The immobile nature of a solid substrate, combined with bonding between surfactant and substrate, results in aggregation and solidification of the adsorbed surfactant at concentrations and temperatures that are, respectively, lower and higher than would be needed for aggregation or solidification in bulk media. The adsorption of a monolayer of surfactant causes hydrophilic substrates to change to hydrophobic surfaces due to the orientation of hydrophobic functional head groups toward the substrate, as shown in fig. 1.3a. Conversely, monolayer adsorption on hydrophobic substrates converts them to hydrophilic substrates, as illustrated in fig. 1.3b, which makes it easier to retain polar lubricants at the surface.

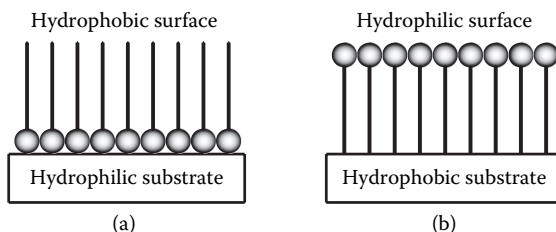


FIGURE 1.3 (a) Surfactant molecules, represented by spheres and lines, adsorbed at a hydrophilic substrate, and (b) surfactant molecules, represented by spheres and lines, adsorbed at a hydrophobic substrate

1.5 SURFACE TENSION

Surface tension is the force that holds an interface together. Molecules in the bulk of a medium can form bonds with molecules in all directions. In contrast, those at an interface with another phase are more restricted in bonding options. The lack of balanced bonding opportunities at the interface gives rise to surface tension. The addition of surfactant to aqueous media results in a higher concentration of surfactant molecules at the air–water interface than in the bulk. The presence of the surfactant at the interface provides an opportunity for water molecules to have more bonding opportunities at the interface and reduces the surface tension. The higher the concentration of surfactant at the interface, the lower the surface tension becomes until a close-packed monolayer of surfactant forms. Concentrations that exceed the level needed for close-packed monolayers result in the formation of micelles, as discussed previously. Consequently, surface tension provides useful information regarding the adsorption of a surfactant at an interface.

The concentration at an interface above the bulk concentration level is known as the surface excess, and it is often calculated using the Gibbs equation [1], which is rearranged to

$$\Gamma = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right) \quad (1.2)$$

in which Γ is the surface excess (mole/m^2), R is the gas constant ($\text{J/mole}\cdot\text{K}$), T is the absolute temperature (K), γ is the surface tension (N/m), and c is the concentration (mole/m^3). The Gibbs equation indicates that the surface excess concentration is linearly proportional to the change in surface tension relative to the logarithm of the surfactant concentration. Consequently, it is anticipated that the slope of a plot of surface tension versus the logarithm of the concentration should be linear. Figure 1.4 shows the anticipated relationship. The gradual change in slope as concentration increases reflects increasing adsorption at the air–water interface. The abrupt change in slope to a nearly horizontal line at the minimum surface tension identifies the concentration as the critical micelle concentration. The reason for the change in slope is the completion of one monolayer at the air–water interface, where the surface tension is determined by measuring the downward pull on a flat plate or ring. As the concentration exceeds the level needed for the completion of a monolayer at the air–water

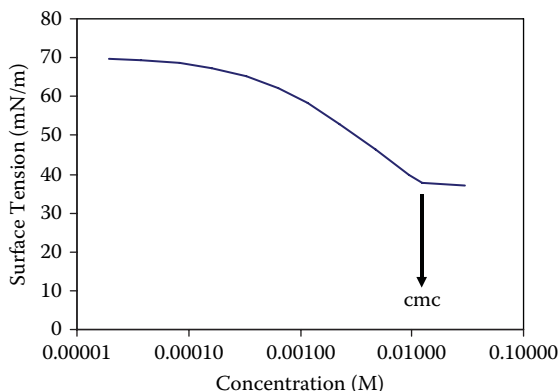


FIGURE 1.4 Plot of surface tension versus concentration for a typical surfactant

interface, additional surfactant has no room to fit in the layer and, therefore, forms micelles in solution or multilayers of surfactant under appropriate conditions. The surface tension does not decrease below the level associated with micelle formation. Consequently, the Gibbs surface excess is only applicable below the CMC.

1.6 CONTACT ANGLE

The adsorption of surfactant usually alters the underlying substrate's interaction with liquids. The interaction of a substrate's surface with a liquid is often characterized by the contact angle. The traditional three-phase contact model is shown in fig. 1.5. Based on the model, a force balance for the interacting surface tension components for each interacting phase combination (γ_{SL} , γ_{LO} , γ_{SO}) leads to Young's equation [2],

$$\gamma_{LO} \cos \theta = \gamma_{SO} - \gamma_{SL} \quad (1.3)$$

in which θ is the contact angle (degree) and γ is the interfacial tension (N/m), where the S subscript denotes the solid, the L subscript denotes the liquid, and the O subscript denotes the other phase, such as a gas or a second liquid.

1.7 ADHESION/COHESION

All molecules experience interaction forces when they encounter other molecules. As atoms approach each other, their orbiting electrons are continually changing positions. Consequently, charge-related interactions are constantly changing, and there is an induced dipole interaction between atoms in adjacent molecules that can provide a strong interaction force at close distances that is part of the van der Waals force. Other interaction forces include electrostatic or coulombic interactions between molecules with a net charge. Other forces that affect interactions are associated with solvent structuring around solute molecules.

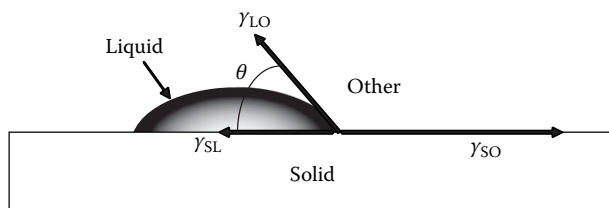


FIGURE 1.5 Typical view of the contact angle for a liquid on a solid substrate in the presence of another phase, such as a gas or a second liquid

Chemical interactions between atoms result in chemical bonding. Chemical bonding between atoms creates molecules. Chemical bonding between molecules such as adsorbate molecules and a substrate result in chemisorption. Chemisorbed molecules are tightly bound to surfaces and can provide a strong anchor for subsequent coatings or lubricant molecules.

Adhesion is one way of characterizing the sum of these interaction forces for different materials in contact. The ability of an adsorbed molecule to resist being forced off a surface by an impinging object with an applied load, which is critical to tribology, is related to the force with which it adheres to the surface. Adhesion is defined in terms of the energy or work per unit area needed to pull apart two different materials. Cohesion is the energy or work required to pull apart a homogeneous material. Thus, adhesion and cohesion are ways to characterize the net force of attraction between molecules in a way that is relevant to tribological applications.

1.8 CONCLUSIONS

Surfactants play an important role in tribology. The role of surfactants in tribology is related to the amphiphilic (dual) nature of surfactant molecules, which is both hydrophilic and hydrophobic. The amphiphilic nature of surfactant molecules leads to aggregation and adsorption, which are important to tribology. Surfactants have the ability to adsorb on metal surfaces to produce hydrophobic surfaces that are more receptive to lubricating oils than unaltered metal surfaces, which are naturally hydrophilic. Surfactants can also impart lubrication properties in the absence of oil. Thus, surfactant molecules play an important role in common tribological applications involving a variety of surfaces and lubricants.

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Part II

Tribological Aspects in Micro- and Nanodevices



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2 Geometry and Chemical Effects on Friction and Adhesion under Negligible Loads

Yasuhisa Ando

2.1 INTRODUCTION

Friction force is proportional to the normal load as stated by Amontons–Coulomb’s law. For microloads less than 1 mN, which are often found in mechanisms such as microelectromechanical systems (MEMS), Amontons–Coulomb’s law is not valid due to the effect of the adhesion force between the contacting surfaces [1]. Studies show that, at such microloads, either the attraction force (adhesion force) caused by the surface tension of water condensed on the surface or the van der Waals force dominates the friction force, and that the friction force is proportional to the sum of the adhesion force (pull-off force) and the normal load [2, 3].

Some studies reported that even a slight roughness decreases the adhesion force significantly [4]. In magnetic storage devices, the technique of creating asperities, called texturing, is often used to prevent sticking at the head and disk interface [5]. The same technique has been used to reduce the sticking of microstructures [6]. Therefore, creating asperities was considered to be an effective way to reduce the adhesion force. However, when applying the friction reduction method by increasing surface roughness to MEMS, random asperities tend to prevent a smooth sliding because the contact area found in MEMS is small and on the order of square microns [7]. In contrast, a periodic array of submicrometer-scale asperities can reduce adhesion and friction forces unless preventing the smooth sliding. It is also very important to use the periodic arrays of asperities to clarify geometric effects on adhesion and friction.

In conventional-sized machines such as an engine system, lubricants are often used to reduce the friction force. Liquid lubricants, however, generate capillary force and often cause stiction in micromechanisms. Moreover, even a low-viscosity liquid tends to increase friction force because viscosity drastically increases when the spacing between solid surfaces becomes narrow and is on the order of nanometers [8]. Therefore, liquid lubricants could cause an increase of the friction force in MEMS. In micromechanisms, one solution for reducing the friction force is molecular boundary lubrication.

Techniques involving Langmuir–Blodgett (LB) films and self-assembled monolayers (SAMs) have been adopted as conventional methods to form organic monolayers on solid surfaces. Under a microload friction, where the normal load is negligible compared

with the adhesion force, organic monolayers are expected to reduce friction force in two ways. One is to *indirectly* reduce the friction force by reducing the adhesion force. Thus, the friction force is indirectly reduced because the friction force is proportional to the adhesion force (pull-off force) when the normal load is negligible [9]. The other way is to *directly* reduce the friction force. These two reduction effects (indirect and direct) might effectively reduce the friction force under microload conditions. Moreover, the friction force might be further reduced by the use of periodic asperity arrays. Therefore, these three means of reducing the friction force under microload conditions need to be clarified.

Surfactants are used for reducing friction. They are found in hair conditioner, fabric softener, etc. Determining the tribological characteristics of LB films and SAMs when the normal load is negligibly small is also important for understanding the friction-reducing effects of surfactants, because the molecular structures of some surfactants are very similar to those of the molecules composing LB films or SAMs.

In this study, we clarified these friction-reduction effects under microload conditions by measuring the friction and pull-off forces for two-dimensional asperity arrays on silicon plates. First, two-dimensional asperity arrays were created using a focused ion beam (FIB) system to mill patterns on single-crystal silicon plates. Each silicon plate had several different patterns of equally spaced asperities. Then, the friction and pull-off forces were measured using an atomic force microscope (AFM) that had a square, flat probe. This report describes the geometry effects of creating asperity arrays and the chemical effects of depositing LB films or SAMs on the friction and pull-off forces.

2.2 CREATION OF PERIODIC ASPERITY ARRAYS BY FOCUSED ION BEAM

2.2.1 FOCUSED ION BEAM SYSTEM AND PROCESSING METHODS

We created two-dimensional arrays of asperities having various heights on a silicon surface by milling with an ion-beam-focusing system, FIB 610 (FEI, Hillsboro, OR). The primary components of this FIB system are a liquid ion metal source (LIMS), ion-focusing column, specimen chamber, and electronics control console. The system extracts positively charged ions from the LIMS by applying a strong electric field, and then focuses the ions into a beam, which then scans the specimen using electrical lenses and deflectors. The nominal minimum diameter of the focused beam is 28 nm. The ion beam removes material from the specimen through a sputtering process and thus mills a narrow groove less than 100 nm wide on the specimen.

A groove can be made by scanning the beam continuously along the desired line on the specimen. The depth and width of the groove are determined by the radius of the beam and the processing time. By milling equally spaced grooves in two orthogonal directions, unmilled parts remained to form a two-dimensional array of "asperities." By varying the milling conditions, the groove depth, groove width, and the spacing between the grooves can be varied. To deposit a platinum film, a deposition gas (methylcyclopentadienylplatinum: $(\text{CH}_3)_3(\text{CH}_3\text{C}_5\text{H}_4)\text{Pt}$) is introduced, which reacts with the area where the ion beam strikes. By varying the processing time, the thickness of the film can be controlled.

2.2.2 SURFACE MODIFICATION USING FOCUSED ION BEAM

A specimen on which the pattern is to be created must be metal or a semiconductor, because the electrostatic charge as the result of irradiation of ions makes the processing difficult. So, in this study, single-crystal silicon was used as the specimen because it has a very smooth surface, and it is much easier to mill a fine groove of about 100 nm width on it than on other materials such as polycrystalline metal.

Figures 2.1–2.4 show examples of periodic asperity arrays used in this experiment, which were measured by a conventional sharp probe that had a nominal radius of curvature of less than 40 nm. Figures 2.1 and 2.2 are two-dimensional

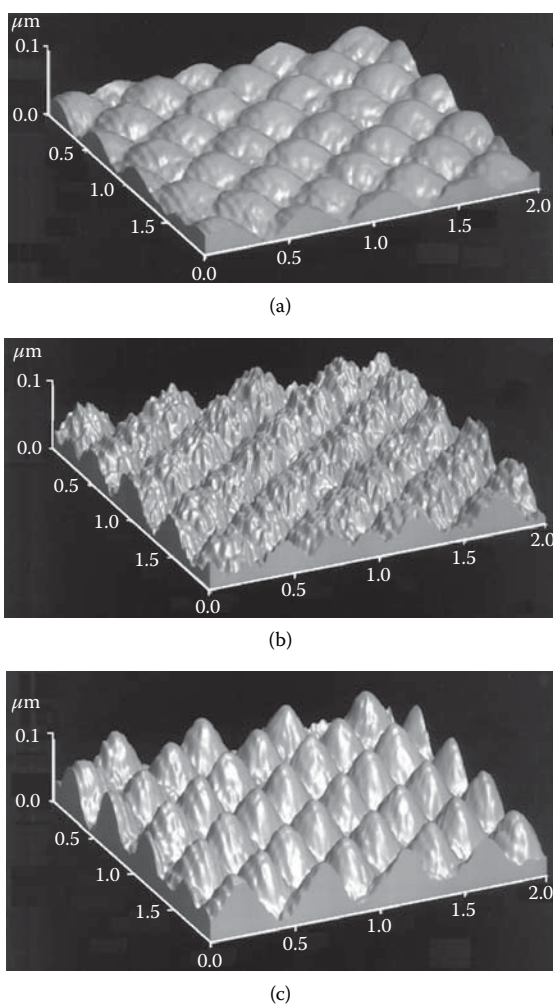
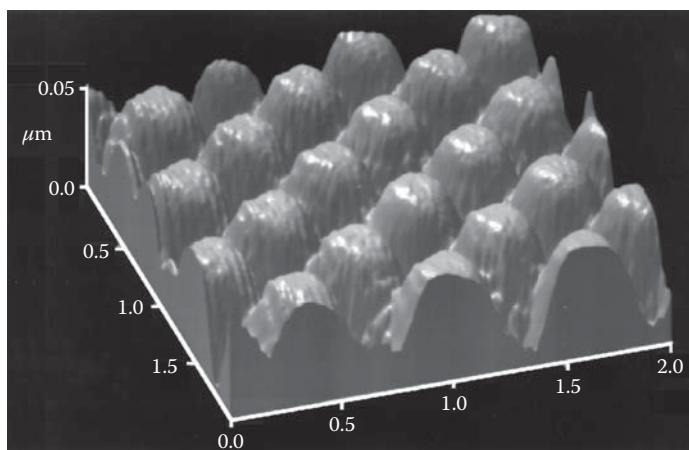
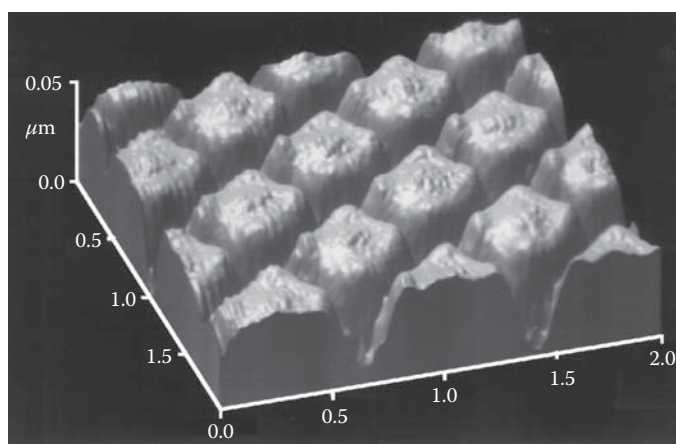


FIGURE 2.1 AFM images of the periodic asperity arrays. Asperity arrays were produced by using an FIB to mill grooves on a silicon surface. Groove depth was calculated from the AFM image. Each groove depth was determined from the topography measurements. (a) 21.2-nm groove depth, (b) 38.7-nm groove depth, (c) 49.2-nm groove depth.



(a)



(b)

FIGURE 2.2 AFM images of periodic asperity arrays of various mound areas on a silicon plate. When fabricating the patterns, the number of scanning lines of the ion beam was varied to control the width of the groove, and the distance between the grooves was varied to control the area of each mound. The ratio of mound width to total width of mound and groove is $2/9$ for (a) and $2/11$ for (b), which were determined from the milling conditions. The groove depth is 23.1 nm for (a) and 19.7 nm for (b), which were determined from the topography measurements.

asperity arrays obtained by milling many grooves in orthogonal directions. With an increase in the processing time, the height of the asperities increased as shown in figs. 2.1a–2.1c. The microsurface roughness of asperities was extremely large for fig. 2.1b due to the different processing conditions. The distance between adjacent peaks was constant in fig. 2.1 and was about 240 nm for each asperity array, which was determined from the milling conditions. In fig. 2.2, the ratio of mound width to total width of mound and groove was varied by varying the spacing between the grooves. The depth of the grooves was relatively constant and was 20 – 27 nm. Figure 2.3

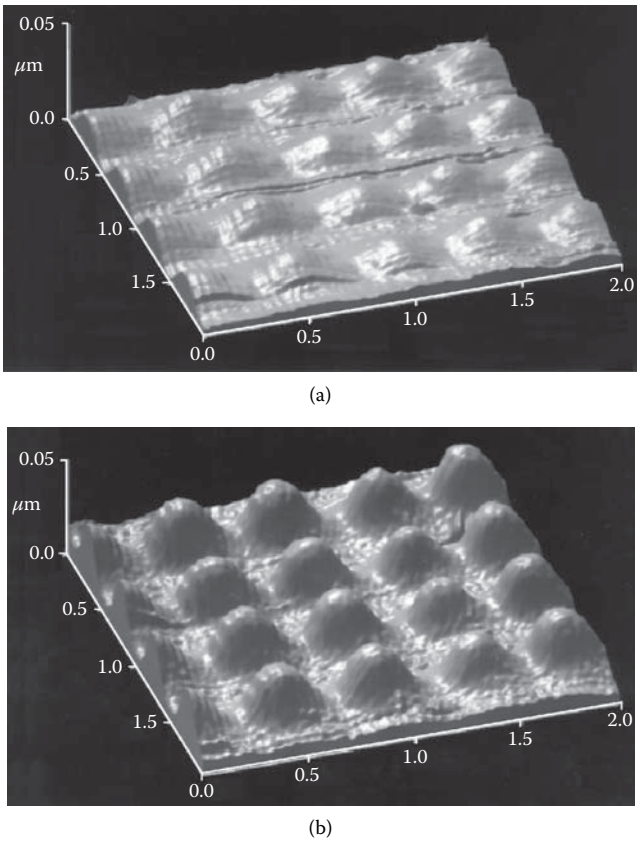


FIGURE 2.3 AFM images of periodic arrays of platinum asperities fabricated on a silicon plate. The asperity array was fabricated by depositing platinum mounds in two orthogonal directions at the same spacing. Each asperity height was determined from the topography measurements. (a) 11.1-nm asperity height, (b) 24.3-nm asperity height.

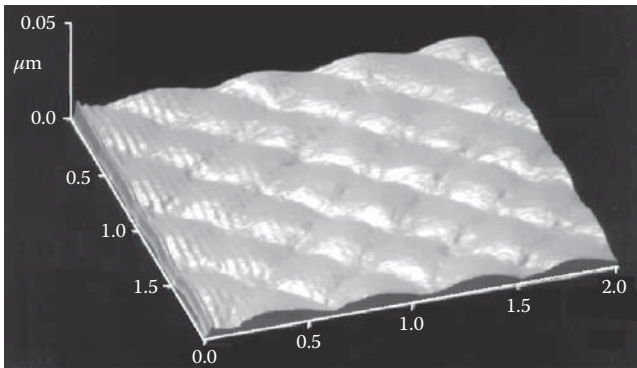


FIGURE 2.4 AFM image of asperity array fabricated on platinum layer that was deposited by FIB (6.5-nm groove depth).

shows an asperity array of platinum that was deposited by focusing small spots of ion beam equally spaced in two orthogonal directions while introducing the deposition gas. With an increase in the irradiation time, the height of the asperities increased, as shown in figs. 2.3a and 2.3b. Although fig. 2.4 also shows an asperity array of platinum, the pattern was obtained by milling many grooves in orthogonal directions in the same way as shown fig 2.1 after depositing a platinum layer in the wider area. The modified area created on the silicon plate was about $5 \times 5 \mu\text{m}^2$.

Table 2.1 summarizes the patterns used to determine the geometry effects and shows material of asperity, groove depth (asperity height), the distance between adjacent peaks (pitch), the ratio of mound width to total width of mound and groove, and the angle between the sliding direction and the direction of the array. The groove depths were obtained from the AFM images. The pitch and the ratio were determined from the milling conditions.

2.2.3 CURVATURE RADIUS CALCULATIONS

Some asperity arrays were selected and the curvature radii of the asperity peaks were calculated to examine the effects of contact geometry in a different perspective. The patterns on test specimen no. 3 in table 2.1 were selected because the curvature radii for the array patterns in this specimen were distributed widely.

The curvature radii of the asperity peaks were calculated from the AFM measurement data, as shown in fig. 2.1. For this calculation, first the AFM topography data were input into a personal computer. Next, we selected more than 10 asperity peaks and fitted each of them with a spherical surface curve. When fitting each peak, we included measured data within a 30–50-nm-radius area of each peak. Each fitted area contained about 80–200 digital data points. Using these data points, we calculated

TABLE 2.1
Patterns Used for Examining Geometry Effects

Specimen no.	Material	Groove depth (nm)	Pitch (nm)	Friction direction
		[mound ratio ^a]		
1	Si	3.0–19.9 [2/7]	245	—
2	Si	17.2 [2/7]	240	0°
		19.3 [2/7]	240	45°
		6.2–49.2 [2/7]	240	45°
3	Si	21.2 [2/7]	240	45°
		19.5 [2/9]	310	
		20.5 [2/11]	380	
		27.2 [4/11]	380	
5	Pt	5.2–43.0	330	0°
6	Pt	2.5–26.2	330	0°
7	Si	3.7–15.5 [2/7]	240	45°
	Pt	3.7–7.9 [2/7]		

^a Ratio of mound width to total width of mound and groove. Each width represents the number of scanning lines of the ion beam used for fabrication of patterns.

TABLE 2.2
Geometry of Asperity Array

Patterns used for determining geometry effects (specimen no. 3)		
Chemical modification	Groove depth (nm)	Average curvature radius (nm) (σ : standard deviation)
None	6.2	790 (σ : 400)
	8.8	640 (σ : 130)
	18.0	330 (σ : 53)
	21.2	290 (σ : 38)
	38.7	170 (σ : 110)
	49.2	86 (σ : 5.5)

the curvature radius for each asperity by means of an approximation program that used a steepest-descent method. Then, we averaged the radius for each asperity array. Table 2.2 shows the geometry of the asperity arrays, i.e., groove depth, averaged curvature radius of the peaks, and standard deviation of the averaged curvature radius.

2.2.4 CHEMICAL MODIFICATIONS OF ASPERITY ARRAYS

In order to determine the effect of chemical modification on the friction and pull-off forces, self-assembled monolayers (SAMs) and Langmuir–Blodgett (LB) films were formed on the silicon surface. Films were formed on the asperity arrays having various groove depths, where the distance between the adjacent peaks was about 240 nm for each asperity array. The SAM and LB films were deposited as follows.

Each plate was cleaned and then coated with a SAM of alkylchlorosilane in a three-step process. First, to remove chemically or physically adsorbed contaminants, the plate was cleaned with a so-called piranha solution (3/7 v/v mixture $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$) at about 70°C for 2 h and then with a 4/6 v/v mixture of benzene/ethanol for 48 h. After each cleaning process, the plate was rinsed with high-purity water. Second, to remove surface contaminants, the plate was placed in a UV (ultraviolet)/ O_3 cleaner (UV output of 25 W) and exposed for 10 min. Finally, to form the SAM coating, the plate was immersed for about 5 s in a 0.5 mM solution of, for example, octadecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$; C_{18}) in hexane. We also prepared a control plate that contained an asperity array without a coating (C_0).

LB films were also formed on the silicon plate after the asperity array was processed by FIB. Before depositing the LB film, we cleaned the silicon wafers in a mixture of benzene and ethanol, rinsed them in pure water, and then exposed them to a UV–ozone atmosphere. Then the plate was immersed in ultrapure water where a monolayer of stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$:CH) or fluorocarboxylic acid ($\text{C}_6\text{F}_{13}\text{C}_{11}\text{H}_{22}\text{COOH}$:CFCH) was confined at a pressure of 30 mN/m. The monolayer on the water migrated onto the silicon surface and formed the LB film (CH-/CFCH-LB film) when the plate was removed from the ultrapure water. The temperature of the ultrapure water was 20°C. Table 2.3 shows the chemical modifications and the geometries of the asperity.

TABLE 2.3
Geometries and Chemical Modifications of Asperity Array

Patterns used for determining chemical effects	
Sample name: Chemical modification	Average curvature radius (nm) (σ: standard deviation)
C ₀ (-SAM): (Uncoated)	250–1500 (σ: 41–1450)
C ₆ (-SAM): n-hexyltrichlorosilane (CH ₃ (CH ₂) ₅ SiCl ₃)	560–2330 (σ: 200–1350)
C ₈ (-SAM): n-octyltrichlorosilane (CH ₃ (CH ₂) ₇ SiCl ₃)	200–800 (σ: 44–83)
C ₁₄ (-SAM): n-tetradecyltrichlorosilane (CH ₃ (CH ₂) ₁₃ SiCl ₃)	1880, 1910 (σ: 680, 770)
C ₁₈ (-SAM): n-octadecyltrichlorosilane (CH ₃ (CH ₂) ₁₇ SiCl ₃)	330–2016 (σ: 85–1700)
CH-LB: stearic acid (C ₁₇ H ₃₅ COOH)	120–790 (σ: 10–150)
CFCH-LB: fluorolurorocarboxylic acid (C ₆ F ₁₃ C ₁₁ H ₂₂ COOH)	95–520 (σ: 6–66)

TABLE 2.4
Contact Angles and Surface Energies on SAM-Coated Plates

Sample name	Contact angle measured after deposition (degrees)		Surface energy (mJ/m ²)	Water contact angle measured after force measurement (degrees)
	Water	CH ₂ I ₂		
C ₀	4–5	39	73	34
C ₆	105	79	24	94
C ₈	105	79	25	—
C ₁₄	111	72	21	103
C ₁₈	112	70	20	—

The wettability of each SAM-coated plate was measured after the formation of SAM to confirm that the alkyl chain in alkylchlorosilane was exposed to the outside. The contact angles of water and diiodomethane (CH₂I₂) were measured by using a droplet on the flat area outside of the patterned area. These two liquids were used because the hydrogen bonding and dispersion force components manifest themselves in the surface energy with water and diiodomethane, respectively. The surface energies of the SAM-coated plates were determined from contact angle measurements by using the Fowkes equation [10]. Table 2.4 summarizes the contact angle measurements and surface energy of each plate.

2.3 MEASUREMENTS OF FRICTION AND PULL-OFF FORCES BY AN ATOMIC FORCE MICROSCOPE

2.3.1 MEASURING APPARATUS (ATOMIC FORCE MICROSCOPE)

Each modified area on the silicon surface was so small ($5 \times 5 \mu\text{m}^2$) that an optical lever type AFM system was used to measure the friction and pull-off forces. Figure 2.5 shows a schematic of the measurement method. The laser beam is deflected by the cantilever and strikes the quad-photodiode detector. When the cantilever probe is pressed against the specimen, the applied force by the cantilever is obtained from the output of the photodiode as $(a + b) - (c + d)$, where a , b , c , and d correspond to the outputs of sensor plates A, B, C, and D, respectively. The output for the height

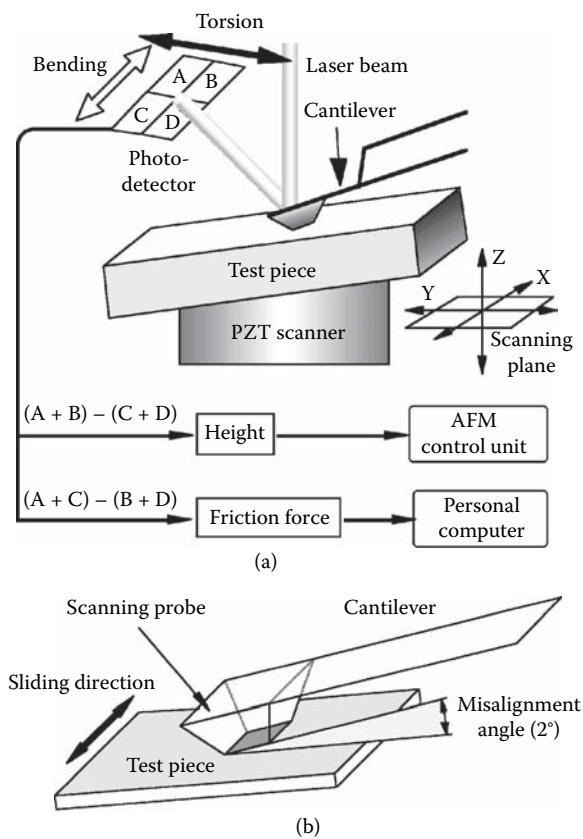


FIGURE 2.5 Schematic drawings of experimental setups (AFM) for measuring friction and pull-off forces. (a) The AFM probe scans along the x -direction, and the torsion and bending of the cantilever are detected by a quad-photodiode detector. (b) Arrangement of probe on a test specimen. The angle between the flat, square tip of the probe and the test piece was 2.5° – 3° .

is used for the conventional AFM system. The friction force between the cantilever probe and specimen is determined from $(a + c) - (b + d)$. The output for the friction force is analog-to-digital converted, and then the average friction force in a scanning is calculated using a personal computer.

To estimate the friction force from the output of $(a + b) - (c + d)$, first we measured the change in the value of the detector's output when tilting the cantilever. Then we calculated the torsional rigidity from the dimensions of the cantilever as 0.36×10^{-9} N·m/rad by using a shear modulus of 57.9 GPa, obtained from Young's modulus of 146 GPa [11] and a Poisson's ratio of 0.26 [12]. The two values (output change and torsional rigidity) were then used to calculate a conversion factor, which was used to convert the photodiode output to the friction force. This factor, however, changes as the position of the laser spot on the cantilever changes. This effect cannot be disregarded when exchanging a specimen or a cantilever. Therefore, we milled various patterns on the same silicon plate and examined the differences between the patterns on that plate.

Although an FIB can mill grooves less than 100 nm wide, this is still larger than the radius of curvature of a conventional AFM probe. The radius of curvature of the probe must be larger than one period of the pattern to examine the geometry effects. The tip of the scanning probe was a flat square, $0.7 \times 0.7 \mu\text{m}^2$. The SEM image of the tip of the scanning probe is shown in fig. 2.6. (This flat probe was used when measuring the pull-off and friction forces, except for the measurement shown in fig. 2.8 later in this chapter, in section 2.4.1.)

Both the installed cantilever and the flat square of the probe were inclined to the scanning plane of the PZT (lead zirconate titanate) scanner. To decrease this misalignment angle and to increase the contact area, the specimen was also inclined, almost parallel to the flat area of the probe (fig. 2.5). The misalignment angle was kept at 2° – 3° , however, as the specimen and the square tip were parallel, the sensitivity of the AFM was significantly decreased.

2.3.2 METHOD FOR MEASURING FRICTION AND PULL-OFF FORCES

When measuring the pull-off force, we used a conventional AFM system that allowed us to use a force–curve mode that showed the force required to pull the scanning probe tip off the specimen. Figure 2.7 shows an example of how we measured the pull-off force from the force–distance curve. The photodiode output $(a + b) - (c + d)$ is plotted on the vertical axis, and the relative position of the specimen in the z -direction is plotted on the horizontal axis. This relative position is based on the applied voltage to the PZT scanner. In fig. 2.7, the probe jumped off the specimen just as the cantilever was pulled a distance H from its neutral position. The pull-off force was calculated using the distance H and the nominal spring constant of the cantilever (0.75 N/m). Because the pull-off force was originally calculated using the applied voltage to the PZT scanner, the measured value included an error caused by the hysteresis in the PZT.

Small particles can easily adhere to the square tip of an AFM probe and can influence the experimental results because the contact area between the flat probe and specimen was much larger than that of a conventional probe tip. Therefore, when

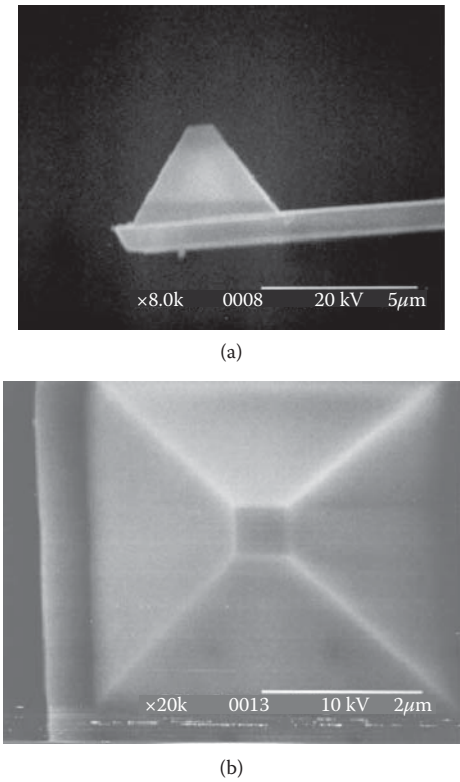


FIGURE 2.6 SEM images of the scanning probe. The flat square of the scanning probe is about $0.7 \times 0.7 \mu\text{m}^2$ from the image. (a) Side view, (b) flat square of the scanning probe.

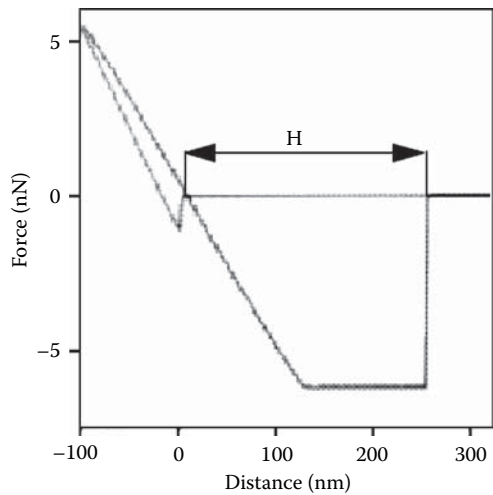


FIGURE 2.7 Force–curve technique used to determine the pull-off force. The force is calculated using the distance H and the spring constant of the cantilever.

TABLE 2.5
Experimental Conditions

Cantilever (Si ₃ N ₄)	
Spring constant (N/m)	0.75/0.37
Torsional rigidity (N·m/rad)	$0.36 \times 10^{-9}/0.20 \times 10^{-9}$
Sliding conditions	
External normal load (nN)	~5 (0 to 10)
Raster scan area (μm ²)	2 × 2
Sliding speed (μm/s)	2
Relative humidity (%)	20–56

examining the difference in the pull-off force between the patterns, first we scanned an area of 20 × 20 μm² including some patterns. Second, these patterns were displayed together in the measurement window for the force–curve mode. Third, we selected more than six measurement points in each pattern, and then the pull-off forces were measured. Because a raster scanning was not performed between measurements, the possibility of any change in probe surface conditions caused by friction was very slim.

The friction force was measured as follows. First, an area of 2 × 2 μm² was selected in a pattern for friction-force measurement. Second, more than six measurement points were selected in that area, and the pull-off force was measured. Third, raster scanning was performed in the scanning direction of *x*, as shown in fig. 2.5a, and the photodiode output (*a* + *c*) – (*b* + *d*) was registered on a personal computer. The personal computer calculated the average of the signal corresponding to the torsion angle of the cantilever over the measurement area. The friction force was obtained by multiplying the average by the conversion factor calculated in section 2.3.1. Finally, the pull-off force was measured again in the same way as before the friction-force measurement. The experimental conditions are summarized in table 2.5.

**2.4 GEOMETRY EFFECTS ON FRICTION
AND ADHESION [9, 13, 14]**

2.4.1 FRICTION AND PULL-OFF FORCES ON SILICON PATTERNS

Figure 2.8 shows the relation between the pull-off force and groove depth. In this figure, solid squares show the pull-off force measured by a flat probe (fig. 2.6), and open triangles show the pull-off force measured by a conventional sharp probe. We did not carry out surface scanning between each measurement due to the possibility of altering the shape of the scanning probe either by a very small amount of wear or by contamination of the surface during friction measurements. Therefore, we assumed that the conditions of the probe were similar for all measurements. In fig. 2.8, the pull-off force measured with the flat probe clearly decreases with groove depth. By

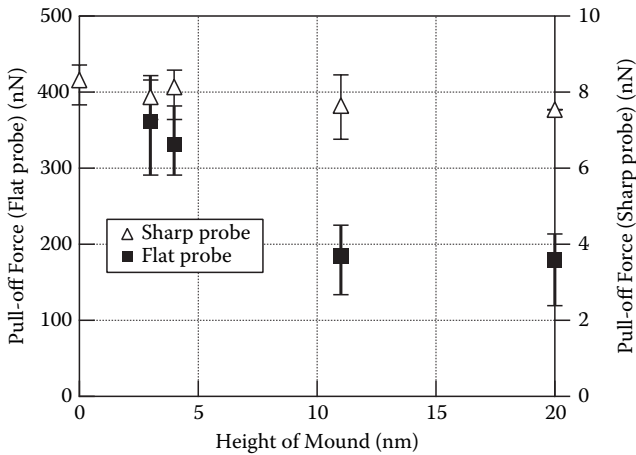


FIGURE 2.8 Relation between pull-off force and groove depth created on the silicon surface. The pull-off force was measured by using a flat probe as well as a normal sharp probe. Each probe was made of Si_3N_4 .

contrast, the pull-off force with the conventional sharp probe remained constant, because the apparent contact area was so small that the contact conditions were not affected by the change in surface topography.

Figure 2.9 shows two kinds of friction forces obtained during surface scanning on the silicon asperity array. The abscissas in both figures represent lapse of time. The direction of the friction force changes when the sliding direction is reversed. Figures 2.9a and 2.9b show the friction force measured along the asperity array (i.e., parallel direction) and at a rotation of 45° to the array (i.e., 45° direction), respectively.

The average friction force during each reciprocating motion increases and decreases periodically, with the period depending on the sliding direction in fig. 2.9. The path of the sliding probe shifted during surface scanning. This shift caused changes in the contact conditions between the probe and the array, resulting in variations in the average friction force between reciprocating motions. When the average friction force is high, during the 3–10-s time period in fig. 2.9a, and 7–10-s and 15–18-s in fig. 2.9b, the probe seemed to be in contact with two rows of asperities simultaneously. This increase in the contact area caused the increase in the average friction force. The difference in the period was caused by the difference in the distances between the peaks along the direction of motion (d_p in fig. 2.9).

Spikes in the friction force are more prominent in fig. 2.9a compared with fig. 2.9b in the high average friction region. When the probe slid along a row of asperities and was in contact with two rows, the edge of the probe square contacted two asperities simultaneously; this did not occur when the probe slid at a 45° direction to the asperity array. The force needed for the probe edge to “climb” the asperities appears as a sharp increase in fig. 2.9a. Since this influence is different in different sliding directions (parallel direction or 45° direction), the sliding direction should be coincided when comparing the friction forces.

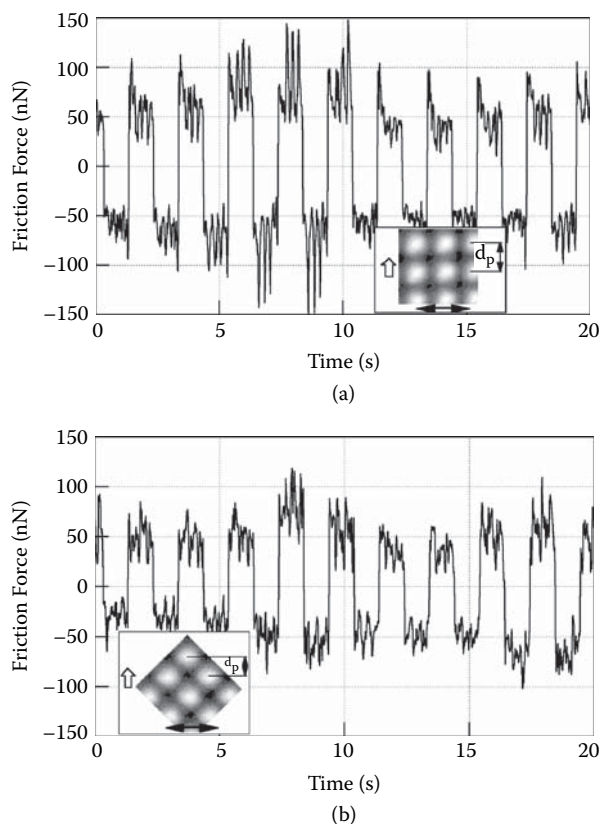


FIGURE 2.9 Friction forces obtained during surface scanning on a silicon asperity array when (a) the scanning direction is along the asperity array and (b) the scanning direction is inclined at 45° to the asperity array. Double arrow shows the primary scanning direction and open arrow shows the secondary scanning direction. The variable d_p shows the distance between the asperity peaks in the secondary scanning direction.

Figure 2.10a shows pull-off forces measured on the same pattern without surface scanning between each measurement (i.e., a no-scan pull-off force). Figure 2.10b shows the friction and pull-off forces measured for the arrays as a function of groove depth. The measured friction force was averaged over a scan area of about 2 to $4\ \mu\text{m}^2$. The pull-off forces in this figure were measured before and after each friction measurement at the same scan area, and were then averaged (i.e., a scan pull-off force).

Figure 2.10b shows that both friction and pull-off forces decrease with increasing groove depth. When measuring the friction force, a surface scan was carried out, and the probe was slid on the specimen not only to measure the friction force, but also to find the measurement position. Although the contact condition can change by this friction, the pull-off force shown in fig. 2.10b decreases with groove depth in the same way as that shown in fig. 2.10a. We also measured the pull-off and friction forces on a flat part of the specimen (i.e., unmilled) at the beginning and end of the series of measurements, and found that the differences were less than 1% and 6% for

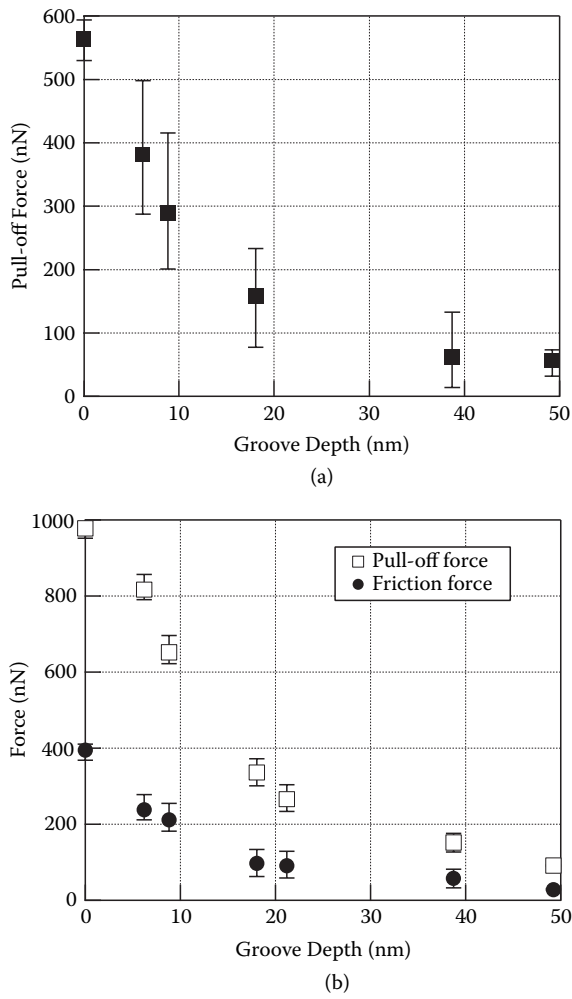


FIGURE 2.10 Friction and pull-off forces measured on a silicon periodic asperity array. (a) Pull-off forces were measured on each pattern without surface scanning between the measurements. (b) Pull-off forces were measured before and after each friction measurement at the same scanning area and were averaged.

the two forces, respectively. Therefore, changes in the friction force were not caused by changes in probe topography (due to wear or contamination) but by the geometry of the silicon asperity.

Figure 2.11 shows the friction and pull-off forces measured for various spacings and widths of periodic grooves using the patterns shown in fig. 2.2. The abscissa represents the ratio of mound width to total width of mound and groove, which was determined from the milling conditions. Both forces increase as this mound ratio increases.

From the topography data shown in fig. 2.1, the depth measured from the highest point in the image is divided into consecutive periods of 0.2 nm, and the surface areas included in all consecutive periods are added together over each period. Figure 2.12

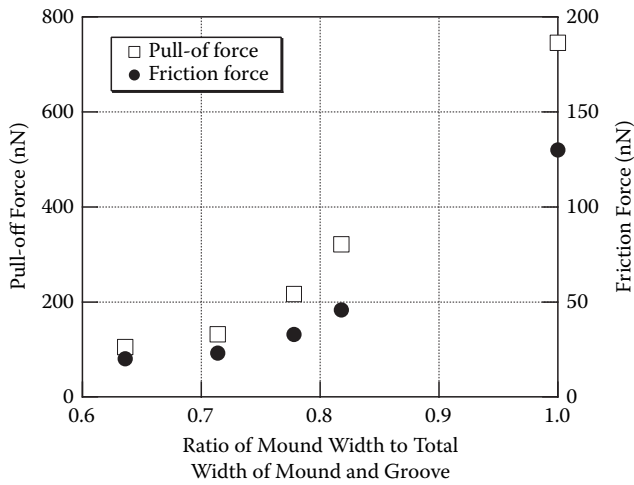


FIGURE 2.11 Friction and pull-off forces as a function of the ratio of mound width to total width of mound and groove.

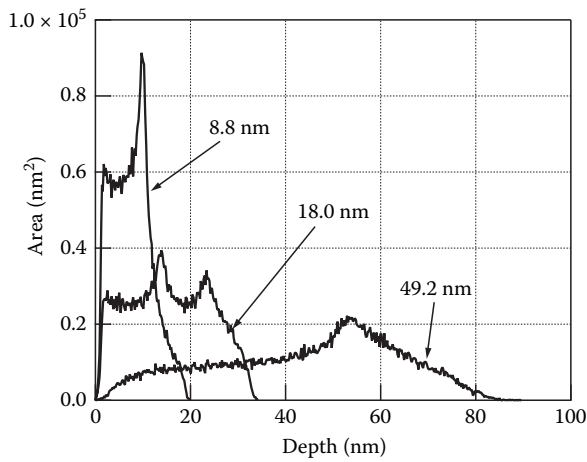


FIGURE 2.12 Depth distribution of silicon asperity arrays. The relations between the area and depth are calculated from topography data of a scanning range of $2 \times 2 \mu\text{m}^2$. The underlined dimension shows the groove depth of each pattern.

shows a distribution of the depth in the silicon patterns calculated as described above. Comparing the sum of the areas included from zero to 5 nm in depth, the included areas of the patterns with grooves of 8.8-, 18.0-, and 49.2-nm depth are calculated to be 1.11, 0.53, and 0.05 μm^2 , respectively. Hence, a deeper groove not only increases the average depth, but also decreases the surface area close to the contact point. The adhesion force was probably strongly affected by this area.

Figure 2.13 shows the relation between the friction force and the pull-off force, from the data in figs. 2.10b and 2.11. Both friction forces are proportional to the

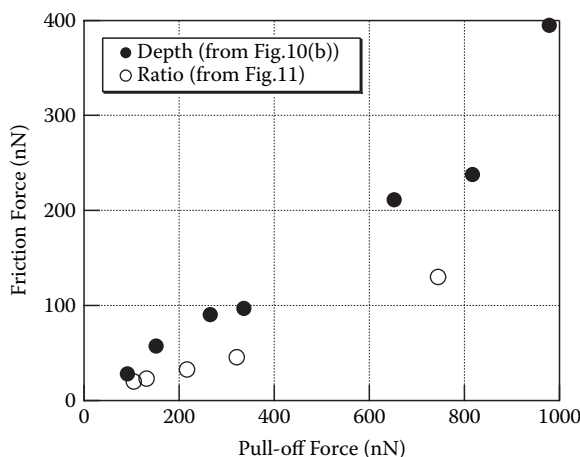


FIGURE 2.13 Relation between friction force and pull-off force measured on two kinds of asperity arrays. Friction forces are extracted from figs. 2.10b and 2.11 and are shown as solid circles and open circles, respectively.

pull-off force. The difference in the gradients of the two friction forces was caused by the difference in the sensitivities of the sensor, as described in section 2.3.1. The friction force is reportedly almost proportional to the sum of the normal load and pull-off force [2, 3]. In fig. 2.13, as the external applied load to the friction surfaces was less than 10 nN and thus was negligible compared with the pull-off force, the assumption that the friction force is proportional to the sum of the normal load and the pull-off force is true when the adhesion (pull-off) force varies.

2.4.2 FRICTION AND PULL-OFF FORCES ON PLATINUM PATTERNS

Figure 2.14a shows the relation between the no-scan pull-off force and the asperity height measured on a platinum pattern as shown in fig. 2.3. The pull-off force was measured without surface scanning between pull-off force measurements. The pull-off force scarcely changed as the asperity height increased. The pull-off force was measured on a silicon pattern by using a conventional sharp probe (fig. 2.8). The effect of groove depth could not be observed for the sharp probe because the contact area was too small to be affected by changes in surface topography. The relation between the pull-off force and asperity height for the flat probe on the platinum pattern (fig. 2.14a) was similar to that of the sharp probe on the silicon pattern. If wear debris were jammed between the probe and the substrate or formed a bump on the flat probe, the square tip of the probe could not make contact with platinum asperities. Thus, the pull-off force was not affected by the difference in asperity height.

Figure 2.14b shows the friction force measured on platinum patterns and the averaged scan pull-off force measured before and after each friction measurement for the same scanned area. In fig. 2.14b, both the friction and pull-off forces decreased as the asperity height increased, but not as rapidly as the forces with silicon groove depth (fig. 2.10b). The difference in contact conditions, as mentioned previously, possibly caused the differences in rates of decrease in the friction and pull-off forces.

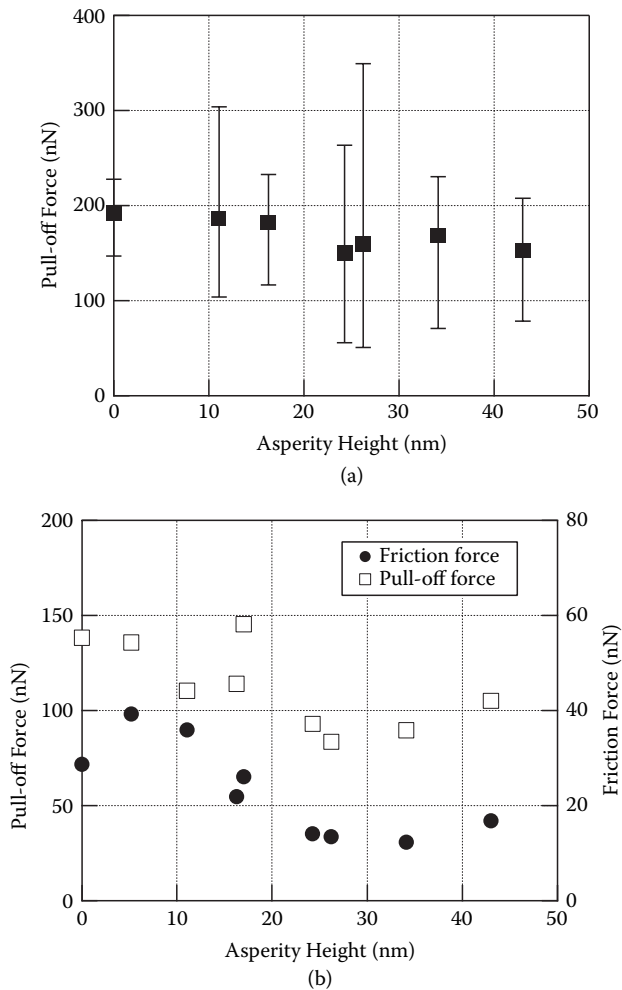


FIGURE 2.14 Friction and pull-off forces measured on platinum asperity arrays as shown in fig. 2.3. (a) Relation between pull-off force and groove depth and (b) effect of asperity height on friction and pull-off forces

If the reaction of platinum by the FIB was not sufficient, the bonding force between the platinum layer and substrate was probably weak, and a part of the deposited platinum easily turned into debris by rubbing. In order to remove the superficial layer that probably had a weak bond to the substrate, the specimen was placed in the FIB system again, and all the pattern areas were sputtered by FIB. Figure 2.15 shows AFM images of the sputtered pattern of the platinum asperities. The patterns shown in figs. 2.3a and 2.3b changed to figs. 2.15a and 2.15b, respectively. As the height of the asperity decreases, the small irregular ridges completely disappear in fig. 2.15.

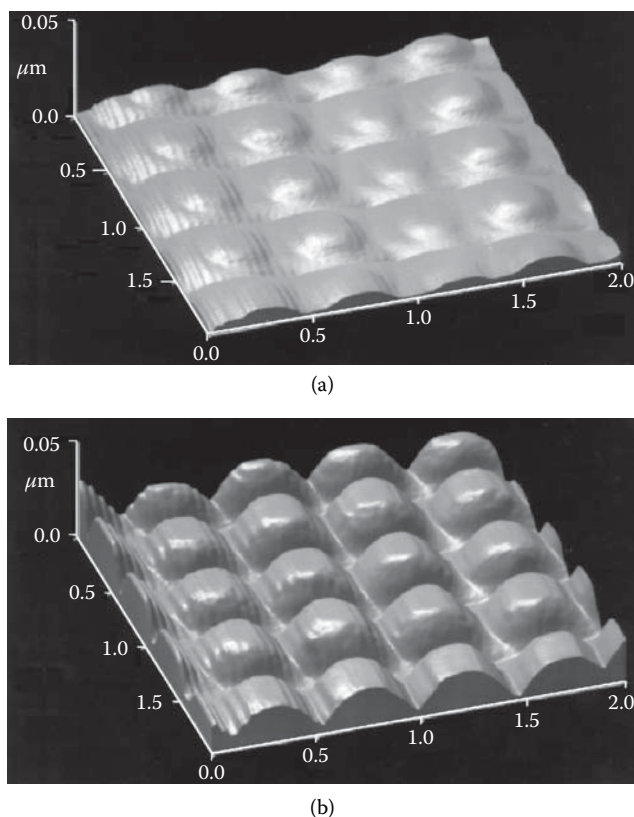


FIGURE 2.15 AFM images of platinum asperity arrays after sputtering. The shape of platinum asperity arrays shown in fig. 2.3 changed after removing the unreacted material. The height of the asperity decreased and the asperity peaks became flat. (a) 6.6-nm asperity height; (b) 17.2-nm asperity height.

Figure 2.16a shows the no-scan pull-off force on the sputtered platinum patterns (fig. 2.15). Figure 2.16b shows the friction and the scanned pull-off force measured on the same specimen. In fig. 2.16b, both the friction and pull-off forces clearly decreased as the asperity height increased. The superficial layer was probably removed by the sputtering process by FIB, because the fluctuation of the forces significantly decreased. In fig. 2.16a, the pull-off forces measured on the pattern of 6.6-nm asperity height showed wide scatter compared with the others because of the lower uniformity of the asperity shape.

Figure 2.17 shows the relation between the friction force and pull-off force, from the data in fig. 2.16b. The friction force was proportional to the pull-off force except for the point (open circle) measured on the silicon surface having no platinum asperity. This difference was caused by the difference in the material. Therefore, the friction force was proportional to the sum of the normal load and the pull-off force for the platinum patterns.

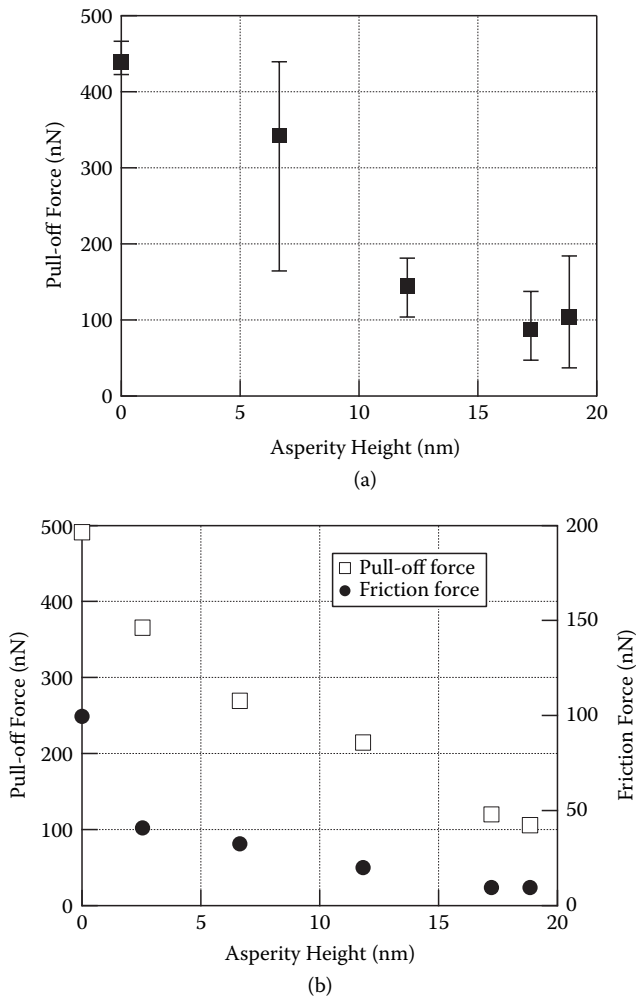


FIGURE 2.16 Friction and pull-off forces measured on platinum asperity arrays after sputtering. (a) Relation between pull-off force and asperity height and (b) effect of asperity height on the friction and pull-off forces.

2.4.3 COMPARISON OF FRICTION AND PULL-OFF FORCES OF SILICON AND PLATINUM

It was difficult to precisely compare the friction forces of different materials on different substrates (figs. 2.13 and 2.17) because the sensitivity of detecting the torsion angle was not always the same for each measurement. Platinum and silicon patterns were made on the same plate, and the friction and pull-off forces were measured to compare the friction coefficients calculated by dividing the friction forces by the pull-off forces for the different materials. Figure 2.18 shows the friction and scanned pull-off forces as a function of groove depth, and these forces were measured for

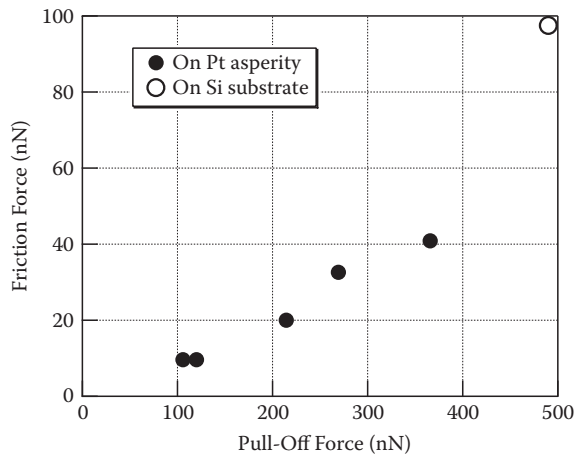


FIGURE 2.17 Relation between friction force and pull-off force measured on a platinum asperity array as shown in fig. 2.15. Friction and pull-off forces are extracted from fig. 2.16. The maximum friction force of 100 nN (shown as ○) was measured at the asperity height of 0 nm in fig. 2.6, which means the friction force was measured on a bare silicon surface without platinum asperities.

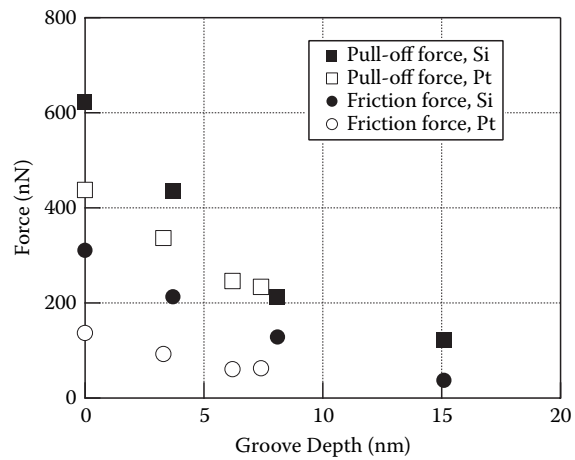


FIGURE 2.18 Comparison of friction and pull-off forces between silicon and platinum asperity arrays. The platinum asperity arrays were fabricated near the silicon asperity arrays on the same silicon plate, which makes it possible to directly compare the difference in the friction and pull-off forces between two different materials.

platinum and silicon asperity arrays on the same silicon plate. This figure shows that the friction force on the silicon asperity array was always greater than that on platinum, although the pull-off forces were rather comparable for both patterns.

Figure 2.19 shows the relation between the friction and pull-off forces using the data from fig. 2.18. The slope of each fitted line that passes through the origin (values

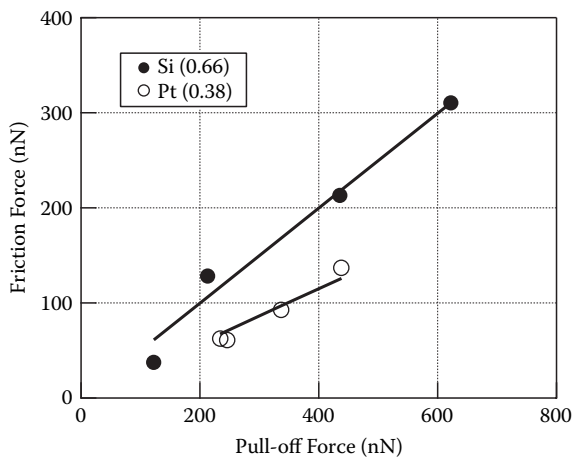


FIGURE 2.19 Comparison of friction force vs. pull-off force on platinum and silicon asperity arrays using data from fig. 2.18. The friction forces measured on each material were fitted with a line that passes through the origin. The gradient of each approximated line is shown in the parentheses in the inset box.

are shown in the inset) appears to correspond to the friction coefficient. This friction coefficient for silicon was about twice than that for platinum.

The pull-off forces shown in fig. 2.18 probably reflected the adhesion forces acting on the surfaces to some extent. If the friction forces were directly caused by the adhesion forces, then the same adhesion force must generate the same friction force. However, in these measurements, the friction coefficient calculated by dividing the friction force by the pull-off force depended on the material. This means that the mechanism causing the adhesion force was different from that causing the friction force, and that the adhesion force acted as a hidden normal load and thus indirectly generated the friction force.

2.4.4 RELATION BETWEEN PULL-OFF FORCE AND CURVATURE RADIUS

Johnson, Kendall, and Roberts (JKR) calculated the Hertzian contact area between two spherical surfaces when the adhesion energy could not be disregarded [15]. They verified their theory by their own experiments using the material combination of rubber and glass. In the JKR theory, it is assumed that adhesion energy is proportional to the contact area and that the attractive force acting on the outside of the contact area can be ignored. The JKR theory is outlined below.

Two spheres in fig. 2.20, with radii R_1 and R_2 , respectively, have a Hertzian contact under normal load P_0 . The apparent Hertzian load P_1 is given by the following equation:

$$P_1 = P_0 + 3\gamma\pi R + \sqrt{6\gamma\pi R P_0 + (3\gamma\pi R)^2} \quad (2.1)$$

where γ is the adhesion energy for the two surfaces and R is the effective radius determined as $R = R_1 R_2 / (R_1 + R_2)$. Considering P_1 as equivalent to the external force,

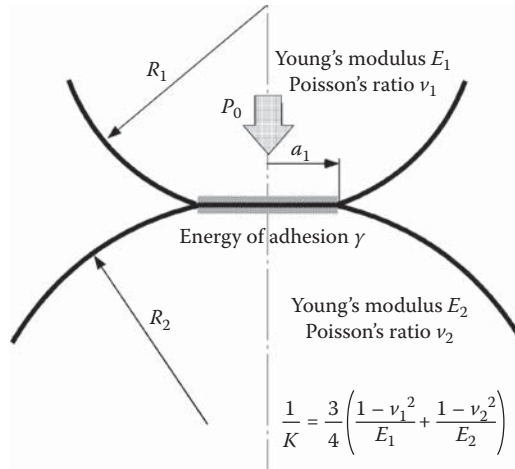


FIGURE 2.20 Contact geometry between two elastic solids showing outline of JKR theory. The two hemispherical surfaces having curvature radii of R_1 and R_2 are in contact under an external load of P_0 . The radius of the contact circle is a_1 . The energy of adhesion γ is generated between the two surfaces.

the radius a of the contact circle derived from the Hertz equation is given by the following equation:

$$a^3 = \frac{R}{K} \left\{ P_0 + 3\gamma\pi R + \sqrt{6\gamma\pi R P_0 + (3\gamma\pi R)^2} \right\} \quad (2.2)$$

where K is the elastic constant calculated from the Poisson's ratio and Young's modulus of each material. The condition in which both surfaces are in a stable contact is expressed as

$$P_0 \geq -\frac{3}{2} \gamma\pi R \quad (2.3)$$

From the above, the pull-off force, $P_{\text{pull-off}}$, which is measured when the surfaces are separated, is given by the following equation:

$$P_{\text{pull-off}} = -\frac{3}{2} \gamma\pi R \quad (2.4)$$

Equation (2.4) shows that the pull-off force is proportional to R . A similar relation would be obtained if a water capillary formed around the contact area and the surface tension of water was considered. When a hemispherical asperity whose radius of curvature is R_s contacts with a flat plane (fig 2.21), water condenses at the narrow spacing around the contact point. If the periphery of the capillary has a concave surface (i.e., a meniscus), the saturated water vapor pressure p_s on the meniscus surface is lower than that on a flat surface. Therefore, liquid water can exist when

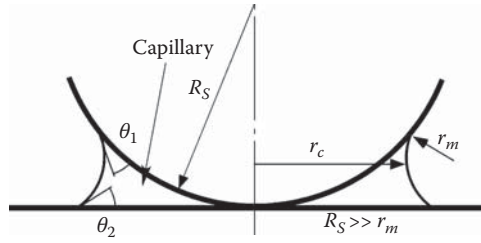


FIGURE 2.21 Capillary formed around contact area between hemispherical and flat surfaces. Size of the capillary can be geometrically determined based on the radius of curvature of the meniscus, contact angle of water, and the radius of curvature of the hemispherical surface.

relative humidity (p/p_s) is less than 100%, and thus r_m is given by Kelvin's equation [16] as

$$r_m = \frac{0.54}{\log(p/p_s)} \quad (2.5)$$

The area of the capillary πr_c^2 geometrically is

$$\pi r_c^2 = 2\pi R_S r_m (\cos \theta_1 + \cos \theta_2) \quad (2.6)$$

where θ_1 and θ_2 are the contact angles of water on the sphere and plane, respectively. The adhesion force F_w generated by the Laplace pressure is then given by

$$F_w = 2\pi R_S \gamma_L (\cos \theta_1 + \cos \theta_2) \quad (2.7)$$

Equation (2.7) shows that F_w is independent of r_m , indicating that the relative humidity does not affect the adhesion (pull-off) force, or F_w , between a hemispherical surface and a flat surface.

From the above discussion, the pull-off force is proportional to the curvature radius in both cases, i.e., whether the adhesion force acts in the contact area or the Laplace pressure acts in a capillary. Thus, the pull-off force must be proportional to the curvature radius of the hemispherical asperity that contacts with a flat plane. The pull-off forces shown in figs. 2.10a and 2.10b are then plotted in fig. 2.22 as a function of curvature radius for each pattern shown in table 2.2. The pull-off forces shown in figs. 2.10a and 2.10b are shown by solid and open squares, respectively. The lines in fig. 2.22 are approximate lines passing through the origin of the graph for the respective data sets. Both sets of pull-off forces were approximately proportional to the curvature radius of the asperity peak, and they agreed with eqs. (2.4) and (2.7). As shown in fig. 2.1b, the microsurface roughness of asperities was extremely large for the radius of curvature of 170 nm. This roughness, however, did not significantly reduce the pull-off force. This verifies that the pull-off force is only dependent on the radius of curvature of a sphere and not on microsurface roughness.

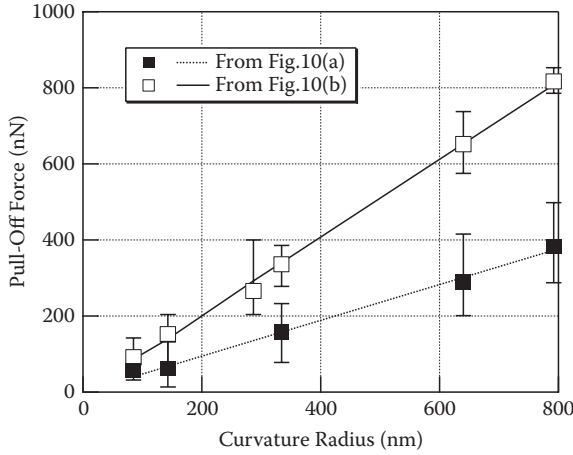


FIGURE 2.22 Relation between pull-off force and curvature radius of asperity peak measured on silicon asperity arrays of various groove depths. The pull-off forces were derived from fig. 2.10. The curvature radii were calculated from the AFM data by using a hemisphere approximation program.

In fig. 2.22, the gradients of the two lines are different. The higher gradient is almost twice the lower value. This is probably because the flat part of the probe was covered with slight contamination. If the probe tip was not flat but had a finite radius of curvature due to deposited contamination, the effective radius at the contact point became lower than the curvature radius of the asperity peak. Moreover, slight contamination affected both the adhesion energy in eq. (2.4) and the contact angles of water in eq. (2.7).

2.4.5 RELATION BETWEEN FRICTION FORCE AND CURVATURE RADIUS

When the friction force was measured, the applied load was very small (<10 nN) compared with the pull-off force. For the applied load P_0 at 0, the apparent Hertzian load P_1 is calculated from eq. (2.1) as

$$P_1 = 6\gamma\pi R \quad (2.8)$$

Then the radius of the contact circle a_1 is calculated from eqs. (2.2) and (2.8) and is given by

$$a_1^3 = \frac{6\gamma\pi R^2}{K} \quad (2.9)$$

Figure 2.23 shows the friction force as a function of R (the asperity curvature for silicon) and $R^{4/3}$ from fig. 2.10b. The friction force was proportional to R , but not to $R^{4/3}$. If the friction force was proportional to the total load that included adhesion force, then from eq. (2.8) the friction force was considered to be proportional to the apparent Hertzian load P_1 [17] as well as to R . If the contact circle between the AFM

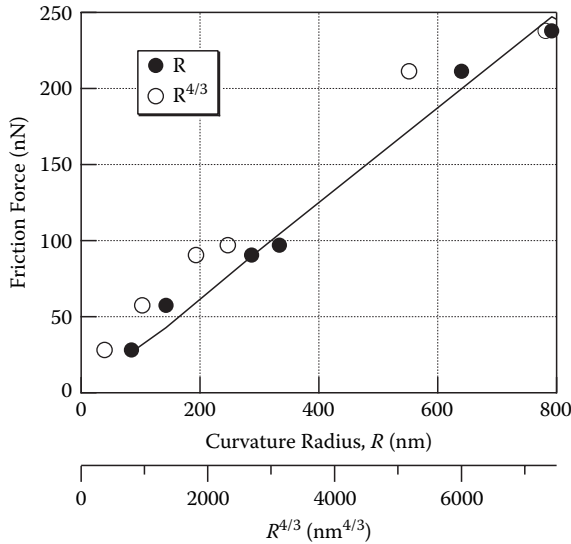


FIGURE 2.23 Relation between friction force and radius of an asperity curvature (R) and $R^{4/3}$.

probe and an asperity calculated from eq. (2.9) was equivalent to the real contact area, then the friction force should have been proportional to $R^{4/3}$. This discrepancy between theoretical and experimental results means that the contact circle given by eq. (2.9) was not a real contact area. This is also confirmed from our result that the friction force was independent of microsurface roughness.

The friction force was reportedly proportional to the contact area when the contact surface was an atomically flat surface, such as a cleavage plane of mica [18]. Under the conditions used in our experiments, the contact surface had a finite surface roughness. The area determined by eq. (2.9) represented only an apparent, not a real, contact area. Adhesion force due to the van der Waals force or capillary force acted on this apparent contact area. Because this adhesion force increased the real contact area as an equivalent normal load, the friction force was proportional to the adhesion force and, as a result, the friction force must be proportional to the radius of curvature.

2.4.6 EVALUATION OF ADHESION ENERGY

From eq. (2.4) and the data in fig. 2.22, we calculated that the adhesion energy γ was from 0.063 to 0.18 J/m². The van der Waals interaction energy per unit area, W , between two flat surfaces is given by [16]

$$W = \frac{-H_{12}}{12\pi d^2} \quad (2.10)$$

where d is the distance between the surfaces, and H_{12} is the Hamaker constant between the two materials (in our case, silicon for the pattern and Si₃N₄ for the probe) expressed as

$$H_{12} = \sqrt{H_1 \cdot H_2} \quad (2.11)$$

where H_1 is the Hamaker constant of silicon and H_2 is the Hamaker constant of Si_3N_4 .

If the adhesion energy is determined by only the van der Waals energy, then γ is equivalent to W ($W = \gamma$). Then, for our case, the calculated average distance d was 0.30 to 0.18 nm when using a Hamaker constant of 2.56×10^{-19} J for silicon [19] and 1.8×10^{-19} J for Si_3N_4 [20]. Because this calculated d was equivalent to the lattice constant of silicon, contact at the atomic level appeared to be generated between the two surfaces over the entire contact area. However, fig. 2.22 shows that the pull-off force was proportional to only the asperity curvature radius and was independent of differences in the microroughness on the asperity (figs. 2.1a–2.1c). Figure 2.23 also shows that the contact area calculated from eq. (2.9) is not the real contact area. Therefore, the surface tension of the condensed water was dominant in the adhesion energy.

It is possible that a capillary condensed water bridge existed between the silicon asperity and the probe plane. When the Laplace pressure is considered, the adhesion force F_w caused by this type of meniscus between a sphere of radius R_s and a flat surface is proportional to the area covered by the capillary water and is expressed as eq. (2.7). When we measured the pull-off force for different asperity curvatures on the same plate, the attractive force F_w was determined only by the curvature, because we assumed that both contact angles were constant. Therefore, the contribution of the attractive force from the Laplace pressure gives a consistent interpretation of eq. (2.7) in agreement with the measured pull-off force shown in fig. 2.22.

The attractive force caused by the condensed water can be estimated using eq. (2.7). For a contact angle of 27° for Si_3N_4 [21] and 70° for silicon [22], the attractive force is, for example, 47 nN (for an R of 83 nm) and 430 nN (for an R of 760 nm). For a contact angle of 43° for oxidized silicon [22], this force is 62 nN (for an R of 83 nm) and 570 nN (for an R of 760 nm). Because these contact angles are easily altered by slight contamination or by a slight degree of oxidation, the difference in the pull-off force in fig. 2.22 was probably due to the difference in the Laplace pressure.

2.5 CHEMICAL EFFECTS ON FRICTION AND ADHESION [23, 24]

2.5.1 PULL-OFF FORCES ON ASPERITY ARRAYS COVERED WITH SAMs

The measured contact angle of water on C_{18} (table 2.4) is similar to that found in the literature, $112^\circ \pm 2^\circ$ [25], which indicates that a SAM of alkylchlorosilane molecules was deposited on all substrates. Figure 2.24 shows the relation between the pull-off force and the curvature radius of the asperity peak covered with SAMs of alkylchlorosilanes. (Note that the x -axis represents the average curvature radius of the asperity peaks shown in table 2.3.) The number (#) of carbon atoms in each alkylchlorosilane is indicated as $C_\#$. C_0 represents an uncoated plate. The data for each plate (SAM) were fitted with a line passing through the origin. For the uncoated plate (C_0) and the SAM-coated plates except C_{14} , the pull-off force increased with increasing peak curvature radius. For C_6 and C_{18} , the SAM-coated plates, the pull-off force was roughly proportional to the curvature radius of the asperity peak. The slopes for

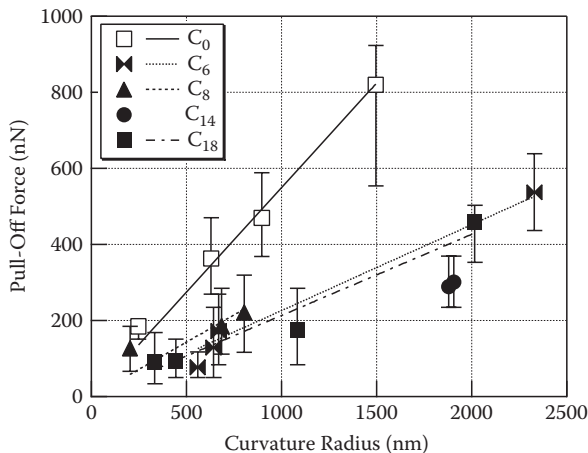


FIGURE 2.24 Relation between the pull-off force and the curvature radius of the asperity peaks for uncoated plate C_0 and SAM-coated plates C_6 to C_{18} . Measured data were fitted by a line that passes through the origin.

the other SAM-coated plates (C_6 to C_{18}) were half, or less, than that for the uncoated plate (C_0).

The experiment in the previous section revealed that the capillary force was predominant between the flat probe and the periodic asperity array. In fig. 2.21, the capillary geometry shows that a capillary can be formed even if one of the surfaces is hydrophobic, and eq. (2.7) shows that the adhesion force exists between the surfaces when $\theta_1 + \theta_2 < 180^\circ$. Thus, the water capillary could form between the hydrophilic probe and SAM-coated asperity peaks, even though the SAM-coated surfaces are hydrophobic and the adhesion force F_w is given by eq. (2.7).

The contact angle of water on SAM-coated or on uncoated silicon (table 2.4) ranged from 4° to 113° after the SAM deposition and from 34° to 103° after the force measurements. For θ_1 , we used the contact angles measured after the force measurements. For θ_2 , we assumed it was 27° for Si_3N_4 [21]. Assuming these values for the contact angles of water, i.e., $\theta_1 = 34^\circ$ to 103° and $\theta_2 = 27^\circ$, then $\theta_1 + \theta_2 < 180^\circ$, which means the condensed capillary could generate an adhesion force. Therefore, from eq. (2.7), the adhesion force is proportional to the radius of curvature of the fitted spherical surface.

If the contact angle for water on the probe is assumed to be 27° , then the adhesion force caused by a capillary on each surface can be calculated using the contact angles shown in table 2.4. Table 2.6 shows the slope of the fitted lines ($\partial P_{\text{pull-off}}/\partial R$) in fig. 2.24 and also shows $2\pi\gamma_L(\cos\theta_1 + \cos\theta_2)$ from eq. (2.7). The $\partial P_{\text{pull-off}}/\partial R$ from the measured data was only 30% to 45% less than $2\pi\gamma_L(\cos\theta_1 + \cos\theta_2)$. (The values from these two expressions would show a better agreement if a higher contact angle on Si_3N_4 were assumed.) Such agreement suggests that there was only one contact point between the asperity array and the probe.

TABLE 2.6
Comparison between $\partial P_{\text{pull-off}}/\partial R$ and Capillary Force on SAM-Coated Plates

Sample name	$\partial P_{\text{pull-off}}/\partial R$ (N/m)	$2\pi\gamma_L(\cos\theta_1+\cos\theta_2)$ (N/m)
C ₀	0.55	0.77
C ₆	0.23	0.36
C ₁₄	(0.16)	0.29

2.5.2 PULL-OFF FORCES ON ASPERITY ARRAYS COVERED WITH LB FILMS

Figure 2.25 shows the pull-off force measured for the asperity arrays covered with two kinds of LB films. The curvature radius on the *x*-axis was shown in table 2.3. The data for each plate with CH(C₁₇H₃₅COOH)-LB or CFCH(C₆F₁₃C₁₁H₂₂COOH)-LB film were fitted with a line passing through the origin. The pull-off force decreased with smaller curvature radius and was roughly proportional to the curvature radius. The pull-off force on the CH-LB film was about 1/5th of the pull-off force on the CFCH-LB film for the same curvature radius.

Figure 2.26 shows the pull-off forces on two kinds of asperity arrays as a function of the relative humidity. The average curvature radius of each asperity array was 150 and 440 nm for the CH-LB film and 95 and 370 nm for the CFCH-LB film. Each plot in fig. 2.26 is the average of 256 pull-off force measurements. The error bar shows the standard deviation for each data point. The average pull-off force clearly increased with higher relative humidity for the asperity array of 370-nm radius with the CFCH-LB film

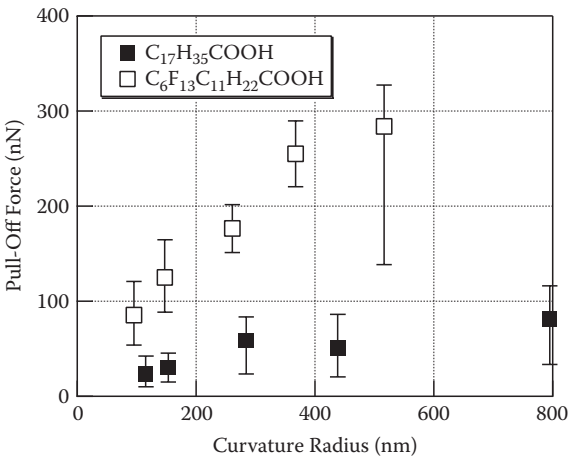


FIGURE 2.25 Relation between the pull-off force and the curvature radius of the asperity peaks for silicon plates coated with CH(C₁₇H₃₅COOH)-LB and CFCH(C₆F₁₃C₁₁H₂₂COOH)-LB films.

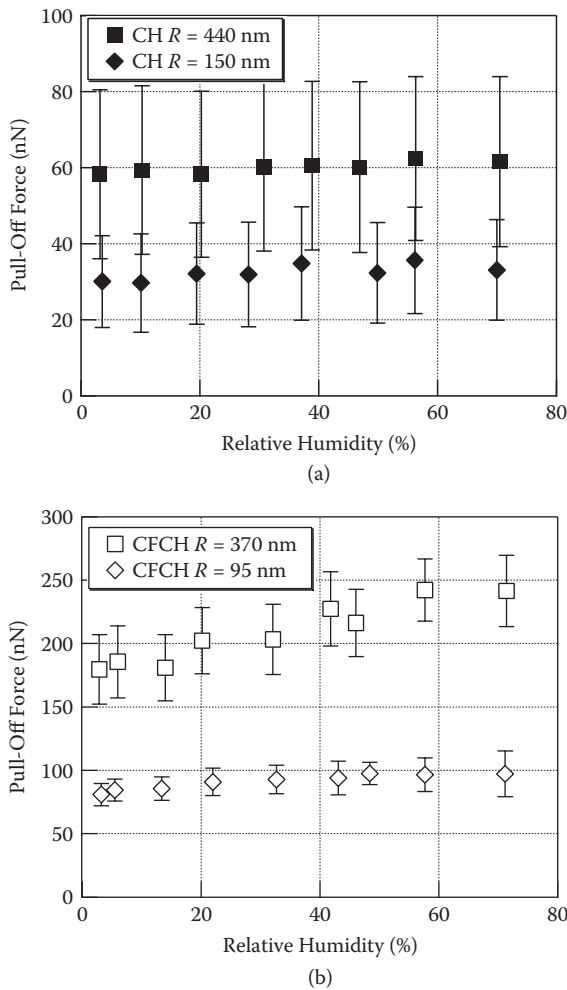


FIGURE 2.26 Relation between pull-off forces and relative humidity measured on asperity arrays. Each plot shows the average of pull-off forces from 256 measurements on (a) CH-LB film and on (b) CFCH-LB film. Two asperity arrays were selected from each plate, and their curvature radii are shown in the inset boxes.

(fig. 2.26b). For the asperity array with the CH-LB film, the pull-off force was nearly constant irrespective of changes in the relative humidity (fig. 2.26a).

In fig. 2.25, the pull-off force fluctuated, but it was nearly proportional to the curvature radius of the asperity peak with each LB film. Assuming that the water contact angle θ_2 on Si_3N_4 was 27° , the Laplace pressure would generate an adhesion force when the contact angle on the LB film was less than 153° , from eq. (2.7). In fig. 2.25, the pull-off force at a curvature radius of 400 nm ranged from about 50 nN for the CH-LB film to 350 nN for the CFCH-LB film. The adhesion force F_w as given by eq. (2.7) is 50 nN for $\theta_1 = 127^\circ$ and 340 nN for $\theta_1 = 0^\circ$, using $\gamma_L = 0.072\text{N/m}$. The

estimated contact angle has a moderate agreement with the value found in a report on the CH-LB film [27]. But, $\theta_1 = 0^\circ$ for the CFCH-LB film is too small. Thus, we should refer to the possibility that average numbers of the contact points might be different for the CH-LB and CFCH-LB films. If the average contact points were *two* for CFCH-LB film, $\theta_1 = 85^\circ$, and this would be a reasonable value. In fig. 2.26, comparing the standard deviation of the pull-off force against the mean value, the standard deviation for the CFCH-LB film (fig. 2.26b) is much smaller than that for the CH-LB film (fig. 2.26a). If the measured pull-off force were the average of two different curvature radii, fluctuation in the data would be suppressed. On the contrary, if the number of contacting points were only one, the pull-off force would be dominated by the curvature radius of one asperity, and thus varied by the contact position (contacting asperity) in the asperity pattern.

2.5.3 REDUCTION OF FRICTION BY ORGANIC MONOLAYER FILMS

Figure 2.27 shows the relation between the friction force and the peak curvature radius measured on SAM-coated plates. The data for each plate were fitted with a line. Similar to the pull-off force, the friction force for the SAM-coated plates increased with increasing peak curvature radius. The degree of reduction in the friction force due to the SAM coating was considerably larger than that in the pull-off force (fig. 2.24). For example, the slopes of the fitted lines for the SAM-coated plates C_6 to C_{18} are less than 1/5th of that for the uncoated plate C_0 . Moreover, those for the SAM-coated plates C_{14} and C_{18} are particularly small.

Figure 2.28 shows the relation between the friction force in fig. 2.27 and the pull-off force in fig. 2.24. The data for each plate were fitted with a line passing through

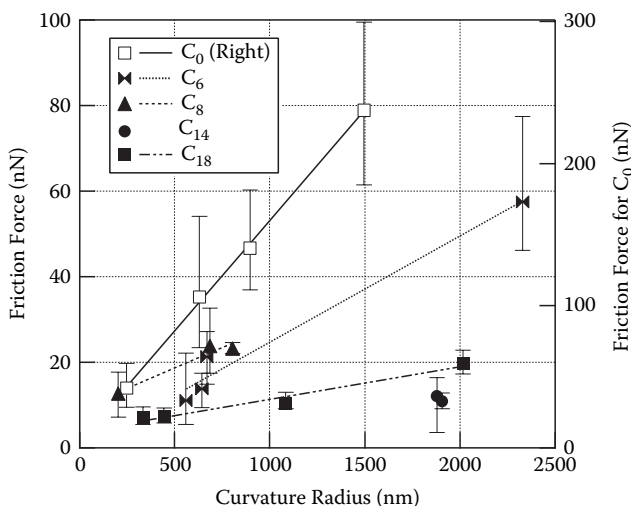


FIGURE 2.27 Relation between the friction force and the curvature radius of the asperity peaks for an uncoated plate C_0 and SAM-coated plates C_6 , C_8 , C_{14} , and C_{18} , where the force measured on the plate C_0 is on a different scale, shown on the right axis. Measured data were fitted with a line.

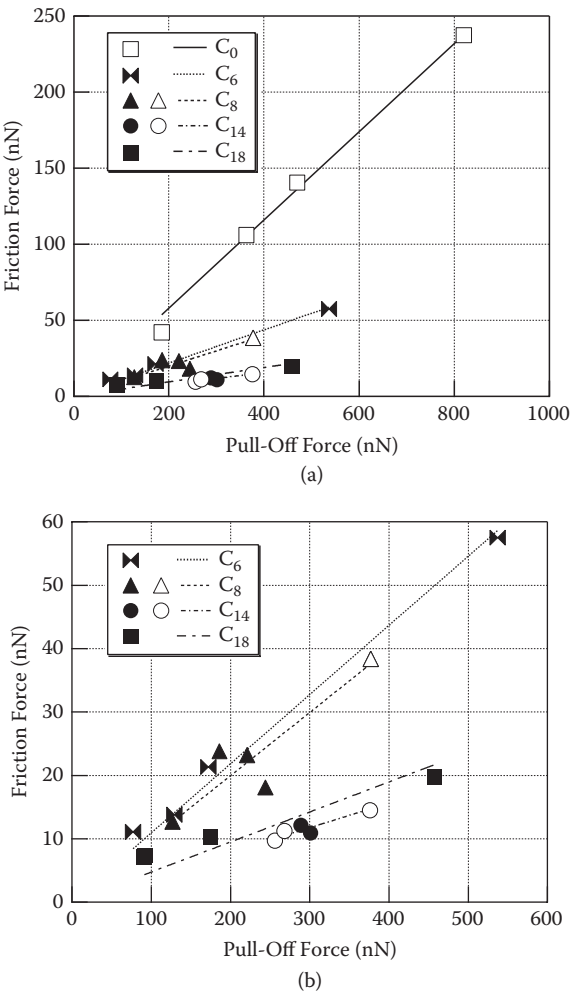


FIGURE 2.28 Relation between friction and pull-off forces for (a) uncoated plate C_0 and SAM-coated plates C_6 to C_{18} and for (b) SAM-coated plates C_6 to C_{18} on an expanded scale for clarity. Measured data were fitted with a line that passes through the origin. The data that are not shown in figs. 2.24 and 2.27 are added and are shown as the open triangles and circles.

the origin. On an expanded scale for clarity, fig. 2.28b shows the data for the SAM-coated plates shown in fig. 2.28a. In addition to the data from figs. 2.24 and 2.27, fig. 2.28 shows data for a patterned area that had an asperity array whose peaks could not be calculated because the height of the asperities was too low. (The curvature-radius-calculating program could not identify asperities whose heights were less than about 3 nm.) The friction force for all the plates is nearly proportional to the pull-off force. The slopes of the fitted lines for the SAM-coated plates are significantly lower than that for the uncoated plate C_0 (fig. 2.28a).

Figure 2.29 shows the friction force measured for the asperity arrays covered with LB films as a function of the curvature radius of the asperity peaks. The error

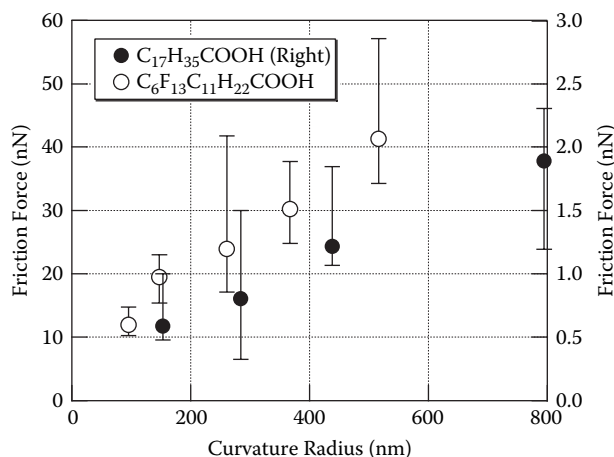


FIGURE 2.29 Relation between the friction force and the curvature radius of the asperity peaks for silicon plates coated with $CH(C_{17}H_{35}COOH)$ -LB and $CFCH(C_6F_{13}C_{11}H_{22}COOH)$ -LB films.

bars in fig. 2.29 show the maximum and minimum values of the pull-off and friction forces. The friction force decreased with smaller curvature radii and was roughly proportional to the curvature radius. The friction force on the CH-LB film was approximately 1/30th of the friction force on the CFCH-LB film for the same curvature radius, whereas the pull-off force on the CH-LB film was about 1/5th of that on the CFCH-LB film (fig. 2.25). The larger reduction rate of the friction force was magnified by the reduction of the pull-off force. Therefore, it is better to compare the gradients of the friction force (i.e., friction coefficients) to discuss the effect on friction.

Figure 2.30 shows the relationship between the friction force and the pull-off force taken from the data in figs. 2.25 and 2.29. The friction force was approximated with a straight line passing through the origin, and the gradient of the fitted line for each friction force (friction coefficient) on each LB film is shown in the parentheses in the plot legend. The friction coefficients for the CH-LB and CFCH-LB films were 0.021 and 0.14, respectively. The friction coefficient on the CH-LB film (0.021) was much lower than the friction coefficient (≈ 0.1) at a higher load measured using a tribology tester [27]. The friction coefficient on the CFCH-LB film (0.14) was comparable to the value (≈ 0.16) found in the same report. If we focus on the differences in the chemical properties between the two kinds of LB films, the surface of the CFCH-LB film exhibits a lower chemical interaction and thus should have a lower friction coefficient. But the CFCH-LB film exhibited a higher friction coefficient than the CH-LB film. If we focus on the mechanical properties, the CFCH-LB film probably had a lower stiffness because of its larger cross-sectional area (0.18 and 0.29 nm²/molecule in the CH-LB and CFCH-LB films, respectively), and because of the lower interaction energy between molecules in the LB film.

Assuming that the CFCH-LB film had lower stiffness than the CH-LB film, the real contact area on the asperities with the CFCH-LB film was larger than that for the CH-LB film. Thus, the CFCH-LB film would exhibit a higher friction force than

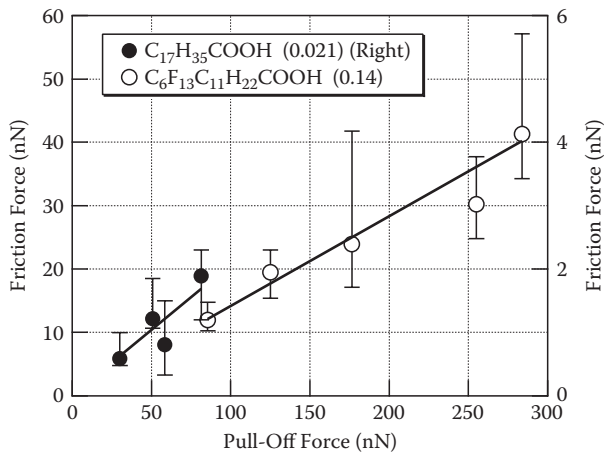


FIGURE 2.30 Friction force vs. pull-off force measured on asperity arrays on silicon plates coated with $CH(C_{17}H_{35}COOH)$ -LB and $CFCH(C_6F_{13}C_{11}H_{22}COOH)$ -LB films. Measured data were fitted with a line that passes through the origin. The gradient of each approximated line is shown in the parentheses in the inset box.

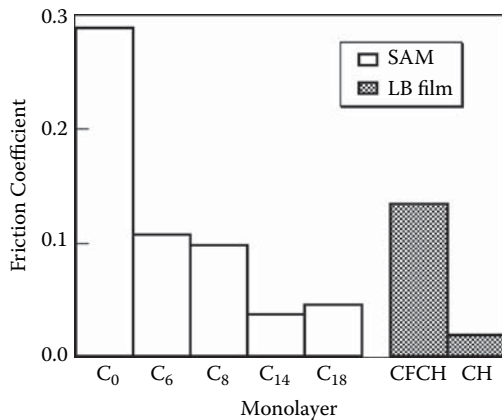


FIGURE 2.31 Friction coefficients for an uncoated plate (C_0) and SAM-coated plates (C_6 – C_{18}) and for plates with LB films (CH-LB and CFCH-LB). Friction coefficients were calculated from the slopes of fitted lines in figs. 2.28 and 2.30.

the CH-LB film if the energy dispersion during sliding per unit area were comparable for each LB film. In our pull-off force measurements, slight differences between the heights of the adjacent asperity peaks could prevent the multipoint contact. If the LB film absorbs the height difference by deformation, capillaries would easily form at two or more asperity peaks, and a higher pull-off force would be obtained.

Figure 2.31 shows the friction coefficient for the uncoated plate (C_0) and the SAM-coated plates (C_6 – C_{18}) and for the plates with LB films (CH-LB and CFCH-LB). These coefficients correspond to the gradients of the fitted lines shown in figs. 2.28 and 2.30. Comparing the SAM-coated plates (C_6 – C_{18}) with the uncoated plate

(C_0), the friction coefficients for the SAM-coated plates were much lower than that for the uncoated plate. The molecular layer probably prevented a direct contact between solids. The friction coefficients for the SAM-coated plates C_{14} and C_{18} were about half that for the other SAM-coated plates. Some reports showed that the friction coefficient was inversely correlated with the alkyl-chain length of the SAM [28, 29]. Similar to the difference in the friction coefficients between CH-LB and CFCH-LB films, the difference in stiffness of the SAMs also might affect the friction force. The stiffness of a SAM is probably correlated with the alkyl-chain length because the van der Waals interaction between alkyl chains increases with longer chain length. The real contact area where the friction force operates is inversely correlated with the stiffness. Based on these assumptions, a longer alkyl chain tends to show a lower friction coefficient.

The length of the alkyl chain (number of carbon atoms) is the same for C_{18} -SAM and CH-LB films; therefore, the van der Waals interaction between the alkyl chains was probably the same for these two kinds of monolayers. The friction coefficient on the CH-LB film, however, was less than half that of the C_{18} -SAM. The difference was likely caused by the difference in the two-dimensional molecular density or in the degree of crystalline perfection. The CH-LB film has a more crystalline structure than the C_{18} -SAM because the structure of SAM on SiO_2 is complex [30]. The difference in the structure would result in differences in the stiffness and contact area. Thus, the CH-LB film showed a lower friction coefficient than C_{18} -SAM.

In this study, we showed that when LB films and SAMs are used to coat a silicon plate, the friction coefficient decreased to 1/3 to 1/12 (fig. 2.31). The friction force was further reduced by optimizing the geometry of the surface roughness. When spherical asperities are added to the surface, the adhesion force can be reduced by using asperities with a smaller curvature radius, thereby reducing the friction force. When this lubrication method involving a combination of an asperity array and a SAM coating is applied to sliding components in micromechanisms such as MEMS, an extremely low friction force can be achieved.

2.6 SUMMARY

Various patterns of two-dimensional asperity arrays were created by using FIB to deposit platinum asperities and to mill patterns on silicon plates and on a platinum layer deposited on the silicon plate. The pull-off and friction forces between the respective patterns and a flat scanning probe of an AFM were measured. Our findings are as follows:

1. The pull-off force decreased with increasing groove depth as well as with decreasing mound ratio, which suggested that the geometry of the asperity peaks dominated the adhesion force.
2. The pull-off force was proportional to the radii of curvature of the asperity peaks and was almost independent of the microsurface roughness of the asperities. The adhesion energy agreed well with the Laplace pressure due to capillary condensed water. These findings indicate that the Laplace pressure was a dominant factor in the adhesion force.

3. The friction force was proportional to the asperity curvature radius R , but not to $R^{4/3}$. This indicates that the friction force was not proportional to the contact area predicted by the JKR theory. This friction behavior was probably caused by the microroughness of the asperities.
4. The friction force was more proportional to the pull-off force than to the curvature radius. The friction coefficient (which was calculated by dividing the friction force by the pull-off force) for the silicon pattern was about twice that for the platinum pattern. These findings indicate that the adhesion force (pull-off force) did not directly affect the friction but, rather, indirectly affected friction, similarly to the effect of an external load.
5. The pull-off force decreased due to the SAM or LB film coatings on the asperity arrays. The magnitude of the pull-off force approximately corresponded to the capillary force calculated using the contact angle of water on the surface.
6. The degree of reduction of the friction force due to the SAM or LB film coatings was considerably larger than that of the pull-off force. While the friction force decreased to 1/10 to 1/30 for the same curvature radius, the pull-off force decreased to 1/2 to 1/5. The larger reduction of the friction force was magnified by the reduction of the pull-off force.
7. The differences in the pull-off and friction forces for the different kinds of LB films and SAM coatings might have been caused by differences in the stiffness of the molecules. The LB film of stearic acid showed the lowest friction coefficient of 0.021, which was probably due to its high stiffness.

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3 Effect of Harsh Environment on Surfactant-Coated MEMS

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and Carlo Carraro*

ABSTRACT

This chapter provides a concise review of the current status of the self-assembled monolayers as molecular lubricants for microelectromechanical systems operating in harsh environments, including elevated temperatures and in fluids. In particular, we focus on the similarities and differences in the structure–property relationships of two SAMs commonly employed to prevent in-use stiction in MEMS, namely octadecyltrichlorosilane (OTS, $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) and perfluorodecyl-trichlorosilane (FDTS, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$). We discuss the effect of harsh environments on these monolayers and how their degradation impacts their properties and the range of conditions for which these monolayers can be employed effectively for MEMS.

3.1 INTRODUCTION

Self-assembled monolayers (SAMs) are commonly used as molecular lubricants in microelectromechanical systems (MEMS) [1, 2]. They have been shown to reduce dramatically the adhesion (stiction) of free-standing or moving microstructures. The most common SAMs deposited on silicon are made from chlorosilane end-groups and alkyl or perfluorinated chains of variable length, with the chemical form RCl_3 . The antistiction properties of a variety of monolayers have been reviewed extensively (see, for example, [3–5]). Relatively few investigations have dealt with the performance of molecular lubricants in harsh environments (such as elevated temperature, liquid and corrosive media, and high electric bias). It is of paramount practical importance to determine to what extent these films can be employed for antistiction in these conditions.

Packaging, biological, and sensing applications commonly involve conditions other than dry air, and it is unlikely that SAMs will have the same antiadhesive properties regardless of the operating conditions. Two important scenarios can occur: one in which the SAMs are briefly exposed to a harsh environment (such as high temperature during packaging), but after the brief exposure the device will be operated at conditions of low to moderate humidity and room temperature. A more demanding situation is one in which the device is constantly operating in a harsh environment and is required to maintain lasting antistiction properties.

The effect of a harsh environment on the structural and functional integrity of siloxane films is poorly understood. Harsh environments can damage the SAM or induce its desorption. A reduction of surface coverage can expose high-surface-energy groups on the silicon oxide surface and accelerate corrosion processes [6, 7]. In addition, for operation in solution, unwanted adsorption can cause failure, and surface treatments for bioMEMS should consider potential fouling issues after passivation. This chapter will cover the effects of elevated temperature and fluid environments on the effectiveness of various surface monolayers to prevent in-use stiction. We will not cover fouling and will focus mainly on two commonly employed anti-stiction monolayers, namely, octadecyltrichlorosilane (OTS, $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) and perfluorodecyltrichlorosilane (FDTS, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$).

3.2 EFFECT OF ELEVATED TEMPERATURE

The effect of annealing on the structural integrity of siloxane monolayers has been investigated at ambient and in ultrahigh vacuum (UHV) environments. Common techniques employed for the characterization of annealing effects on SAMs are contact angle measurements, x-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS). This section reports on how thermal cycling affects surface coverage of monolayers deposited on smooth, single-crystal silicon wafers. It is important to note that MEMS involve rough surfaces, and, as will be discussed in the next section, the antistiction behavior of SAMs at elevated temperature is strongly affected by the presence of multi-asperity contacts.

Table 3.1 shows the reported temperature values for the onset of a significant, and irreversible, change in the structural integrity of OTS and FDTS films caused by annealing in different environments and for periods of time varying between 2 to 15 min. The large range in temperature values published in the literature is likely to be caused by the specific sensitivities of the various techniques employed to characterize the impact of thermal annealing on the surface films. As an illustration, for both OTS and FDTS, a 15%–20% loss of coverage is readily observed from XPS measurements but does not cause a significant change in static water contact angle values [8, 9].

The reported desorption mechanisms for OTS and FDTS are quite different. Thermal desorption of OTS has been shown to follow a “shaving” mechanism, i.e., the loss in the carbon content occurs via cleavage of the C-C backbones and successive

TABLE 3.1
Temperature for the Onset of Structural Change
in the Siloxane Monolayer on Silicon

	OTS	FDTS
Air	125°C–240°C [9, 27]	100°C–300°C [12, 13]
N ₂	400°C [1]	400°C [28]
UHV	475°C [10, 11]	100°C–300°C [12]

Note: The reported relative humidity for the measurements in air was 40%–50% [1, 9, 12].

shortening of the chain. The mechanism appears to govern the annealing both in air and in UHV [9–11]. Perfluorinated monolayers, such as FDTS, have been shown to desorb via the loss of a whole chain for temperatures as low as 100°C in vacuum. The desorption mechanism is believed to follow first-order kinetics, as it does not depend on the monolayer coverage. It is likely that the loss of coverage at low temperatures is caused by the desorption of physisorbed chains or chains that are poorly bonded to the silicon surface. Chain desorption is accompanied by a tilting of the monolayer, which allows the static water contact angle to maintain a value above 90° after annealing at 300°C and a loss of 20% of the fluorine content [8, 12]. The level of cross-linking for the monolayer can be varied by replacing one or two reactive Si-Cl groups by unreactive Si-CH₃ groups. Reducing the extent of cross-linking for perfluorinated monolayers has been shown to require a longer deposition time, often creating monolayers that are not fully packed, and to reduce the thermal stability [8, 13]. This effect is accentuated for annealing in air (compared with vacuum) for perfluorinated monolayers.

The stability of the monolayer at an elevated temperature depends on the duration of the annealing step. Using contact angle measurements, Zhuang et al. [13] have shown that FDTS can maintain a static water contact angle above 90° ($\theta > 90^\circ$ is the minimum contact angle value necessary to avoid capillary forces) for up to 90 min at 400°C. On the other hand, the monolayer made out of a very similar tail, but not cross-linked, tridecafluoro-1,1,2,2,-tetrahydrooctyl (CF₃(CF₂)₅(CH₂)₂(CH₃)₂SiCl), can maintain a water contact angle above 90° for only 10 min.

3.3 IMPLICATION OF MONOLAYER DESORPTION ON STICTION

Intuitively, the capability of a monolayer to retain its structural integrity when exposed to an elevated temperature is a requirement for lasting antistiction properties. We have shown, however, that the relationship between the restructuring of a monolayer at elevated temperatures and its antistiction properties can be more complex. This is especially the case for highly hydrophobic surfaces, such as the ones produced with OTS or FDTS monolayers. As long as MEMS surfaces maintain their hydrophobicity, near-contact interactions are not dominated by capillary forces. Instead, they are governed by weaker forces, such as van der Waals interactions between surfaces that are quite rough. The complex surface topography and texture of the monolayer in the presence of defects create challenges to the modeling of surface interactions in real devices, especially when operating in hostile environments [14].

The behavior of FDTS monolayers under thermal stress offers an example of this complexity and of the counterintuitive results it can produce. We have shown that the monolayer can lose 25% of its fluorine content *and* display lower adhesion compared with when the surface is covered by a full monolayer, as can be seen from fig. 3.1. The lowering of the apparent work of adhesion (W_{adh}) at high temperatures is surprising, considering the fact that both water and hexadecane static contact angles decrease after the same annealing steps. Detailed XPS studies have shown that the low-temperature desorption of entire FDTS molecules is accompanied by a tilting of the remaining chains. It is also suspected that, due to the larger size of the fluorine molecule (compared with hydrogen), proper cross-linking of FDTS is difficult and that highly reactive Si-OH groups are left on the surface. Another indication that

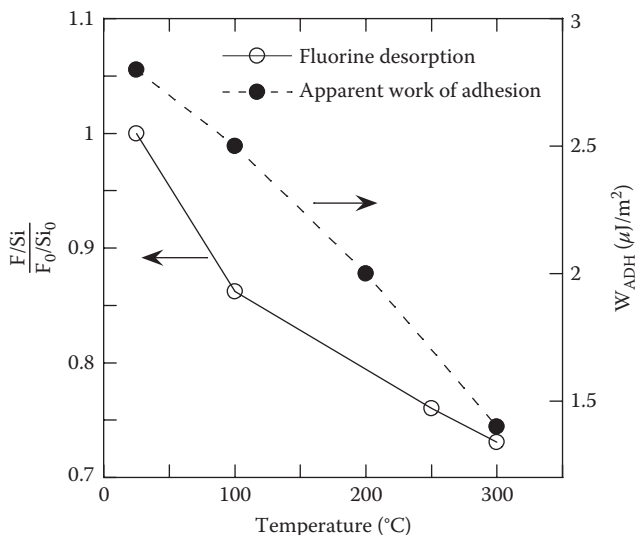


FIGURE 3.1 Temperature dependence of the fluorine loss and adhesion for a FDTD monolayer. The fluorine content is measured from the $F(1s)/Si(2p)$ ratio obtained before (indicated by subscript 0) and after annealing in the XPS chamber. The adhesion is obtained from cantilever beam arrays actuated at different temperatures. The adhesion is measured at the reported annealing temperature (and not after cooling to room temperature).

desorption occurs via the loss of whole, poorly cross-linked, chains comes from the similar losses in fluorine content for annealing in air and in UHV. This is not the case for alkylsiloxane monolayers that desorb via cleavage of C-C bonds, a reaction catalyzed by oxygen that displays accelerated desorption for annealing in air compared with UHV. Overall, it is suspected that the removal of some fluorine, chain tilting, and high temperature allow for the remaining Si-OH groups to react and cause the reduced adhesion upon annealing. The presence of buried Si-OH groups is unlikely to affect contact angle on a flat surface, but rough asperities involved in MEMS contact can pierce through the monolayer. These results illustrate both the importance of directly evaluating stiction at the device level and of understanding the desorption mechanisms of the film to be employed in harsh environments.

The effect of annealing on stiction of MEMS cantilevers covered with OTS has also been investigated by Ali et al. [15]. As shown in fig. 3.2, they first observed an increase in adhesion during annealing up to 200°C. Between 200°C and 300°C, they report a decrease in adhesion. Note that the reported values are for the sticking probabilities of cantilever beams with lengths between 480 and 540 μm ; the detachment length or the apparent work of adhesion was not reported in their work. Also, it is important to note that the carbon desorption plotted in fig. 3.2 corresponds to the XPS data of Kim et al. [9]; therefore, correlation between the two curves is qualitative at best. Reported temperature values for “significant” structural damage caused by annealing in air of an OTS monolayer are between 125°C and 200°C. Similar to our work with FDTD, stiction appears to decrease in this temperature range in spite of the monolayer degradation. This reduction of adhesion can be caused by a loss of

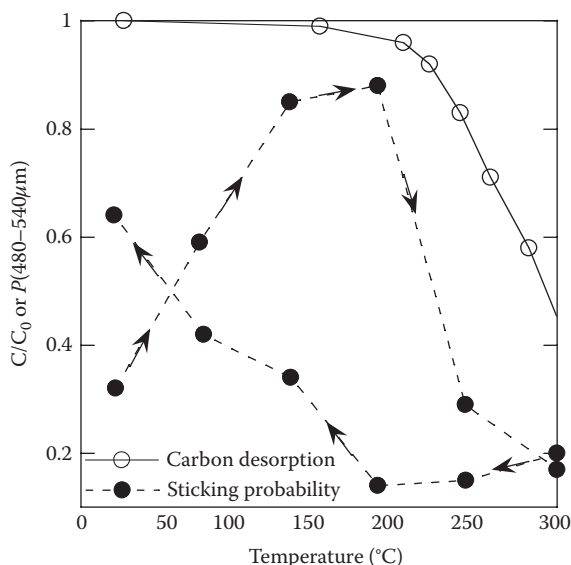


FIGURE 3.2 Desorption of OTS monolayers on Si(100), presented as C/C_0 , where C_0 and C are carbon concentrations before and after annealing, respectively (data taken from Kim et al. [9]), and sticking probability for 480–540- μm cantilever beams (data taken from Ali et al. [15]). The loss in coverage is plotted as a function of annealing temperature. An increase in sticking probability corresponds to an increase of adhesion between the cantilever and the landing pad. The arrows indicate the hysteresis between heating and cooling.

water from the monolayer or via a process similar to the one described for FDTS. Interestingly, Ali et al. report XPS data showing 75% carbon loss after annealing to 300°C, while their detachment length appears to decrease from 710 to 590 μm . This change in detachment length corresponds to a significant increase in stiction, but the monolayer maintains a good degree of antistiction properties after sustaining serious damage. Further annealing cycles did not show more carbon loss or a further increase in stiction (as can be deduced from the sticking probability data).

Using atomic force microscopy (AFM), Kasai et al. [16] have also investigated how adhesion and friction between surfaces covered with FDTS and OTS respond to temperature variations. The temperature range investigated was 20°C–115°C. For both the OTS and FDTS monolayers, increasing the temperature was shown to decrease both the adhesion and friction between the tip and the surface. The decrease in both friction and adhesion was attributed to a loss in the water content within the monolayer. The adhesion and friction forces dropped by a factor of two over the temperature range investigated.

3.4 ADHESION IN FLUIDIC ENVIRONMENTS

Investigation of stiction in fluid environments is gaining importance due to the emergence of microfluidic devices and their technological applications for biological assays. There have been only a very few reports, however, on the investigation of

stiction in fluid environments, especially for fluids at high or low pH. An additional issue is electrostatic actuation in a salt solution, as the establishment of the electrical double layer [17] prevents typical DC actuation. The problem can be circumvented by using high-frequency AC actuation [18]. Moreover, adhesion forces in a fluid environment are not the same as in air. Capillary forces are not present in a liquid environment, but double-layer repulsion, acid–base interaction, and hydrophobic forces can all play a major role [19].

Parker et al. [20] systematically investigated common antistiction SAMs (such as OTS and FDTS) for potential applications in various fluidic environments (such as water, isopropyl alcohol, iso-octane, and hexadecane). For operation in water, it was shown that bare silicon oxide was by far more effective in reducing stiction compared with any hydrophobic monolayers (three different monolayers and two different deposition conditions were investigated). Interestingly, adhesion with a bare silicon oxide surface was much lower than adhesion in air with surfaces covered with FDTS. The low adhesion between hydrophilic SiO_2 surfaces in solution can be explained by a reduced van der Waals interaction and double-layer repulsion (SiO_2 surfaces tend to have a negative surface potential of around -60 mV [21]). On the other hand, interactions between hydrophobic surfaces in solution can be very strong, especially in aerated solutions where air bubbles and cavitation can cause very strong adhesion [22]. A report by Parker et al. [20] on the use of hydrophobic SAMs (OTS and FDTS) as antistiction monolayers for operation in solution indicates that they are indeed detrimental, most likely because of hydrophobic interactions. Stiction did not appear to be an issue for any of the surface treatments (even bare SiO_2) for actuation in isopropyl alcohol. For operation in nonpolar solvents (hexadecane and iso-octane), stiction was greatly reduced with the use of a hydrophobic monolayer compared with a hydrophilic oxide surface.

An AFM image of an FDTS monolayer after it has been in water for a prolonged period of time shows a weblike structure, as shown in fig. 3.3, highlighting the pos-

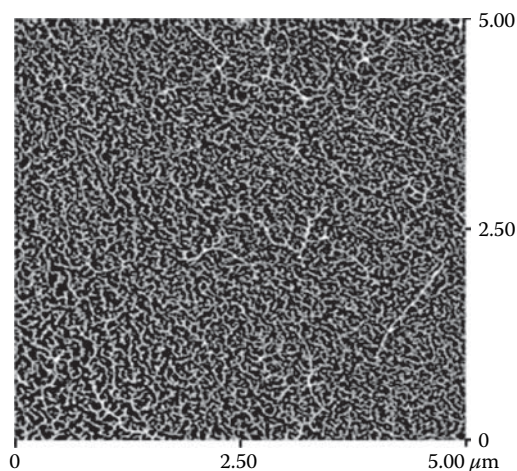


FIGURE 3.3 Tapping-mode AFM image of an FDTS film after immersion in water for 6 weeks. The z -scale is 10 nm. Figure taken from [12].

sibility of poor cross-linking (as also mentioned in section 3.2 about the effects of elevated temperature) and a result similar to hydrophobic surfactants adsorbed on mica after being in an aqueous solution [23, 24].

Geerken et al. [25] investigated the chemical and thermal stability of OTS and a perfluorinated equivalent (perfluorinated octyltrichlorosilane) in liquids as a function of time (up to 200 h), temperature (50°C–80°C), and pH (2–13). They evaluated the stability of the monolayers (not stiction) by measuring water and hexadecane contact angles after exposure to harsh conditions. They reported that perfluorinated monolayers were more stable than OTS in all the conditions they investigated.

3.5 CONCLUSIONS

Hydrophobic siloxane monolayers are effective at preventing capillary adhesion in MEMS operating in ambient air. However, the use of SAMs to prevent stiction in harsh environments (elevated temperature or fluids) has been investigated to a lesser extent. Packaging or specific application conditions can expose MEMS to elevated temperatures. Similarly, the advent of bioMEMS and microfluidic devices opens the door to a wide range of applications in liquid environments.

A brief review of the literature shows that, for applications at elevated temperatures, it is important to avoid testing solely the change in monolayer integrity (as measured with contact angle). It is shown that for both FDTs and OTS, a reduction of coverage does not necessarily directly lead to a significant increase in stiction. In particular, for an FDT monolayer, we show that a small loss in fluorine content leads to improved antistiction behavior, justifying annealing the devices during, or right after, the monolayer deposition [26].

For MEMS operating in a fluid environment, a survey of the literature shows that the choice of surface treatment depends on the operating fluid. For operation in aqueous solutions, a hydrophilic surface is preferable to avoid strong hydrophobic interactions. A hydrophobic monolayer decreases adhesion for actuation in nonpolar fluids such as iso-octane and hexadecane.

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4 Surfactants in Magnetic Recording Tribology

T. E. Karis and D. Pocker

ABSTRACT

Surfactants play key roles in the mechanical systems of magnetic recording disk drives. The most notable arena for surfactants is at the slider-disk interface, where the lubricant ensures reliable operation of a nanometer scale recording gap between the slider and the disk. The low surface energy and surface activity of functional end groups on the lubricant hold a monolayer in place for the lifetime of the disk drive. This chapter focuses on the novel development of a low surface energy coating of poly (1H,1H-pentadecafluorooctyl methacrylate) fluorohydrocarbon surfactant on the magnetic recording slider to improve tribological performance. Application of the film and methods for film characterization are detailed. Subambient pressure tribological test results show the ability of this film to reduce lubricant transfer and disk scratching as good as or better than several other low surface energy coatings.

4.1 INTRODUCTION

Even though magnetic recording is ubiquitous and pervasive in all aspects of modern society, one scarcely recognizes the miraculous harmony of physics and engineering embodied within these data-storage devices. A disk drive comprises magnetic recording disks and sliders in an enclosure. Each slider contains a magnetic recording head to read and write the data. The disks are rotated by a centrally located motor, and the heads are positioned over the magnetic data tracks by a servomechanism. The disks are typically rotating between 3,600 and 15,000 rpm, while the slider maintains the head within a few nanometers of the disk surface to detect the magnetic domain orientation. For reliable operation of the slider-disk interface, the disk is coated with approximately 1 nm of a perfluoropolyether lubricant with polar hydroxyl end groups [1]. The disk lubricant is an amphiphilic fluorosurfactant [2, 3].

The clearance between the slider and disk is extremely small, and an accumulation of lubricant on the slider can lead to wicking underneath the nanometer-thick spacing gap, causing data errors, scratching of the disk overcoat, and potential crashing of the slider. Accumulation of lubricant on the slider [4–6] must be avoided. Low-surface-energy coatings of fluorohydrocarbon surfactants [7] help to keep the slider clean. The focus of this chapter is the application and properties of slider surface coatings.

Various surface modifications can be done to the surface of the slider without significantly increasing the head-disk spacing gap. A low-surface-energy sputtered Teflon or chemical vapor-deposited fluorocarbon film can be applied at the slider-row level during

slider fabrication. Another means to lower the surface energy of the slider is by solution-casting a thin film of fluoropolymer on the completed head gimbal assembly (HGA) by dip coating. For use in manufacturing, it is essential to have methods for precise and reproducible control of the film thickness and properties. This chapter describes x-ray photoelectron spectroscopy (XPS) and ellipsometry procedures developed to measure fluoropolymer film thickness. Ellipsometry was done to measure the film thickness on test samples consisting of slider rows, carbon- and non-carbon-overcoated silicon strips, and silicon wafers. XPS was needed to measure the fluoropolymer film thickness on the air bearing surface of sliders because of their small size. Thickness measured by XPS on the air bearing surface is compared with that measured by ellipsometry on strip test samples dip coated at the same time as the sliders. XPS is also employed to study the chemical composition of the fluorohydrocarbon surfactant thin films [8].

Since the slider coating film may be in contact with disk lubricant, it is possible that the lubricant may dissolve in and soften the film. This could potentially lead to some flow of the slider coating at the elevated temperatures inside the disk drive. To assess the possibility of film shear flow from the slider, or development of tackiness, the rheological properties of the fluorosurfactant and various concentrations of lubricant were measured. The fluorosurfactant coating is also compared with several other types of alternative coatings in an accelerated tribological test for the ability of the coating to inhibit lubricant transfer and abrasion of the disk by the slider.

4.2 EXPERIMENTAL

4.2.1 MATERIALS

The fluorohydrocarbon surfactant that is the focus of this chapter consists primarily of the poly (1H,1H-pentadecafluorooctyl) methacrylate chemical structure shown in fig. 4.1a and is referred to as PFOM. A small amount of fluorocarbon side group isomer is also detected by nuclear magnetic resonance (NMR). The monomer molecular weight is 468 g/mole. The degree of polymerization $n \approx 640$ was determined from the weight average molecular weight of 300,000 g/mol by light scattering. The glass transition temperature is $\approx 50^\circ\text{C}$, and the index of refraction $n_f = 1.36$. The PFOM was obtained from commercial sources.

Several different types of substrates were employed to develop the film thickness measurement procedures. The first type of substrate was slider rows. Slider rows are strips (2.5×47 mm, 0.44 mm thick) of N58 ($\text{TiC}/\text{Al}_2\text{O}_3$ ceramic) overcoated with a nominally 12.5-nm-thick layer of sputtered carbon. Silicon wafers 0.4 mm thick (International Wafer Service, Santa Clara, CA, www.siwafar.com) were cut into strips having the same lengths and widths as the slider rows. Some of the silicon strips were overcoated with a nominally 12.5-nm-thick layer of sputtered carbon. Other silicon wafers 25.4 mm in diameter and 0.2 to 0.3 mm thick were used without cutting (Virginia Semiconductor, Inc., Fredericksburg, VA, www.virginiasemi.com). Film thickness was also measured on the air bearing surface of production-level sliders mounted on head gimbal assemblies (HGA).

To simulate exposure of the surfactant films to disk lubricant, PFOM films containing various amounts of perfluoropolyether Zdol 2000 were prepared for rheological

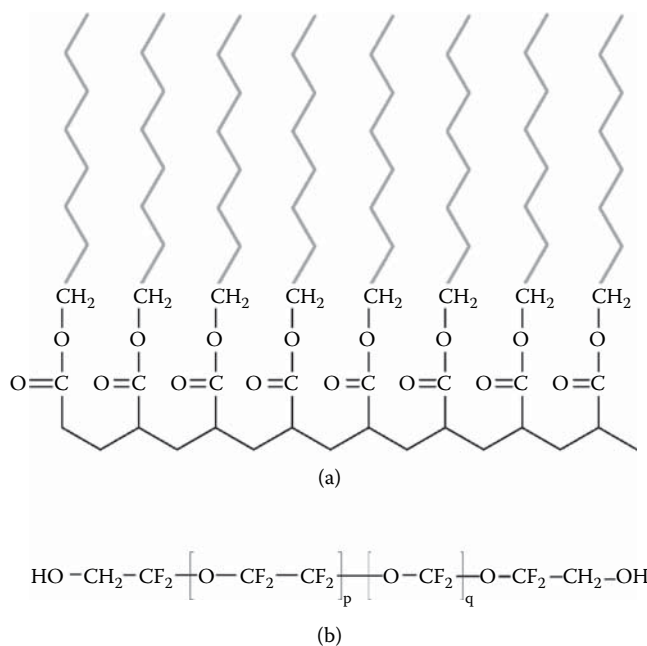


FIGURE 4.1 (See color insert following page 80.) (a) poly (1H,1H-pentadecafluorooctyl) methacrylate (PFOM), molecular weight 300000 (g/mol); (b) Hydroxyl terminated perfluoroether Fomblin Zdol, molecular weight 2000 or 4000 (g/mol), $p/q = 2/3$.

measurements. The chemical structure of Zdol is shown in fig. 4.1b. Ztetraol has the same perfluoropolyether chain as Zdol, but the hydroxyl end groups have been reacted with glycidol, which doubles the number of hydroxyl groups at the chain ends. (Zdol and Ztetraol are products of Solvay Solexis, Inc., West Deptford, NJ.)

Sliders were coated with three other types of low-surface-energy coatings for tribological measurements in comparison with PFOM. Fluorinated carbon overcoat (FCOC) was prepared by plasma deposition of fluorinated monomers onto the slider [9]. ZNa, the sodium salt of Fomblin Zdiac [10], was deposited from dilute solution in 3M™ Novec™ Engineered Fluid HFE-7100 (nonafluorobutyl methyl ether) solvent. Zdiac has the same perfluoropolyether chain as Zdol, but with acid rather than hydroxyl end groups. Another coating tested was 3M Novec Electronic Coating EGC-1700, which was dip coated from solution in 3M Fluorinert™ Electronic Liquid FC-72 (perfluorohexane) solvent (www.3m.com/product).

4.2.2 METHODS

A motorized stage was employed to withdraw the test samples and HGAs from a PFOM solution tank at specified rates.

Ellipsometric measurements were done using a Gaertner model L-115B ellipsometer (HeNe laser, wavelength 632.8 nm, Gaertner Scientific, Chicago, IL). Six points were measured on the dip-coated slider rows and silicon strips. Three points were measured on the dip-coated silicon wafers. The PFOM thickness was calculated from

the ellipsometric angles Δ and Ψ using the standard software package provided by Gaertner.

X-ray photoelectron spectroscopy (XPS) was done on some of the silicon test samples and on all the sliders. The narrow dimensions of the air bearing surface of the slider are difficult to measure using ellipsometry, while the spot size of the XPS is small enough to measure in these regions. The XPS measurements were done on Surface Science Labs SSX-100 spectrometers (Al K_{α} source) at resolution 3 with a 300- μm spot size. These conditions yield an Ag $3d_{5/2}$ line width of about 1.13 eV. The anode power was 50 W, and the irradiated area was about $300 \times 500 \mu\text{m}$ because of the 35° angle of incidence. The XPS measurements were performed within 25 min to minimize film thickness erosion due to gradual ablation of the PFOM by the incident x-ray beam.

Tribological measurements, consisting of subambient pressure frictional hysteresis loop measurements, were carried out inside a sealed disk tester with a controlled leak (CETR Olympus, Center for Tribology, Campbell, CA). The disk rotation rate was 7200 rpm, and the slider suspension was mounted on a strain-gauge block to measure the friction force. Scratch measurements on the surface of the tested track were done with an optical surface analyzer.

Rheological measurements were performed in a stress rheometer fixture with a 2-cm cone and plate having a 1° cone angle and gap of 27 μm . Dynamic shear moduli were measured at 0.5% strain between 0.1 and 100 rad/s. Creep compliance was measured with a constant applied stress in the range of 0.1 to 5 kPa. Both measurements were performed over a series of temperatures to obtain data for time-temperature superposition.

Glass transition temperature measurements on the solutions of Zdol in PFOM were performed in a temperature-modulated differential scanning calorimeter.

The procedure for estimating the PFOM thickness from an XPS spectrum [11] requires calculating d/λ . This is the ratio of the PFOM film thickness d to the electron mean free path λ in the PFOM film. It is calculated from the XPS as described below. The electron emission intensity is corrected for the Scofield capture cross section of each element. The escape depths are corrected for kinetic energy E according to $E^{0.7}$ by the spectrometer analysis routine. Note that this kinetic energy correction is rigorously correct only for bulk samples and may cause some error when applied to thin films.

The C1s and O1s regions of the XPS spectrum on the air bearing surface of a slider coated with 2.5 nm of PFOM are shown in fig. 4.2. The binding energy of the peaks used in the calculation are indicated by the arrows in fig. 4.2. The peaks in the C1s spectrum, fig. 4.2a, are assigned to the chemical environments shown in table 4.1. The measured C1s, O1s, and F1s regions of the spectrum are peak fitted at each of the binding energies listed in table 4.1, and the total integrated area under the peaks is normalized to 100%. In the case of PFOM on non-carbon-overcoated silicon, the Si2p peak area is also included. Part of the C1s spectrum is assigned to the PFOM, and the remaining portion of the spectrum is assigned to carbon in the substrate. The contribution of oxygen from the substrate is then determined from the known stoichiometry of the PFOM. The difference between the raw O1s percentage and the percentage assigned to the PFOM is due to the substrate. All the F1s signal is from the PFOM. Details of the calculation are given below.

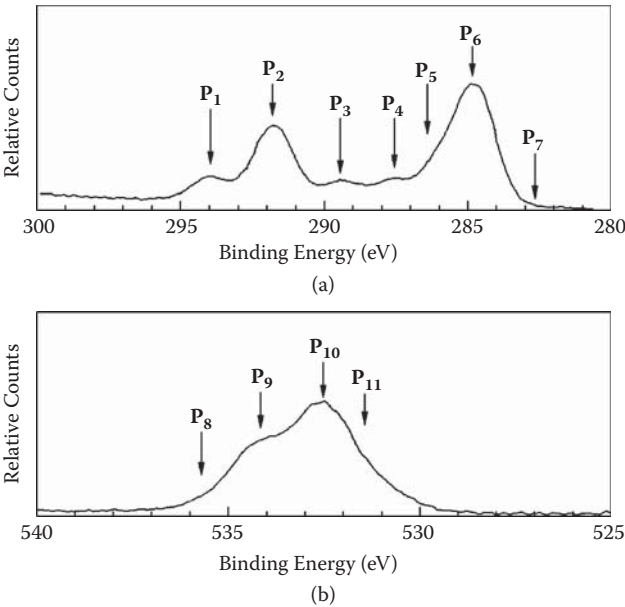


FIGURE 4.2 XPS spectra of a 2.4 nm thick film of PFOM on the air bearing surface of a slider. C1s spectrum (a), and O1s spectrum (b). The arrows indicate the binding energies of atoms with different chemical environments.

TABLE 4.1
Peak Assignments Used in Analysis of the XPS Spectra to Determine PFOM Thickness on the Air Bearing Surface of the Slider

Element	Label in fig. 4.1 ^a	Binding energy (eV)	Chemical environment ^b
C1s	P ₁	294	–CF ₃
	P ₂	291.8	–CF ₂ –
	P ₃	289.5	–CF + –COOCH ₂ –
	P ₄	287.7	–CF ₂ CH ₂ O–
	P ₅	286.3	CH ₃ CCOO–
	P ₆	284.8	–CH ₃ + –CH ₂ –
	P ₇ ^c	282.3 ^c	+carbon overcoat
O1s	P ₈	535.9	—
	P ₉	534.3	—
	P ₁₀	532.7	—
	P ₁₁	531.3	—
F1s	—	691.1 ^c	—
	—	689	—
	—	686.5 ^c	—

^a The locations of peaks P_i are indicated by the arrows in the spectra in fig. 4.2.
^b The underscore shows which carbon atom/chemical environment is emitting at the specified binding energy.
^c Small peaks are due to non-Gaussian skirts arising from imperfections in the spectrometer transmission characteristics.

Among the carbons in the PFOM, fig. 4.1, there are seven carbons attached to fluorine ($-\text{CF}_3$ and $-\text{CF}_2-$), there is one ester carbon ($-\text{COOCH}_2-$), and there is one carbon in the ($-\text{CF}_2\text{CH}_2\text{O}-$) environment, i.e., the α carbon of the fluorocarbon side-chain. These nine carbons give rise to the four peaks with the higher binding energies in fig. 4.2a and table 4.1. The sum of these easily recognized parts of the PFOM in the C1s spectrum is given by

$$\sum_{i=1}^4 P_i$$

In the calculations, P_i refers to the integrated area under peak i at the binding energy listed in table 4.1. The remaining C1s peaks at lower binding energies include both the PFOM and the carbon overcoat. The integrated area of the peaks at lower binding energies (table 4.1, P_{5-7}) is

$$\sum_{i=5}^7 P_i$$

There are three PFOM carbons in this region of the C1s spectrum. The contribution of the three PFOM carbons is subtracted from the integrated area of the peaks at lower binding energies to get the contribution to the atomic% substrate from the carbon overcoat in the C1s spectrum,

$$\sum_{i=5}^7 P_i - (3/9) \times \sum_{j=1}^4 P_j$$

The next step is to determine the contribution to the atomic% substrate from the carbon overcoat in the O1s region of the spectrum. The oxygen-to-carbon ratio of the PFOM is (2/12), and the oxygen-to-fluorine ratio is (2/15). Thus, there are two ways to estimate the contribution of the PFOM to the O1s spectrum: (1) multiply the F1s percentage by (2/15), and (2) multiply the atomic% of carbon from the PFOM in the C1s spectrum by (2/12), i.e.,

$$(2/12) \times (1 + (3/9)) \times \sum_{i=1}^4 P_i = (2/9) \times \sum_{i=1}^4 P_i$$

The average of the two estimates from methods (1) and (2) above is then subtracted from the raw O1s percentage

$$\sum_{i=8}^{11} P_i$$

to estimate the contribution to the atomic% substrate from the O1s region of the spectrum.

The atomic% substrate in the spectrum is then the sum of the substrate portions of the C1s and O1s integrated areas (plus the integrated area of the Si2p spectrum in the case of a non-carbon-overcoated silicon substrate). The ratio of the PFOM film

thickness to the electron mean free path d/λ measured by the XPS for determining PFOM thickness is given by

$$\frac{d}{\lambda} = \sin(\theta) \times \ln\left(\frac{100\%}{\text{atomic\% substrate}}\right) \quad (4.1)$$

where θ is the electron take-off angle from the sample to the detector (35°). In this work, the electron mean free path λ in eq. (4.1) was empirically determined as follows. Ellipsometry was used to measure PFOM thickness d , XPS was used to measure d/λ on the same samples, and an experimental λ was estimated from these data. The substrate signal was detectable for all of the PFOM films measured by XPS in this study. (The PFOM film thickness can be measured as long as the signal from the substrate is detectable in the spectra.)

For the rheological measurements, the PFOM was dissolved at 2 wt% in FC-72 cosolvent with Zdol, and the solvent was evaporated, leaving behind the mixture. The mixtures were melted into the fixtures of the rheometer to measure creep compliance and dynamic moduli.

For the tribological measurements, the radial position of the slider during the tests was halfway between the inner and outer diameters of the disk, and the pivot-to-center distance was adjusted so that the slider skew angle was close to 0° . The disk rotation was started with the slider suspension on the load/unload ramp just off the edge of the disk. The slider was accessed to the test radius. The pressure control and measurement of the frictional displacement were performed with The National Instruments LabView software on a PC with interface cards. Average displacement and peak amplitude were recorded after each pressure decrement/increment (4000 samples at 20 kHz for 200 ms). The pressure inside the tester was varied linearly from ambient (100 kPa) to 15 kPa and back up to ambient over about 3 min in approximately 1-kPa increments. At the end of the test, the slider was translated back to the load/unload ramp before stopping the disk rotation.

4.3 RESULTS

4.3.1 MULTIPLE DIP TEST

A test series was carried out to determine the effects of multiple dip-coating cycles on the PFOM thickness on slider rows. It was necessary to measure the substrate optical constants n_s and k_s for each row before dip coating because of the significant variation from one row to another. These values for the uncoated slider rows are listed in table 4.2. The slider rows were dip coated and the PFOM thickness was measured. This procedure was repeated until some of the rows had been dipped up to four times (4 $\times$). The PFOM thickness measured after each dip-coating cycle is given in table 4.3.

4.3.2 DIP-BAKE-DIP TEST

A test was done to study the effects of multiple dip-coating cycles with baking in between on the PFOM thickness. Slider rows were dipped; the PFOM film thickness

TABLE 4.2
Substrate Optical Constants on Slider Rows, N58 Overcoated with 12.5 nm of Carbon

Average <i>n</i>	Standard deviation	Average <i>k</i>	Standard deviation
2.039	0.011	0.385	0.009

Note: Sample size = 20.

TABLE 4.3
PFOM Thickness as Measured by Ellipsometry on Carbon-Overcoated Slider Rows Showing the Effect of Multiple Dip Coatings

	No. of dips			
	1×	2×	3×	4×
Sample size	12	8	4	4
Average thickness (nm)	2.2	4.3	4.7	4.6
Standard deviation (nm)	0.6	0.4	0.5	0.4

Note: PFOM concentration 700 ppm, withdrawal rate 1.6 mm/s, 12.5-nm carbon overcoat on N58 ceramic.

was measured by ellipsometry; the rows were baked at 70°C for 15 h; and the PFOM thickness was measured by ellipsometry after the bake. The dip and bake process was repeated until the rows had been dipped four times. The results of this test are shown in table 4.4.

4.3.3 RELATIVE HUMIDITY EFFECTS

The effect of relative humidity (RH) on the apparent PFOM film thickness measured by ellipsometry was studied. The PFOM thickness on slider rows was measured after equilibration at 51% RH and 26% RH. These rows were then placed in a vacuum desiccator to be thoroughly dried, and the apparent thickness was measured. The thickness was remeasured following equilibration at 50% RH. The results of this test are shown in table 4.5.

4.3.4 CARBON-OVERCOATED SILICON STRIPS

Since the air bearing surface of the slider is carbon-overcoated, the same carbon overcoat was placed on some of the silicon strips to evaluate the PFOM film thickness and ellipsometric measurement procedure on carbon- and non-carbon-overcoated substrates. A nominally 12.5-nm-thick layer of sputtered carbon was deposited on silicon strips, and the strips were dip coated with PFOM. The ellipsometric angles Δ and Ψ were measured. The two-layer model (two films on an absorbing substrate) was used with the optical constants for the materials listed in table 4.6 in calculating the PFOM thickness from Δ and Ψ on carbon-overcoated silicon. The apparent

TABLE 4.4
PFOM Thickness as Measured by Ellipsometry on Carbon-Overcoated Slider Rows, Showing the Effect of Multiple Dip Coatings with Baking in Between

	Process step						
	Dip	Bake	Dip	Bake	Dip	Bake	Dip
Sample size	8	8	8	4	4	4	4
Average thickness (nm)	2.8	2.8	3.9	2.9	4.6	3.9	5.4
Standard deviation (nm)	0.4	0.5	0.6	0.2	0.8	0.6	0.9

Note: Bake for 15 h at 70°C, PFOM concentration 700 ppm, withdrawal rate 1.6 mm/s, and 12.5-nm carbon overcoat on N58 ceramic.

TABLE 4.5
PFOM Thickness as Measured by Ellipsometry on Carbon-Overcoated Slider Rows, Showing the Effect of Relative Humidity and Drying

Treatment	Thickness (nm)		
	Average	Standard deviation	Sample size
51% RH	2.9	0.2	3
26% RH	3.4	0.3	3
4 h in vacuum desiccator	3.6	0.4	3
18 h in vacuum desiccator	4.2	0.1	3
34 h in vacuum desiccator	4.2	0.3	3
71 h at 50% RH	3.0	0.1	2

Note: PFOM concentration, 700 ppm; withdrawal rate, 1.6 mm/s; 1× dip; and 12.5-nm carbon overcoat on N58 ceramic.

TABLE 4.6
Optical Constants from Ellipsometry and Ellipsometric Angles Δ and Ψ for the Carbon-Overcoated Silicon Strips

Material	<i>n</i>	<i>k</i>	Ψ	Δ
PFOM	1.36	0	—	—
Carbon overcoat	1.84	0	—	—
Si/SiOx	3.853	0.212	10.54	171.25

Note: Measurements taken at wavelength 632.8 nm.

PFOM thickness, assuming two different carbon-overcoat thicknesses in the calculation, is given in table 4.7. Two of the PFOM-coated strips were measured by XPS. The d/λ from XPS and the corresponding thicknesses are listed in table 4.7.

TABLE 4.7

PFOM Thickness on Carbon-Overcoated Silicon Strips as Measured by Ellipsometry and as Estimated from XPS d/λ

Strip	Ellipsometry thickness (nm) ^a		Δ	Ψ	XPS ^b	
	12.5-nm carbon	13.5-nm carbon			d/λ	Thickness (nm)
1	3.4	2.1	126.15	13.02	—	—
2	4.1	2.7	124.98	13.20	—	—
3	4.9	3.5	123.91	13.37	—	—
4	4.3	3.0	124.71	13.24	—	—
5	4.3	3.0	124.83	13.23	—	—
XPS 1st ^c	—	—	—	—	1.08	2.9
XPS 2nd ^c	—	—	—	—	1.10	2.9
Average	4.2	2.9	—	—	1.09	2.9

Note: Carbon-overcoat thickness, nominally 12.5 nm; PFOM concentration, 650 ppm; withdrawal rate, 1.6 mm/s; 1× dip.

^a Indicates the carbon thickness used in the calculation of the PFOM thickness from ellipsometric angles Δ and Ψ .

^b Estimate from XPS d/λ is based on the mean free path determined from PFOM on non-carbon-overcoated silicon in table 4.8, $\lambda = 2.66$ nm.

^c XPS 1st and 2nd were measured on two separate strips that were coated at the same time as strips 1–5.

4.3.5 NON-CARBON-OVERCOATED SILICON STRIPS AND WAFERS

Since an additional ellipsometric measurement would be needed to determine the carbon-overcoat thickness, the ellipsometric measurement of PFOM thickness directly on non-carbon-overcoated silicon is more straightforward. Silicon strips and wafers were dip coated with PFOM. The PFOM thickness measured by ellipsometry and the d/λ from XPS are listed in table 4.8. The thickness measured by ellipsometry was divided by the d/λ from XPS for each sample (last two columns in table 4.8). The experimentally determined average electron mean free path for PFOM film is $\lambda = 2.66$ nm. Sliders were dip coated with PFOM at the same conditions as the silicon wafers and strips, and d/λ was measured on the air bearing surface of each slider by XPS. These d/λ were multiplied by $\lambda = 2.66$ nm, as determined above, to estimate the PFOM thickness on the air bearing surface. These results are listed in table 4.9. The concentration of the PFOM solution was 650 ppm, and the withdrawal rate was 1.6 mm/s.

4.3.6 CONCENTRATION AND WITHDRAWAL RATE

Tests were done to determine the effects of PFOM concentration and withdrawal rate on the PFOM film thickness deposited on the air bearing surface of sliders. The PFOM film thickness was estimated using XPS. The film thickness as a function of PFOM concentration is shown in fig. 4.3a. Run 1 was made in a prototype coating tank using a developmental procedure. Run 2 was made with the coating tank and

TABLE 4.8
PFOM Thickness as Measured by Ellipsometry on Silicon Strips and Wafers, and the Mean Free Path Determined from XPS Measurement on the Same Samples

Sample no.	Ellipsometry thickness (nm)		d/λ		λ (nm)	
	Si strip	Si wafer	Si strip	Si wafer	Si strip	Si wafer
1	2.9	2.3	1.08	0.923	2.69	2.49
2	2.6	2.4	0.989	0.95	2.63	2.53
3	2.8	2.4	0.948	0.897	2.95	2.67
Average	2.8	2.4	1.01	0.923	2.66	

Note: PFOM concentration, 650 ppm; withdrawal rate, 1.6 mm/s; 1× dip.

TABLE 4.9
PFOM Thickness as Estimated from XPS Measurements on the Air Bearing Surface (ABS) of Magnetic Recording Sliders

Slider ABS	XPS	
	d/λ	Thickness (nm)
1	1.14	3.0
2	1.32	3.5
3	1.23	3.3
4	1.01	2.7
5	1.19	3.2
6	1.05	2.8
Average	1.16	3.1

Note: Magnetic recording sliders were dip coated at the same time and conditions as the silicon strips and wafers in table 4.7 using the experimental average mean free path $\lambda = 2.66$ nm from table 4.8.

procedure intended for manufacturing. The 2× dip was done to determine the effect of a rework cycle on PFOM thickness. The PFOM thickness as a function of withdrawal rate between 0.2 and 1.6 mm/s is shown in fig. 4.3b.

4.3.7 CONTACT ANGLES AND SURFACE ENERGY

Three reference liquids with known polar and dispersion surface-energy components were employed to determine the surface energy of the surface coatings 2–3 nm thick on silicon wafers. The surface energy and its components for water, hexadecane, and Zdol and their contact angles measured on silicon wafers coated with PFOM and several other low-surface-energy coatings are listed in table 4.10. The Girifalco–Good–Fowkes–Young equation [12],

$$\cos \theta = -1 + \frac{2}{\gamma_1} \left[\left(\gamma_s^d \gamma_1^d \right)^{1/2} + \left(\gamma_s^p \gamma_1^p \right)^{1/2} \right] \tag{4.2}$$

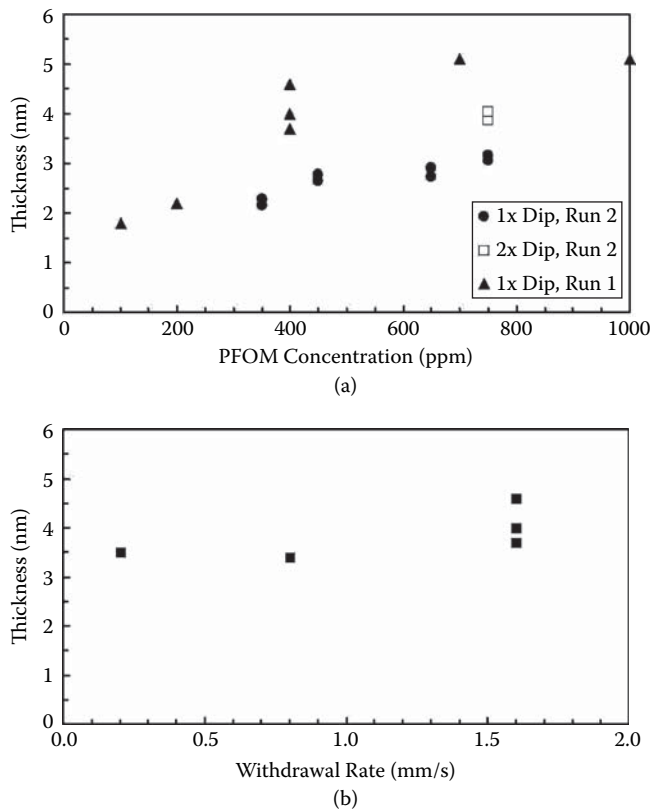


FIGURE 4.3 PFOM thickness estimated from XPS measurements on the air bearing surface of sliders as a function of PFOM concentration at a 1.6 mm/s withdrawal rate (a) and thickness as a function of withdrawal rate at a PFOM concentration of 400 ppm, 1× dip (b).

was used to determine the surface energies from the contact angles measured on the test samples. The superscripts *d* and *p* denote the dispersion and polar components of the surface energy; the subscripts *s* and *l* denote the solid (test sample) and reference liquid, respectively; and the total surface energy $\gamma = \gamma^d + \gamma^p$. The surface energies of the reference liquids are listed in the footnotes to table 4.10.

4.3.8 RHEOLOGICAL PROPERTIES

The storage and loss shear moduli, *G'* and *G''*, vs. oscillation frequency ω , and the creep compliance *J* vs. time *t*, measured at each concentration and temperature, were temperature shifted with respect to frequency or time. These temperature master curves at each concentration were then shifted to overlap one another along the frequency or time axis. The dynamic shear moduli master curves as a function of reduced frequency $\omega a_{T a_C}$ are shown in fig. 4.4, and the shear creep compliance master curves as a function of reduced time $t/a_{T a_C}$ are shown in fig. 4.5. Master curves

TABLE 4.10**Contact Angles and Surface Energies of Low-Surface-Energy Coatings on Silicon Wafers**

Coating	Contact angle (degrees)			Surface energy (mJ/m ²)					
				(water-hexadecane) ^a			(Zdol-hexadecane) ^b		
	water	hexadecane	Zdol 4000	γ^d	γ^p	γ	γ^d	γ^p	γ
PFOM	59.8	68.7	38.6	12.8	28.4	41.2	12.8	4.0	16.7
3M Novec EGC-1700	70.3	58.8	24.6	15.9	17.8	33.6	15.9	3.6	19.5
ZNa	33.8	62.0	16.5	14.8	46.5	61.3	14.8	5.4	20.2
FCOC	104.3	52.3	8.4	17.9	1.2	19.0	17.9	3.5	21.3

^a Calculated from reference liquids water $\gamma^d = 22.1$ mJ/m², $\gamma^p = 50.7$ mJ/m², and hexadecane $\gamma^d = 27.47$ mJ/m², $\gamma^p = 0$, and contact angles.

^b Calculated from reference liquids Zdol $\gamma^d = 15$ mJ/m², $\gamma^p = 6$ mJ/m², and hexadecane, and contact angles.

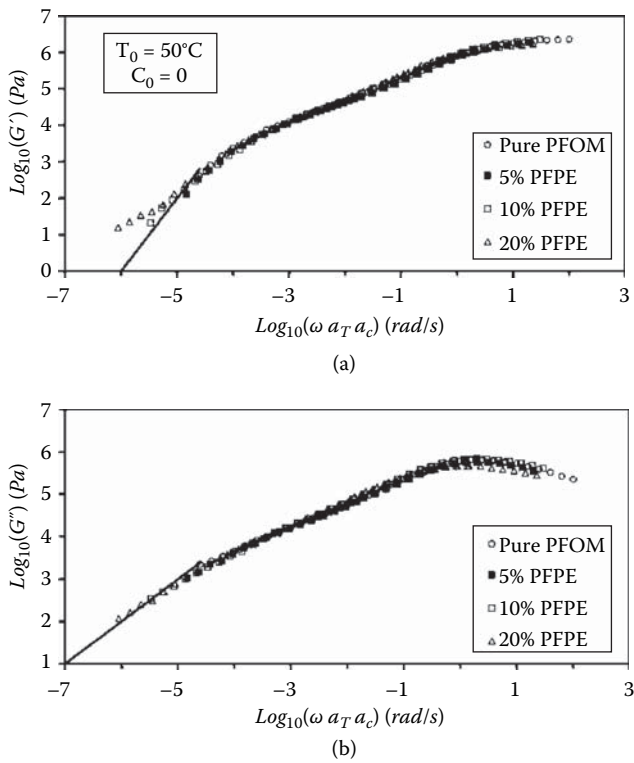


FIGURE 4.4 Dynamic shear moduli temperature-concentration shifted master curves for PFOM with dissolved PFPE Zdol: (a) storage modulus and (b) loss modulus.

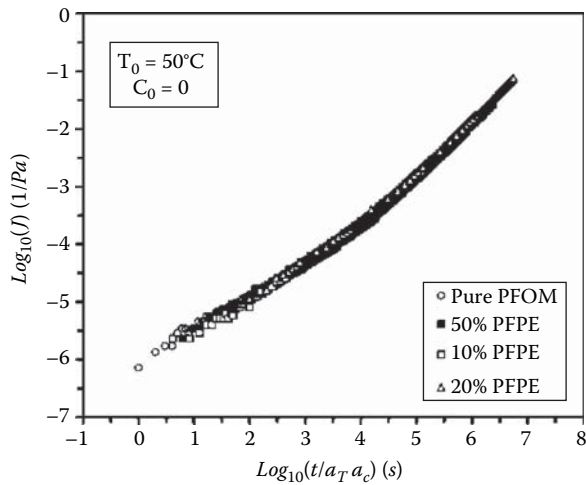


FIGURE 4.5 Shear creep compliance temperature-concentration shifted master curves for PFOM with dissolved PFPE Zdol.

are referenced to 50°C and pure PFOM ($a_T = a_C = 1$). The result is a set of temperature shift factors, a_T , and concentration shift factors, a_C . The shift factors are plotted in fig. 4.6 and are listed along with the glass transition temperatures in table 4.11.

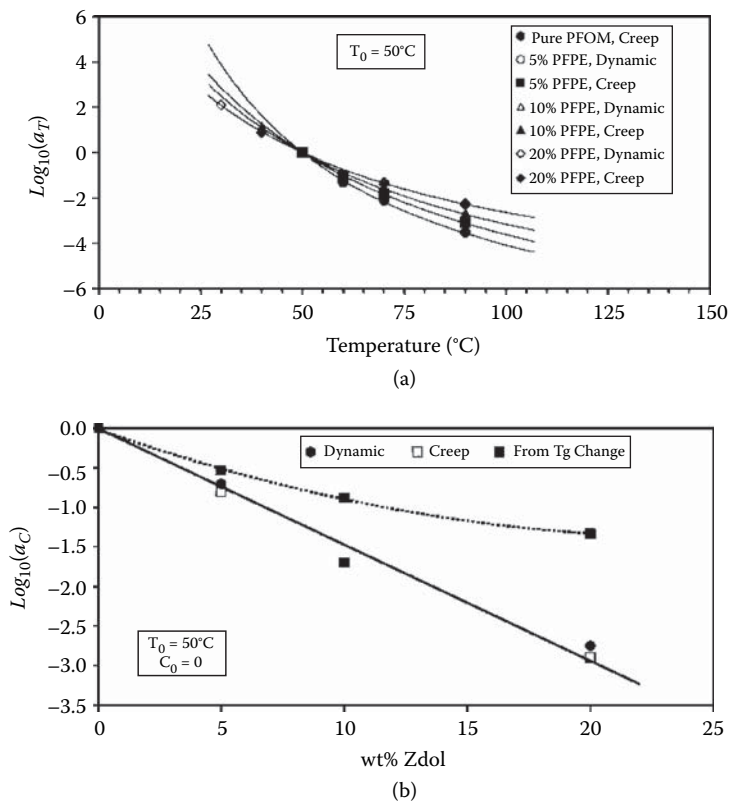


FIGURE 4.6 Shift factors from dynamic and creep rheological measurements on Zdol 2000 in PFOM: (a) temperature shift and (b) concentration shift.

TABLE 4.11
Concentration Shift Factor (a_C) from Dynamic and Creep Rheological Measurements, Glass Transition Temperature (T_g), WLF Coefficients (C_1 and C_2 [reference temperature $T_0 = 50^\circ\text{C}$]), and the Expected Contribution of T_g Change with Concentration to the Concentration Shift Factor

PFPE (%)	$\log_{10}(a_C)$		T_g (°C)	C_1	C_2	Log shift due to T_g change with concentration
	Dynamic	Creep				
0	0	0	45	9.84	70.77	0
5	-0.70	-0.80	40	10.21	91.50	-0.529
10	-1.70	-1.70	35	8.91	91.50	-0.878
20	-2.75	-2.90	25	7.43	91.50	-1.333

The WLF coefficients [13, 14] were calculated from the temperature shift factors a_T by nonlinear regression analysis using the functional form

$$\log(a_T) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (4.3)$$

where the reference temperature $T_0 = 50^\circ\text{C}$, and C_1 and C_2 are the WLF coefficients with respect to T_0 .

4.3.9 TRIBOLOGICAL PERFORMANCE

Three metrics were employed to compare the performance of low-surface-energy coatings on sliders in the subambient pressure frictional hysteresis loop test: (1) frictional hysteresis, (2) lubricant accumulation on the slider during the hysteresis test, and (3) disk scratches. The typical friction force on the slider during loop tests, each carried out with a separate slider, is shown in fig. 4.7. Four test runs were done, each

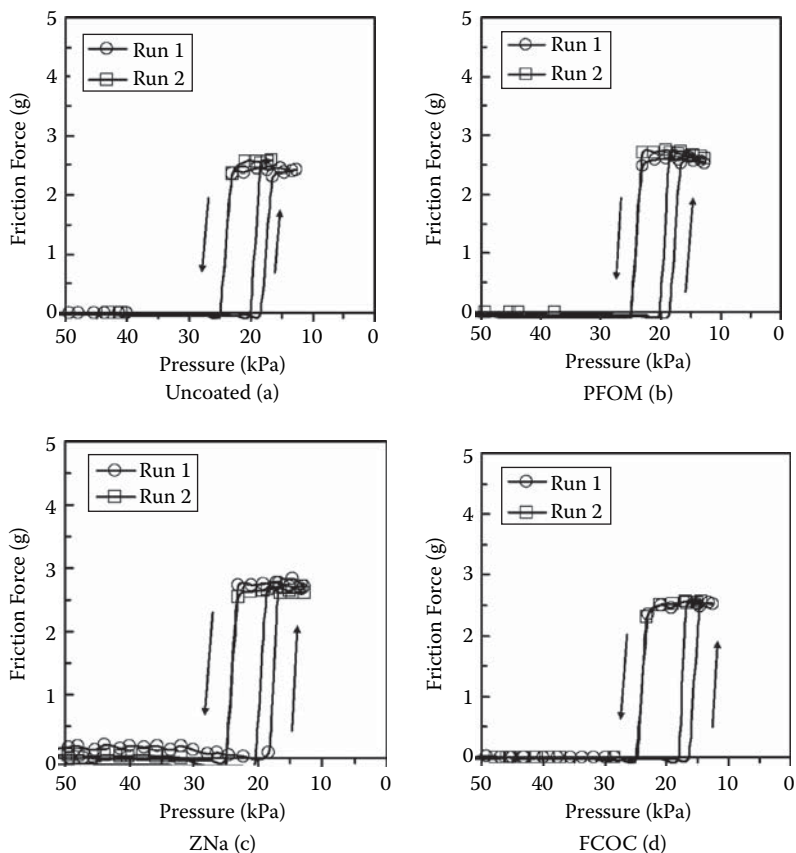


FIGURE 4.7 Results of subambient pressure frictional hysteresis loop tests on low surface energy slider coatings: (a) uncoated, (b) PFOM coated, (c) ZNa coated, and (d) FCOC coated.

with a different slider on a fresh disk test track near the middle diameter of the disk. The touch-down pressure (TDP), where the friction first increases as the air pressure is being decreased, was usually higher on the second run than on the first with a given slider/track. Representative optical micrographs of the slider taken within minutes after the end of the test on uncoated and coated sliders are shown in fig. 4.8. The splotchiness, which is more apparent on some of the sliders, is disk lubricant that was transferred to the slider. After 20 days, the splotchiness had mostly disappeared because the lubricant had spread out by surface diffusion. The increase in the number of scratches relative to the background before the test on the surface during the subambient pressure hysteresis loop tests is shown in fig. 4.9. Test tracks on two disk sides were measured. Most of the scratches were formed in the disk tests using the uncoated slider.

Overall, the tribological tests provide a ranking for the performance of the low-surface-energy slider coatings:

- Lubricant transfer to the slider: uncoated > ZNa > PFOM > FCOC
- Friction and hysteresis: no significant difference
- Disk scratches: uncoated > FCOC > PFOM > ZNa

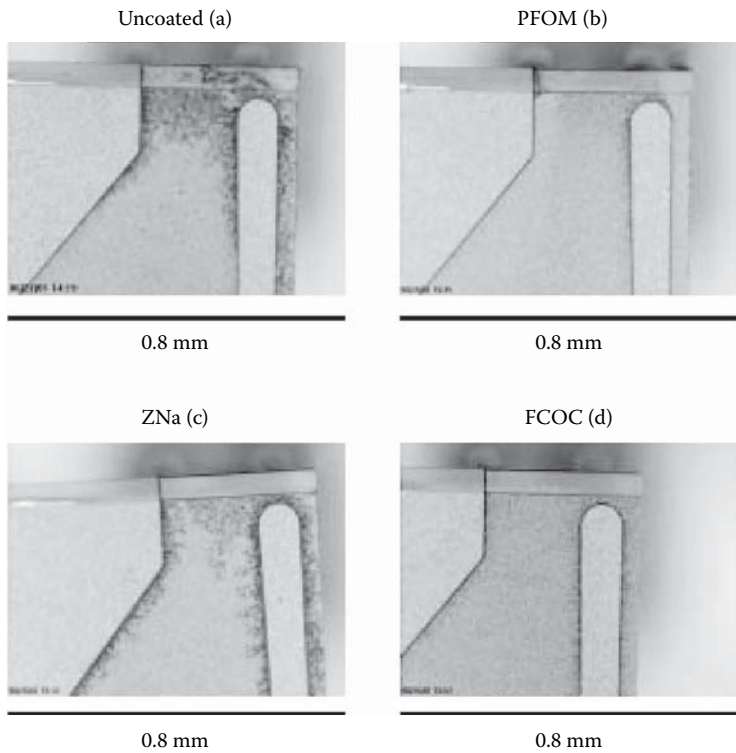


FIGURE 4.8 (See color insert following page 80.) Optical micrographs showing the relative level of lubricant accumulation on the slider during the subambient pressure frictional hysteresis loop tests on low surface energy slider coatings (a) uncoated, (b) PFOM coated, (c) ZNa coated, and (d) FCOC coated.

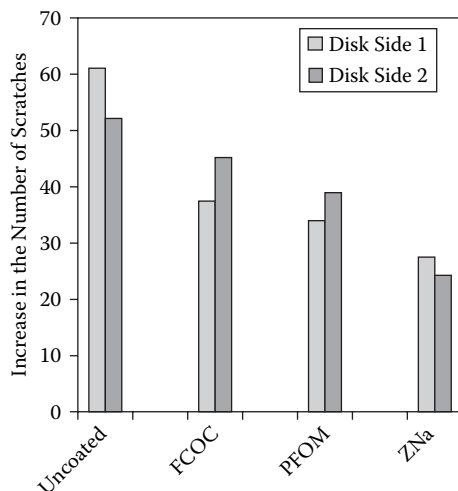


FIGURE 4.9 Scratches formed on the disk during the subambient pressure frictional hysteresis loop tests on low surface energy slider coatings.

None of the low-surface-energy coatings completely prevented disk scratching or lubricant transfer to the slider in the subambient pressure frictional hysteresis loop test. Friction and hysteresis were unaffected by the presence of the coating.

4.4 DISCUSSION

4.4.1 LOW-SURFACE-ENERGY DIP-COATING THICKNESS

The initial ellipsometric measurements on the PFOM films were done using the TiC/ Al_2O_3 ceramic slider rows coated with 12.5 nm of carbon. Due to the variability of the ceramic optical properties and/or the carbon-overcoat thickness, n_s and k_s had to be measured for each row before coating with PFOM. A test was done to evaluate the effects of multiple dip-coating cycles (to simulate multiple dip-coating cycles during manufacturing rework) (see table 4.3). The largest increase in the average PFOM thickness was from 2.2 to 4.3 nm, following the second dip-coating cycle. There was no significant increase in PFOM thickness with further dip-coating cycles beyond $2\times$ up through $4\times$.

The effect of baking at 70°C for 15 h in between dip-coating cycles was studied (table 4.4). The bake was intended to accelerate aging of the film between repeated dip-coating cycles.

Changes in the storage humidity produced significant changes in the apparent PFOM film thickness as measured by ellipsometry (table 4.5). A test was done to study the effect of extreme changes in humidity by subjecting coated slider rows to drying in a vacuum desiccator followed by equilibration at ambient 50% RH. A slider row without any PFOM coating was also subjected to the same drying cycle, and this produced no detectable changes in the optical properties of the substrate. The effect of the drying cycle on a 5-nm-thick PFOM film surface on silicon was measured by atomic force

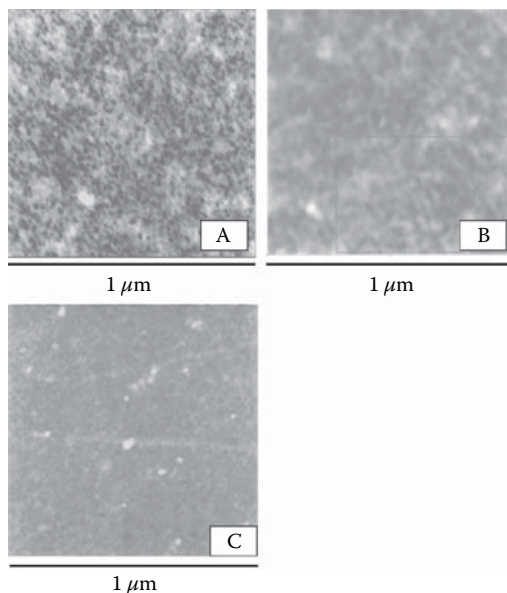


FIGURE 4.10 Atomic force images from $1 \times 1 \mu\text{m}^2$ scans on 5 nm thick PFOM film on silicon equilibrated at ambient 50% relative humidity, 0.26 nm rms roughness (a), the same PFOM film as in (a) following equilibration in a vacuum desiccator, 0.17 nm rms roughness (b), and an uncoated silicon strip, 0.09 nm rms roughness (c).

microscopy (AFM). Figure 4.10A shows an AFM micrograph of the PFOM film equilibrated at ambient 50% RH. Visible texture is apparent in this film, and the root mean square (rms) roughness was 0.26 nm. Figure 4.10B shows the same film after being dried in the vacuum desiccator. The micrograph of the dried PFOM film shows the absence of the texture observed in fig. 4.10A. The rms roughness of the dried PFOM film was 0.17 nm. The AFM micrograph of the uncoated silicon is shown in fig. 4.10C. The rms roughness of the silicon substrate was 0.09 nm. The PFOM film increased the surface roughness. The dried PFOM film was smoother than the film equilibrated at ambient 50% RH. However, these changes in the PFOM film texture upon drying cannot account for the observed variations in the apparent film thickness between ambient humidity and the dried film as measured by ellipsometry.

The increase in the apparent PFOM film thickness upon drying as measured by ellipsometry is attributed to polymer chain orientation within the film. For example, consider row 3 of table 4.5. In this row, the substrate $n_s = 2.052$ and $k_s = 0.393$. These were unaffected by drying in the vacuum desiccator. The ellipsometric angles measured at ambient humidity were $\Delta = 38.11^\circ$ and $\Psi = 11.67^\circ$, and those measured after drying were $\Delta = 40.15^\circ$ and $\Psi = 11.64^\circ$. The ellipsometric angle Ψ is related to attenuation during reflection, and was unaffected by drying. The ellipsometric angle Δ is the phase shift between the light polarized parallel and perpendicular to the plane of incidence. The value of Δ is determined by n_s , k_s , and the PFOM film thickness d and index of refraction n_f . The increase in the apparent thickness with drying is a result of the increase in Δ . Since the actual thickness d is unaffected by drying, and the AFM

showed only a small change in film texture with drying, drying appears to change n_f . Since the n_f of a material depends primarily on its composition and density, n_f is often treated as a material property. However, anisotropy of stress or orientation causes small but significant differences between the values of n_f in the directions parallel and perpendicular to the plane of incidence. This effect is referred to as birefringence, or optical anisotropy. A molecular model of PFOM was studied to understand how molecular orientation could occur in the PFOM film. The monomer is shown in fig. 4.11a (energy minimized). The four-unit polymer in its energy-minimized free-space configuration is shown in fig. 4.11b. In this state, the side chains are randomly oriented, and the film is isotropic. Drying of the film removes water, increasing the interaction of the polar ester groups with the SiO_x surfaces. In fig. 4.11c, the side chains have been rotated about the C–O bonds (which have a low rotational energy barrier) to bring the ester groups closer to the surface. The effect of this configurational rearrangement is to produce a net orientation of the side chains perpendicular to the surface. In the oriented state, the value of n_f perpendicular to the surface $>$ n_f parallel to the surface, leading to the apparent increase in thickness upon drying as measured by ellipsometry.

The time scale for the configurational rearrangement process is hours. When the sample was placed in the vacuum desiccator after equilibration at ambient humidity, more than 4 h were required for equilibration. Consequently, as long as the ellipsometric thickness measurements are done within about 4 h of dip coating, the PFOM film remains isotropic, and the ellipsometry provides an accurate value for the film thickness.

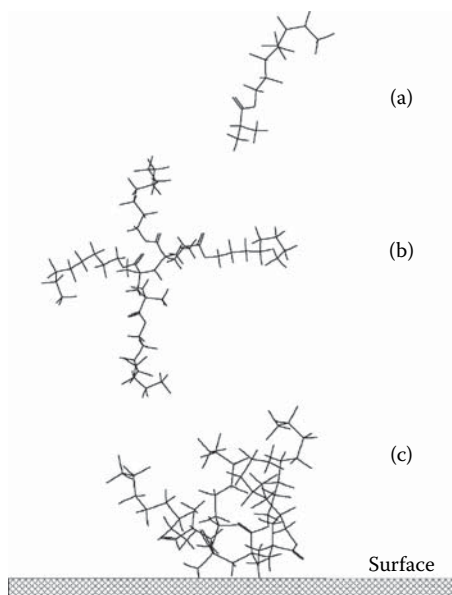


FIGURE 4.11 Wire frame image of PFOM monomer, energy minimized (a); polymer with 4 monomer units, energy minimized (b); and polymer with 4 monomer units, having side chains rotated about the C–O bonds, allowing the polar ester groups to more closely approach the surface (c).

In general, the deposition rate from solution during the dip-coating process is a function of the surface chemistry (surface tension and the heat of adsorption). A carbon overcoat was deposited on the silicon to match the surface properties of the carbon overcoat on the slider rails. However, when the single-layer model was used for analysis of ellipsometric measurements on the PFOM with the carbon-overcoated silicon strips, the calculated PFOM thickness was much too low. The ellipsometric model using two layers on a substrate was necessary. The two-layer model requires knowing the optical properties of the silicon, carbon overcoat, and PFOM (table 4.6), as well as the carbon-overcoat thickness, to calculate an unknown PFOM film thickness from the ellipsometric angles Δ and Ψ . The PFOM thickness calculated using the nominal carbon-overcoat thickness of 12.5 nm (table 4.7, column 2) seemed unusually high, so that the PFOM thickness was also calculated assuming a carbon-overcoat thickness of 13.5 nm (table 4.7, column 3). Two of the strips were also measured by XPS to obtain d/λ from eq. (4.1). The PFOM thickness estimated using the mean free path $\lambda = 2.66$ nm is in the last column of table 4.7. The PFOM thickness from XPS is closest to the PFOM thickness from ellipsometry calculated with a carbon-overcoat thickness of 13.5 nm. As a result of the tests with the carbon-overcoated silicon, it was concluded that measurement of the carbon-overcoat thickness would also be needed in conjunction with the more complicated two-layer model for the ellipsometry calculation if the carbon-overcoated silicon strips were to be used.

A test was done to evaluate the use of non-carbon-overcoated silicon wafers and strips as PFOM thickness monitors. The PFOM thickness on the silicon wafers and strips is shown in table 4.8 along with the d/λ from XPS measured on the same samples. The data in table 4.8 were employed to derive the experimental mean free path relating PFOM thickness from ellipsometry with d/λ from eq. (4.1) as

$$\text{thickness (nm)} = (2.66 \text{ nm}) \times (d/\lambda) \quad (4.4)$$

The electron mean free path of $\lambda = 2.66$ nm is within the range of mean free paths reported for polymer thin films on surfaces [8]. Equation (4.4) was used to estimate the PFOM thickness on air bearing surfaces from d/λ . The values of d/λ and PFOM film thicknesses are given in table 4.9. The PFOM film was 0.5–0.7 nm thicker on the carbon-overcoated air bearing surfaces (table 4.9, column 3) and on the carbon-overcoated rows (table 4.7, columns 3 and 7) than on the silicon wafers (table 4.8, column 3). This is attributed to the difference between the surface chemistry of the SiO_x surface of the uncoated silicon and that of the carbon overcoat.

In conclusion, for the PFOM film thickness measurement, the non-carbon-overcoated silicon wafers can be used to monitor the thickness of PFOM being deposited on the air bearing surface as long as the presence of an offset in the deposited film thickness between the two types of substrates is taken into account.

The effects of PFOM concentration and withdrawal rate on the PFOM thickness deposited on slider rails during dip coating of HGAs were studied. The first PFOM concentration dependence run was done with a prototype coating tank and procedure (triangles in fig. 4.3a). The three triangles at 400 ppm are from three solutions separately formulated at the same concentration. Points above and below 400 ppm were from the same batch of formulation as the highest triangle at 400 ppm.

The points shown by the circles in fig. 4.3a were dip coated using an improved version of the tank and coating cycle designed for use in manufacturing. The squares are from a 2× dip using the latter conditions. The second dip, at 750-ppm PFOM concentration, increased the PFOM thickness by ≈ 0.8 – 1.0 nm. This is less than the average of ≈ 2.1 -nm increase in thickness after 2× dips found on the slider rows with 700-ppm PFOM concentration (table 4.3). The second dip-coating cycle after baking increased the average PFOM thickness on slider rows by ≈ 1.0 nm (table 4.4).

For both of the PFOM concentration studies shown in fig. 4.3a, the PFOM thickness linearly extrapolated to zero PFOM concentration intercepts the vertical axis at about 1.5–2.0 nm. This thickness is nearly the same as the length of the monomer unit of the PFOM polymer shown in fig. 4.11a. Since the PFOM thickness-vs.-concentration curve must pass through zero, it seems that a layer of the PFOM forms on the surface at a very low concentration. The PFOM film thickness is also relatively independent of withdrawal rates between 0.2 to 1.6 mm/s, as shown in fig. 4.3b. The interpretation of the rapid layer formation, which is nearly one monomer unit thick, can be extended to suggest that the formation of a uniform layer may be possible at very low PFOM concentrations. An apparent nonzero intercept of the film thickness-vs.-concentration plot, and the film thickness being relatively independent of withdrawal rate, can also arise from rapid evaporation at the meniscus of a solvent that does not wet the substrate. It would be of interest to explore the region of even lower concentration to avoid excess PFOM deposit on surface topography features of the slider that accumulate a meniscus or pendant drops of solution.

4.4.2 SURFACE ENERGIES OF SLIDER COATINGS

Hexadecane spreads out completely on bare carbon overcoat. To avoid this problem, the surface energy of the bare carbon overcoat can be evaluated with water and methylene iodide [15]. In this study, the dispersion surface-energy components of the low-surface-energy coatings were evaluated with either water–hexadecane or Zdol–hexadecane liquid pairs. The polar component varies considerably and is strongly dependent on the reference liquids used for measurement. For the fluorohydrocarbon surfactants and FCOC, the Zdol reports a lower polar surface energy component than water with hexadecane as the nonpolar reference liquid. This may be related to the hydrogen bonding density difference between water and Zdol, because Zdol only has hydrogen bonding at each end group, separated by the polymer chain in between. The ranking for surface energy of the coatings is based on the dispersion contribution, because this was most nearly independent of the reference liquids employed for measurement:

$$\text{FCOC} > \text{ZNa} > \text{PFOM}$$

The PFOM is probably the lowest because it has the most highly fluorinated interface arising from the fluoro-octanol ester chains being concentrated at the surface.

4.4.3 RHEOLOGY OF PFOM AND MIXTURES WITH ZDOL DISK LUBRICANT

PFOM mixtures containing less than 40 wt% Zdol remained single-phase solutions. The 40 wt% sample was initially a transparent viscoelastic liquid at room temperature. When

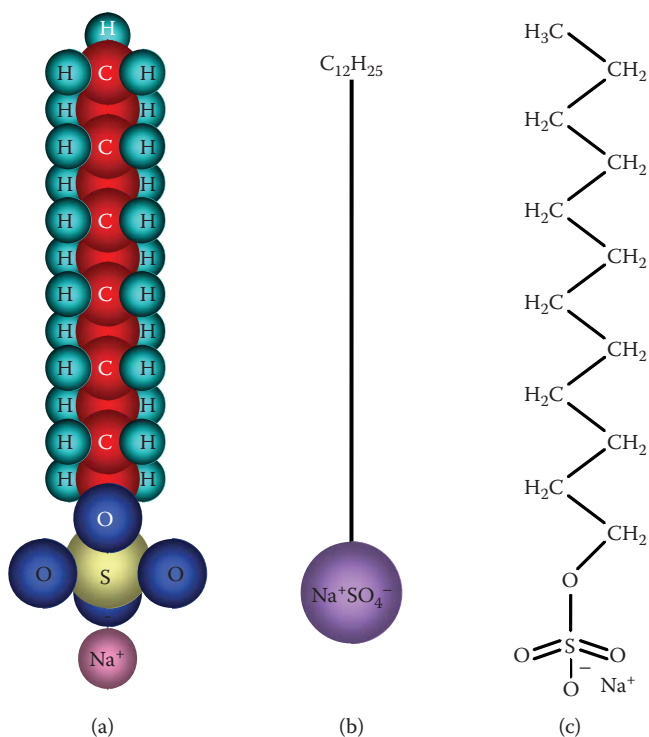


FIGURE 1.1 Comparison of (a) space-filling atomic, (b) simplified, and (c) simplified atomic views of sodium dodecyl sulfate. The letters represent the atomic symbols. These views represent the lowest energy state. However, due to molecular vibrations, the actual shape varies with time, and the average shape is not a straight chain as shown. Note that the angle for these views does not reveal the fact that the repeating carbon-hydrogen section of adsorbed sodium dodecyl sulfate is not perpendicular to the surface.

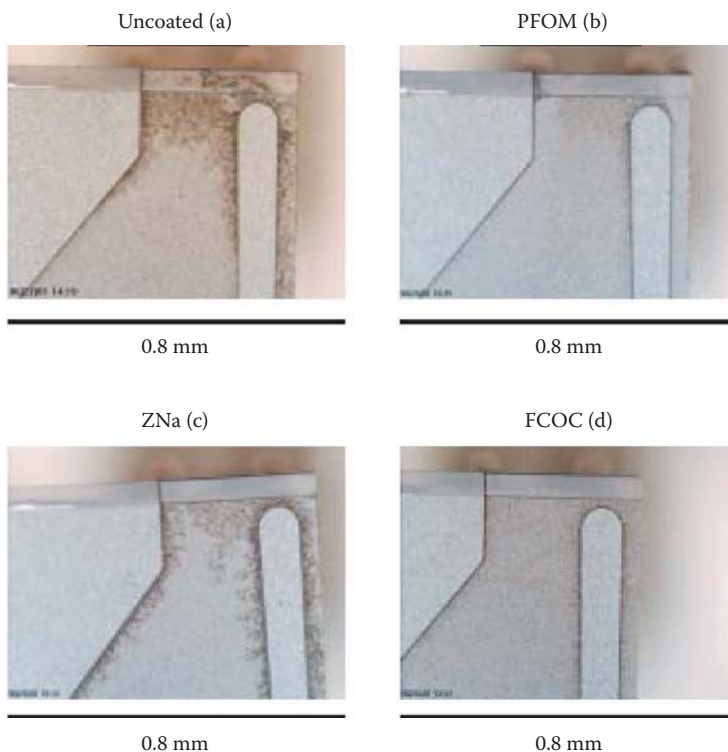


FIGURE 4.8 Optical micrographs showing the relative level of lubricant accumulation on the slider during the subambient pressure frictional hysteresis loop tests on low surface energy slider coatings (a) uncoated, (b) PFOM coated, (c) ZNa coated, and (d) FCOC coated.

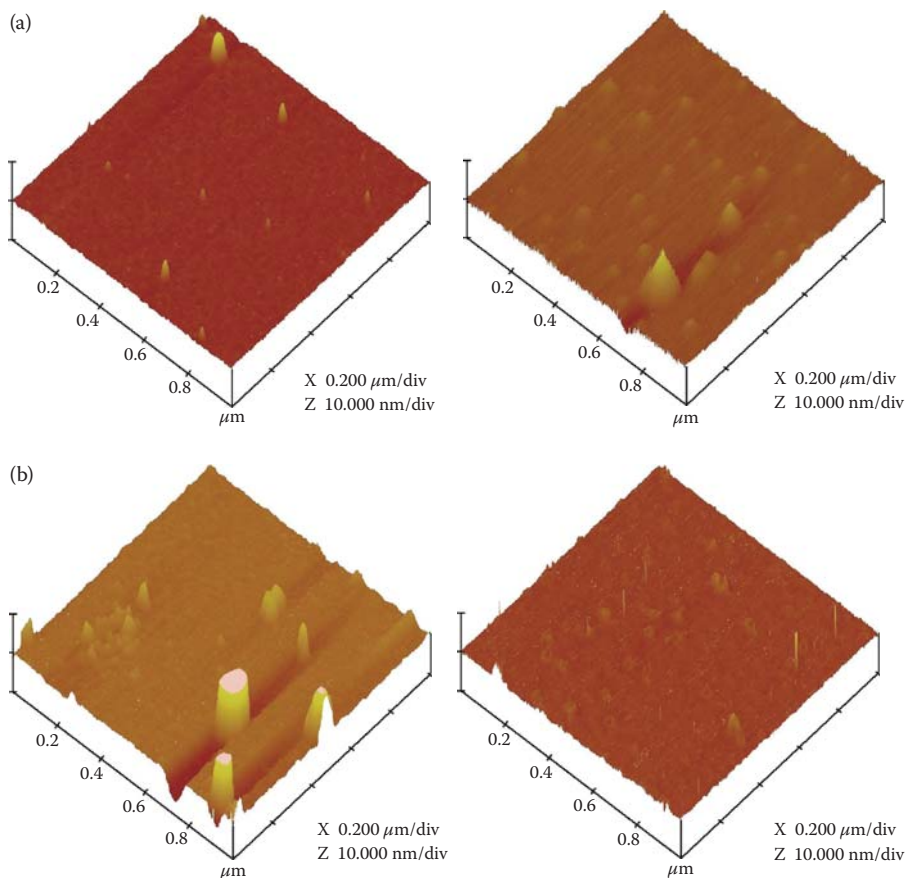
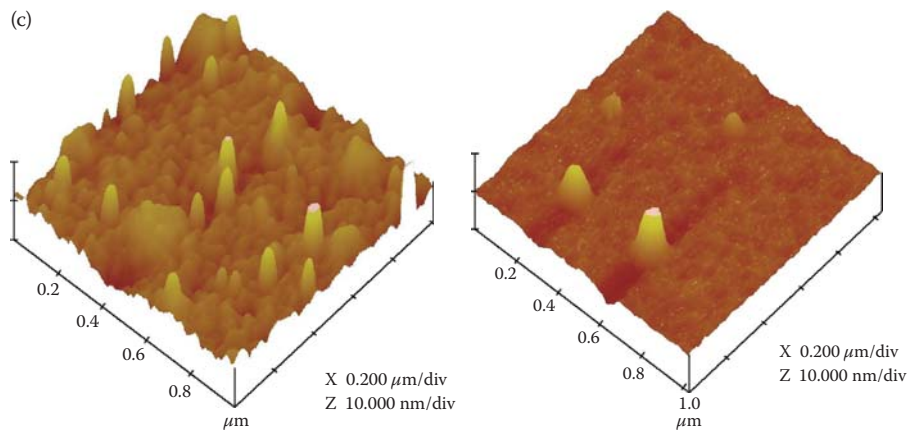


FIGURE 6.2 AFM images of (a) bare Si, (b) Si/OTS, (c) Si/APTMS, and (d) Si/GPTMS before (left image) and after (right image) coating with PFPE. The vertical scale is 10 nm in all images.

(c)



(d)

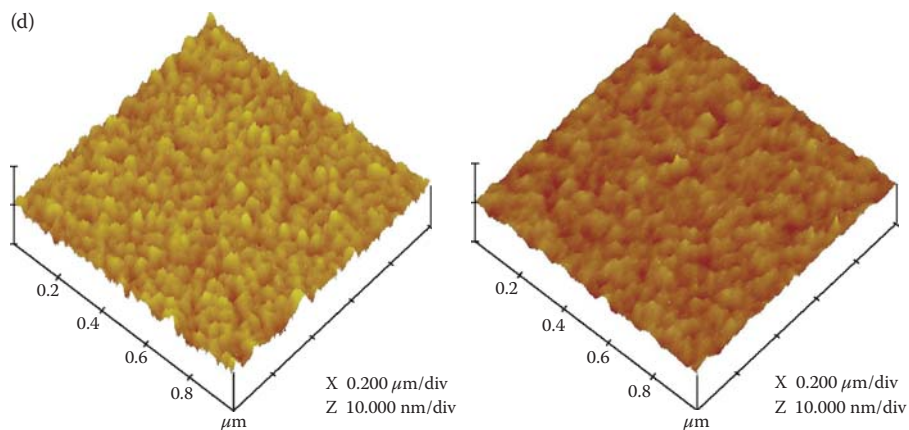


FIGURE 6.2 (CONTINUED) AFM images of (a) bare Si, (b) Si/OTS, (c) Si/APTMS, and (d) Si/GPTMS before (left image) and after (right image) coating with PFPE. The vertical scale is 10 nm in all images.

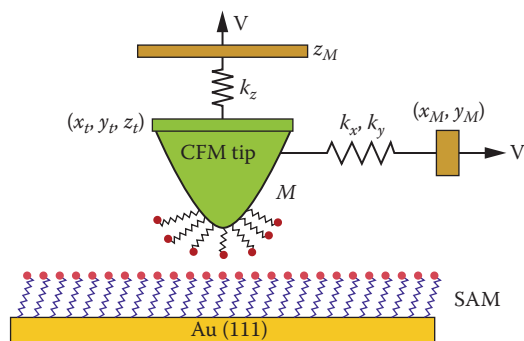


FIGURE 7.10 Mechanical model for the simulation system [80]. The tip was dragged by the support (z_M) through the spring (k_z) at a velocity v while the support (x_M, y_M) was fixed. (From Ghoniem, N. M., et al. 2003. *Philos. Mag.* 83: 3475. With permission.)

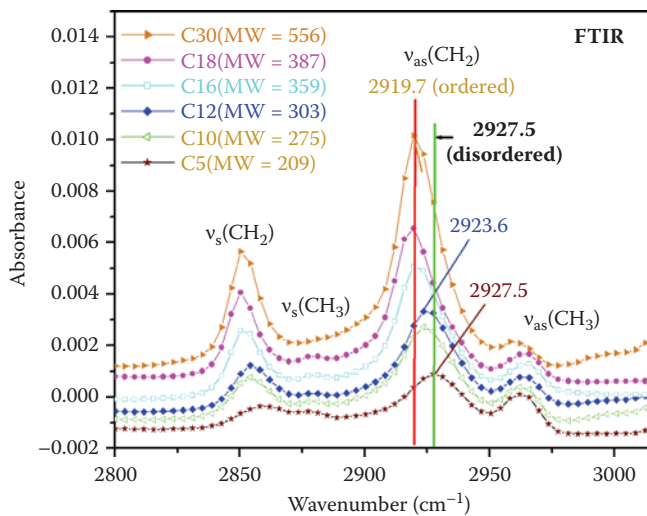


FIGURE 8.3 FTIR spectra in reflection mode of trichlorosilane SAMs with carbon chain lengths C_5 – C_{30} on silicon. The asymmetric CH_2 band maxima are observed in the range of 2927–2912 cm^{-1} . Symmetric CH_2 stretches, observed at 2853–2846 cm^{-1} , are also indicated for various SAMs.

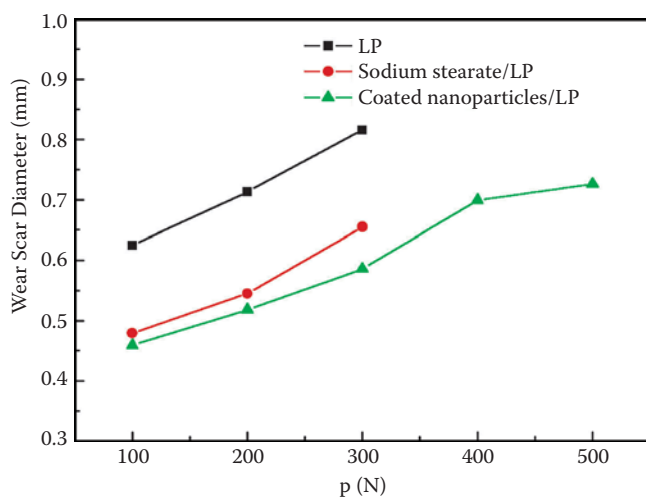


FIGURE 10.6 Effect of load on wear-scar diameter (four-ball test machine; additive concentration in liquid paraffin (LP): 0.1%; speed: 1450 rpm; test duration: 30 min).

heated to 90°C, the 40 wt% solution undergoes apparent crystallization within minutes. The crystallization occurs more slowly at 50°C. The 40 wt% sample turned from clear to cloudy when cooled to 10°C, apparently due to phase separation of the Zdol. This phase separation is reversible. The 40 wt% solution cleared upon heating to 20°C. The 60 wt% solution is a milky viscoelastic liquid; it cleared reversibly upon heating to 30°C. Apparent crystallization occurs in the 60 wt% solution over a day at room temperature.

The pure PFOM and its solutions with Zdol at and below 20 wt% Zdol concentration were thermorheologically simple fluids in that they superimposed on one another with a horizontal shift along the time or frequency axis. They also shifted to superimpose with respect to Zdol concentration (figs. 4.4 and 4.5). The temperature-shift factors are shown in fig. 4.6a. The smooth curves are fitted to the WLF equation, eq. (4.3). The concentration-shift factors plotted in fig. 4.6b show that both the dynamic and creep rheological measurements provided the same values. For typical glass-forming liquids, the shift factors follow the changes in the glass transition temperature induced by variations in molecular structure, hydrogen bonding, or molecular weight [16]. Specifically, the reference temperature in eq. (4.3) is expected to be offset by an amount equal to the change in the glass transition temperature with concentration. For the solutions of Zdol in PFOM, the concentration shift was more than expected from the change in the T_g alone. Within the context of the free-volume model, it may be that the Zdol not only mediates the intermolecular force between the PFOM chains, but also facilitates segmental translation. The temperature dependence of the shift factor in fig. 4.6a is consistent with a decrease in the flow activation energy with increasing Zdol concentration.

There was some concern that the PFOM on the slider exposed to Zdol disk lubricant might become runny and flow from the slider to the disk at the disk drive operating temperature. The rheological temperature–concentration master curves can be used to calculate the linear viscoelastic properties: zero shear viscosity η , equilibrium recoverable compliance J_e^0 , and characteristic time $\tau_c = \eta J_e^0$. These are derived from the limiting low-frequency moduli according to $G''\{\omega a_T a_C \rightarrow 0\} = \eta \omega a_T a_C$ and $G'\{\omega a_T a_C \rightarrow 0\} = \eta^2 J_e^0 (\omega a_T a_C)^2$. The limiting low-frequency fit is shown by the solid lines in fig. 4.4. A hint of network formation, or phase separation, with 20 wt% PFPE in PFOM is suggested by the upward deviation of the low-frequency G' data in fig. 4.4a from the power-law slope [17]. The viscoelastic properties from the dynamic rheological data are given in table 4.12.

TABLE 4.12
Linear Viscoelastic Properties of PFOM and Its Solution with 20 wt% PFPE Zdol at 50°C

Property	Pure PFOM		20% PFPE Zdol	
	From dynamic	From creep	From dynamic	From creep
η (Pa·s)	1.6E+07	5.6E+07	2.4E+04	8.4E+04
J_e^0 (1/Pa)	1.0E-04	—	1.5E-07	—
τ_c (s)	1.6E+03	—	2.4	—

A steady viscosity is also provided by the steady-state creep compliance according to $J(\{t/a_{T\alpha_C}\} \rightarrow \infty) \approx (t/a_{T\alpha_C})/\eta$. The power-law slope of the long-time creep compliance in fig. 4.5 is 0.984. The zero-shear viscosity from creep data is given in table 4.12. It is larger than the zero-shear viscosity value from the dynamic measurement. The difference is attributed to the slope of the long-time creep data being slightly less than 1. The viscoelastic properties are also calculated for 20 wt% PFPE in PFOM at 50°C with the average concentration log shift factor of -2.825 , and these values are listed in table 4.12. For comparison, the viscosity of Zdol with molecular weight 2250 is 0.03 Pa-s, and the viscosity of another common disk lubricant Ztetraol 2000 is 0.6 Pa-s at 50°C. Thus, even if some lubricant becomes dissolved in the PFOM, a film of PFOM is not expected to flow from the slider.

Another possible concern, given the sensitivity of sliders to contamination, is that the combination of PFOM with disk lubricant could become tacky and collect particles. Over the range of temperature from 50°C to 90°C, the plot of the dynamic properties of PFOM and its solutions with Zdol (G' vs. G'') transitions through the region of what is known as the viscoelastic window [18] for pressure-sensitive adhesives (PSAs). At high temperature, they should have the properties of a removable PSA, at intermediate temperature those of a general purpose PSA, and at low temperature those of a high-shear PSA. To test this assertion, PFOM solution was dip coated onto glass slides; glass particles with a size range from 5 to 50 μm were sprinkled onto the slides after heating to a series of different elevated temperatures; and the loose particles were blown off with an air gun. Micrographs showing the different amounts of glass particles remaining stuck in the PFOM film are shown in fig. 4.12. The number of residual particles clearly increased as the temperature was increased from 60°C to 70°C for the pure PFOM. With 20% Zdol in the PFOM, the transition to high adhesion for the glass particles was at a much lower temperature, between 20°C and 50°C. With the presence of PFOM coating on the slider, care must be taken to avoid particulate contamination in the disk drive to prevent particle accumulation on the slider.

4.4.4 TRIBOLOGICAL PERFORMANCE OF LOW-ENERGY SLIDER COATINGS

All of the low-surface-energy coatings improved the tribological performance of the slider. The ranking of their relative surface energies and performance is summarized in table 4.13. The lowest-surface-energy coating PFOM had the next-to-the-least lubricant transfer and scratching. The FCOC had the least lubricant transfer.

In the absence of lubricant on the slider, the adhesion stress is taken to be the tensile strength of the interface between the slider carbon overcoat (material 1) and the disk lubricant (material 2). It is the force per unit area to separate the two materials. Only dispersion-force contributions to the tensile strength are included in the following, because the high velocity between the slider and disk asperities does not allow time for dipole orientation [19], and there are relatively few polar end groups per unit area of disk surface. An approximate expression for the tensile strength with atoms separated by distance r_{12} is derived as follows [20].

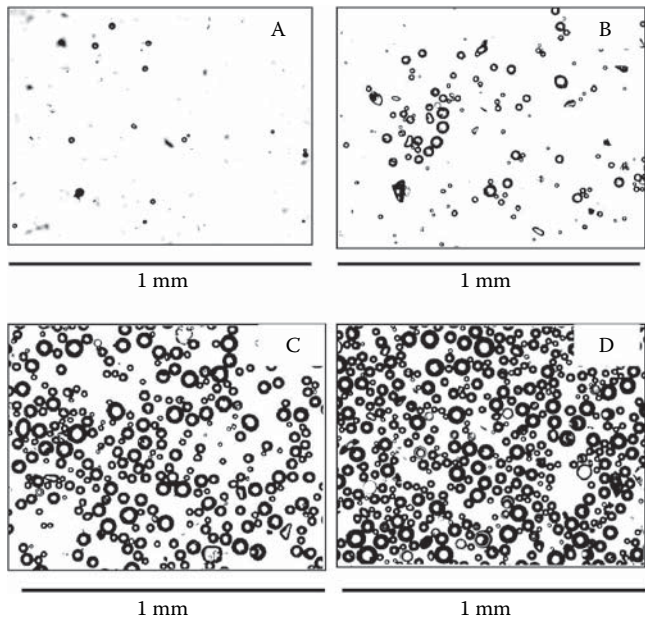


FIGURE 4.12 PFOM film dip coated on glass slide from 2 wt% solution in FC72. 5–50 μm glass microspheres dusted on dried polymer film at indicated temperature. Excess particles removed with 60 psi (414 kPa) air gun. Film thickness 50 nm, image area 1 × 1 mm. (a) 50°C, (b) 60°C, (c) 70°C, (d) 80°C.

TABLE 4.13
Ranking of Surface Energy, Lubricant Transfer, and Disk Scratches during the Subambient Pressure Loop Test

Ranking	Surface energy/ adhesion stress (MPa)	Transfer	Scratching
Highest	Uncoated/300	Uncoated	Uncoated
	FCOC/190	ZNa	FCOC
↓	ZNa/175	PFOM	PFOM
Lowest	PFOM/160	FCOC	ZNa

In this approximation, the dispersive interaction energy is

$$\sum_{12}^d \propto 1 / r_{12}^2$$

and the interaction force is

$$d \sum_{12}^d / dr_{12} \propto -2 \sum_{12}^d / r_{12}$$

The interaction energy per surface is then taken to be

$$\sum_{12}^d \approx \sqrt{\gamma_1^d \gamma_2^d}$$

hence the adhesion stress is approximately given by

$$\sigma_{12} \approx \frac{4}{d_0} \sqrt{\gamma_1^d \gamma_2^d} \quad (4.5)$$

where $d_0 = 0.317$ nm is the distance of closest approach between the surface atoms [21].

The thick-film limit of the lubricant dispersion surface energy is $\gamma_2^d \approx 13$ mJ / m² [22]. The dispersion component of the surface energy of the slider is γ_1^d . For the uncoated slider, $\gamma_1^d \approx 43$ mJ / m², and the coated slider values are given in table 4.10. The adhesion stress is listed in table 4.13. Further discussion of adhesion-controlled friction is given in the literature [23].

Lower adhesion stress is expected to reduce the tendency of the slider to pitch down and scratch the disk. The scratch ranking follows the adhesion stress except that the PFOM and ZNa are reversed. However, the adhesion stress values for both of these are nearly the same, so that the scratch count may be equivalent within the statistics of the measurement. Overall, the best coating for reduction of both scratches and lubricant transfer is PFOM.

4.5 SUMMARY

The development of an industrial procedure for applying a magnetic recording slider coating and for measuring the coating thickness was described. Both ellipsometry and XPS were employed to complement one another for thickness measurement and calibration. Ellipsometric measurement cannot be performed on slider rails, so it was done on slider rows or on silicon strips cut into the shape of slider rows. XPS was necessary to obtain the resolution needed for manufacturing process control.

The surface energy and tribological performance of poly (1H,1H-pentadecafluorooctyl methacrylate) fluorohydrocarbon surfactant were compared with several other types of slider coatings. The surface energy of the fluorinated acrylate polymer was the lowest, and it provides the best compromise for reduction of both lubricant transfer and scratches. The improvement is consistent with a reduction in the adhesion stress by the low-surface-energy coatings on the slider.

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Part III

*Self-Assembled Monolayers
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