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## Solid-Like Lubricating Films, Self-Assembled Films

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### Definition

As a new lubrication regime, thin film lubrication has been well studied since the 1990s. Lubrication with ordered films is a common practice in many modern technical devices. Generally, ordered films can be formed on surfaces (substrates) by several approaches, including the Langmuir–Blodgett (LB) method, self-assembly, adsorption, and evaporation. Among these, the self-assembly technique has generated substantial interest not only for its simple preparation procedure but also for its wide potential applications in many fields, such as surface modification, boundary lubricant coatings, sensors, photoelectronics, and functional bio-membrane modeling.

Self-assembled films (SAFs) are ordered molecular assemblies formed on a solid surface through a spontaneous process driven by certain forces. SAFs can be divided into two categories based on the number of layers in

the film: self-assembled monolayers (SAMs) and self-assembled multilayer films (SAMFs).

## Scientific Fundamentals

### Self-Assembled Monolayers (SAMs)

SAMs are molecular assemblies that are formed spontaneously on a solid surface by the immersion of a substrate into a solution containing active surfactant (Fig. 1a, Ulman 1996). A self-assembling precursor surfactant molecule includes three parts: a head group, an alkyl chain, and a tail group (Fig. 1b). Each part has great influence on certain properties of SAMs (Tsukruk 2001). Briefly, the head groups adhere to the substrate through certain strong chemical interactions and play an important role in determining the affinity of SAMs. The alkyl chains are packed together through interchain van der Waal forces and influence the pack density of the assemblies. The tail groups are exposed to the environmental atmosphere and serve as the surface layer, determining surface properties such as wettability, reactivity, and so on.

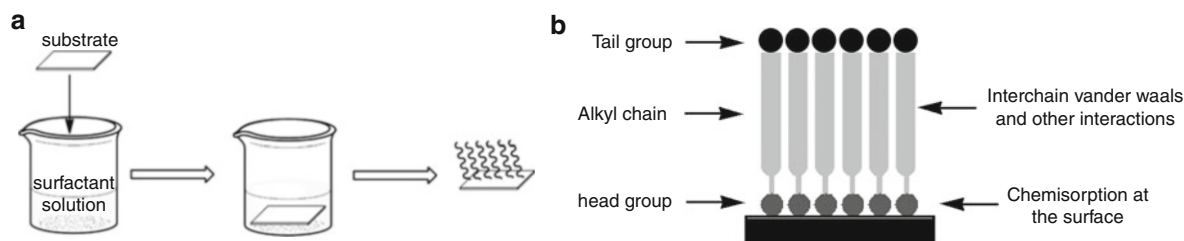
According to the interaction between head group and the substrate, SAMs can mainly be divided into the following three categories.

### Organosilane Monolayers

SAMs of organosilanes, such as alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes, are generally formed on the hydroxylated surface of oxide ( $MO_x$ ), such as  $SiO_2$  and  $Al_2O_3$ . The driving force for this self-assembly is the in situ formation of Si–O–M interfacial bonding. Taking the assembly of *n*-octadecyltrichlorosilane (OTS) as an example, it is supposed that the OTS molecules would first be hydrolyzed under the attack of the adsorbed water molecules on the substrate or the dissolved water in the organic solvent. Then, the hydroxylated OTS molecules are adhered to substrate. Finally, Si–O–M anchoring and lateral bonding are formed by the condensation between Si–OH and M–OH.

From the above example, it can be inferred that the water inducing the hydroxylation of surfactant is a key factor for the assembly of organosilane. So, it is clear that OTS molecules can only be physically absorbed on the substrate without the absorbed water or in the solvent without the dissolved water.

Temperature is another important factor affecting SAM formation (Ulman 1996). This can be attributed to the competition between the reaction of hydrolyzed (or partially hydrolyzed) trichlorosilyl (or alkoxy-silyl) groups

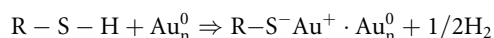


**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 1** A typical preparation process for SAMs (a); the molecular structure of a SAMs (b)

with other such groups in solution to form a polymer, and the reaction of such groups with surface  $M-OH$  moieties to form a SAM. As temperature increases, the surface reaction is suppressed and the thermal disorder in the forming monolayer increases. Thus, there must exist a critical temperature ( $T_c$ ), below which an ordered monolayer can be formed. It is reported that the critical temperature of  $T_c$  is a function of chain length. Particularly, a linearity between  $T_c$  and the number of carbon ( $N_C$ ) was observed when  $N_C$  is in the range of 10–22 (Ulman 1996).

### Organosulfur Monolayers

Due to the excellent coordination to the transition metal surface, organosulfides, such as  $R-SH$ ,  $R_1-S-R_2$  and  $R_1-S-S-R_2$ , can be strongly attached to the surface of  $Au/Ag/Cu/Pt/Hg/GaAs/InP$  to form ordered SAMs (Ulman 1996). However, the most studied SAMs are those of alkanethiols on  $Au(111)$  surfaces. In a typical assembling process, a fresh  $Au$  layer deposited on silicon or mica substrate was immersed into a solution (the solvent can be ethanol, hexane, acetone, or dichloromethane) of alkanethiol with a concentration of  $10^{-3}$ – $10^{-1}$  mol/L for a period of time (several minutes to several days). In such cases, the interfacial reaction may be formally considered as an oxidative addition of the  $S-H$  bond to the  $Au$  surface, followed by a reductive elimination of the hydrogen. When a clean  $Au$  surface is used, the proton probably ends as an  $H_2$  molecule (Ulman 1996):



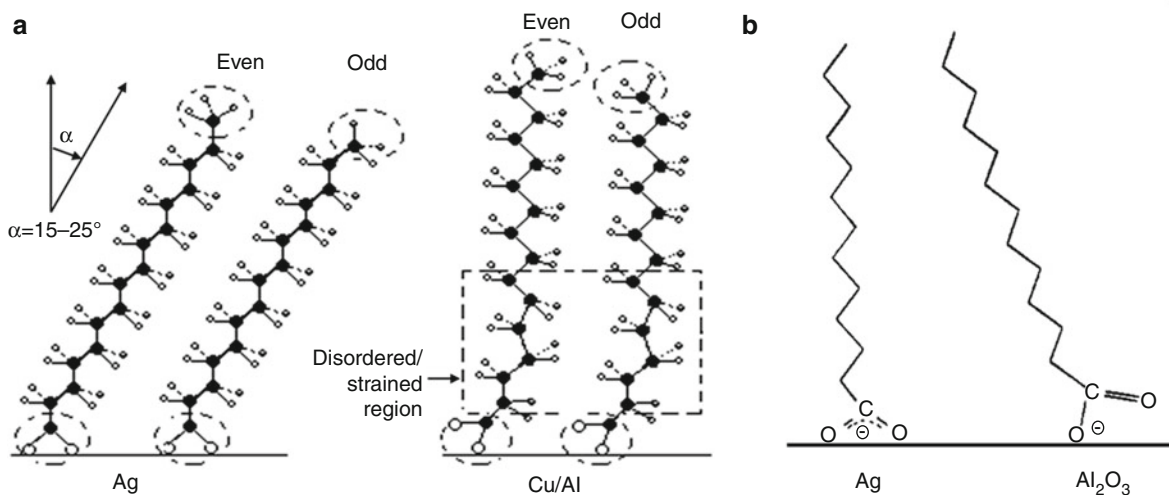
The adsorbing species of  $RS^-$  has been evidenced by characterizations of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and electrochemistry. The

homolytic bond strength of such bonding is as high as  $\sim 40$  kcal/mol.

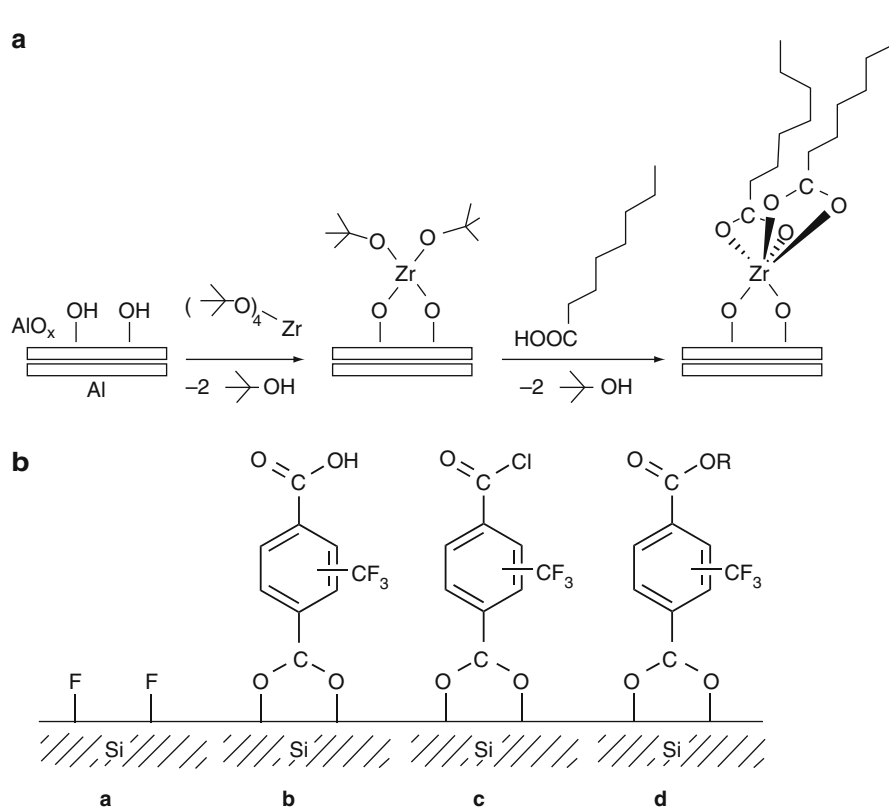
### Fatty Acid Monolayers

Long-chain  $n$ -alkanoic acids ( $C_nH_{2n+1}COOH$ ) can be spontaneously adsorbed onto the natively oxidized metal surfaces (such as  $Ag/Cu/Al$ ) to form stable assemblies. The substrate of such metal oxide is positively charged and can be regarded as Lewis acid; the ionized  $n$ -alkanoic acid is a Lewis base. So, the self-assembly is an acid–base reaction. The driving force is the formation of surface salt between carboxylate anions and surface metal cations. The as-formed SAMs are very stable, with interface ionic bonding as high as 120 kJ/mol. It was discovered that the spatial structures of the as-formed interfacial ionic bonding are not unique. To be specific, as discovered by Tao (1993), the two oxygen atoms of carboxylate bind to the  $Ag$  surface almost symmetrically and the molecular chain extends trans zigzag, forming tile angles between  $15^\circ$  and  $25^\circ$ , while on the surface of  $Cu/Al$  the carboxylate binds asymmetrically to the surface and the molecular chains pack straight up for the long chain acid (Fig. 2a). Moreover, the orientation of tail groups (i.e.,  $-CH_3$ ) vary as the carbon number in alkyl chain changes from even to odd. However, as to the orientation of the alkyl chain, contrary phenomena have been observed by Pemberton et al. (Fig. 2b, Thompson and Pemberton 1995). Such a contradiction may be caused by the different smoothness of the substrates.

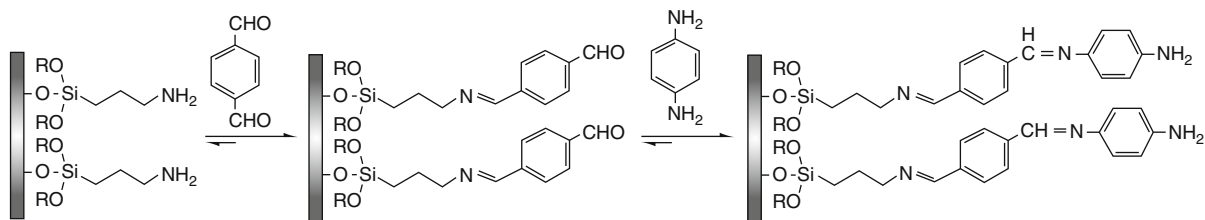
In some specific situations, interfacial covalent bonding also can be realized. For instance, mediated by an alkoxide of zirconium,  $n$ -octanoic acid can be covalently adsorbed onto the  $Al_2O_3$  surface and the as-formed SAMs is stabilized (Fig. 3a, Aronoff et al. 1997). In the case of a fluorinated silicon surface, aromatic dicarboxylic acid



**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 2** The proposed structure of *n*-alkanoic acid monolayer on different substrate



**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 3** Covalent adsorption of *n*-octanoic acid onto the Zr alkoxide treated hydroxylated Al surface (**a**) and aromatic dicarboxylic acid onto the fluorinated silicon surface (**b**)



**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 4** Formation of  $\pi$ -conjugated azomethine oligomers by controlled iminization of aromatic dialdehydes and diamines onto an amino-functionalized substrate

can be covalently bonded and can serve as an active layer to induce further assembling (Fig. 3b, Mitsuya and Sugita 1997).

### Self-Assembled Multilayer Films (SAMFs)

The exposed tail groups of SAMs not only determine the surface properties but also can serve as the reactive points to construct SAMFs. For example, the reactive tail groups, such as amine, carboxyl, hydroxyl, and epoxy, can undergo different reactions to fabricate various SAMFs. Taking advantage of the condensation between amine ( $-\text{NH}_2$ ) and aldehyde ( $-\text{CHO}$ ) groups (Fig. 4), SAMFs composed of aromatic dialdehydes and diamines can be formed on an amino-functionalized substrate (Dinglasan et al. 2002). Moreover, in Yang's group, a series of SAMFs has also been constructed based on the surface amidation between the amine tail group and carboxyl ( $\text{COOH}$ )/acid chloride ( $\text{COCl}$ ) (Song et al. 2008; Ou et al. 2009).

The  $\text{COOH}$  tail groups of SAMs are generally modified by amino compounds through amidation. However, it is well known that the amidation between  $\text{COOH}$  and amine groups is difficult to realize under normal conditions. To boost such a reaction, a dehydrating agent such as 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) is often added. Another effective way to improve the reactivity of  $\text{COOH}$  is to convert it into  $\text{COCl}$ . The  $\text{COOH}$  exposed to  $\text{SOCl}_2$  steam can be converted into  $\text{COCl}$ , which then reacts with alkyl mercaptan to produce multilayer film (Kim et al. 1995).

The tail hydroxyl is another popular group that is often used to induce the interfacial reactions. As depicted in Fig. 5, the hydroxyl group can be further modified by different reagents to construct various multilayers (Ulman 1996).

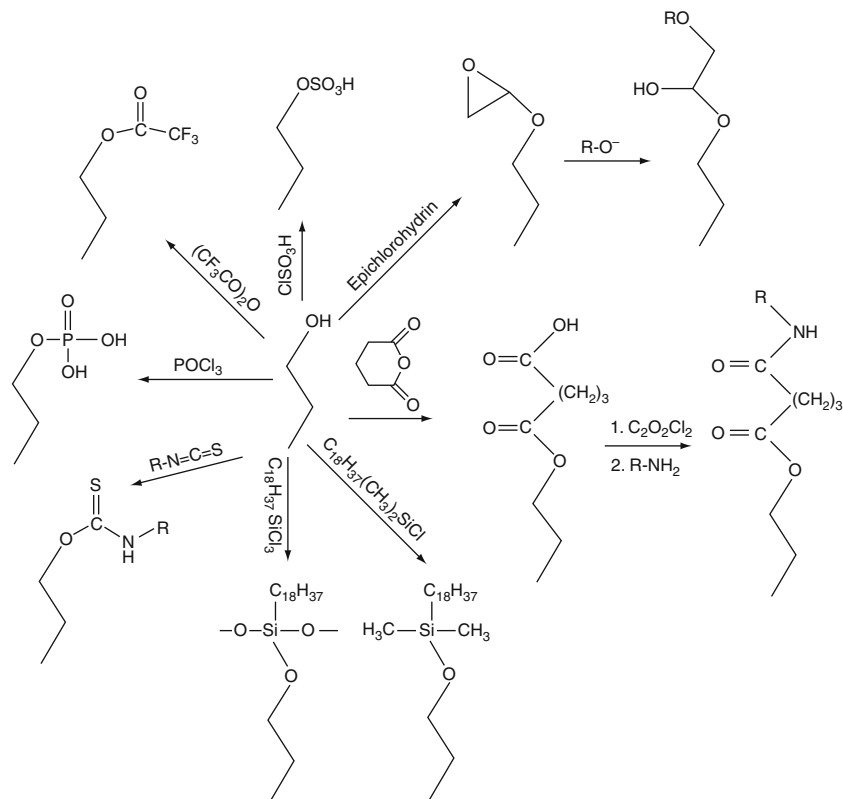
Gamma-glycidyloxypropyl trimethoxysilane (GPTMS) SAM is widely studied as the adhesive layer to construct multilayer films based on the reactions between epoxy and amine/hydroxy/carboxy (Zhao et al. 2009). For example,

taking advantage of the ring-opening reaction between epoxy and amine groups, 3-aminopropyl triethoxysilane (APTES) was grafted onto the GPTMS-SAMs. Subsequently, OTS can be further grafted onto the APTES surface by the hydrolysis-condensation process. Thus, a trilayer film (coded as GAO) composed of GPTMS, APTES, and OTS was successfully obtained (Fig. 6).

To date, the most studied SAMFs are produced by an electrostatic layer-by-layer (ELbL) self-assembly technique, which is schematically shown in Fig. 7a. Briefly speaking, this ELbL involves immersion of a charged substrate into different solutions with oppositely charged materials. In addition to the electrolytes listed in Fig. 7b, other species (such as DNA, protein, nanoparticles of  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and ions of  $\text{Tb}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Zr}^{4+}$ ) have also been incorporated into the multilayered systems (Ariga et al. 2007).

However, this electrostatic LbL technique is confined to charged materials. To expand the application of the LbL, a novel non-electrostatic LbL (NELbL) assembly technique has been invented in Yang's group (Ou et al. 2011). The newly reported polydopamine (PDA) serves as the building block due to its special nature, i.e., high adhesion to almost all solid surfaces and the active surface with functional groups (such as  $-\text{OH}$  and  $-\text{NH}_2$ ). As schematically illustrated in Fig. 8, PDA can be chemically grafted onto the amine groups of APTES-SAMs (Fig. 8, Process II) or hydroxyl groups of  $\text{ZrO}_2$  film (Fig. 8, Process IV). In addition, the  $\text{ZrO}_2$  clusters formed in the  $\text{Zr}(\text{SO}_4)_2$  solution can deposit onto the PDA surface via chelation (Fig. 8, Process III). Therefore, the sequential deposition of  $\text{ZrO}_2$  and PDA can present a novel non-electrostatic strategy to construct  $\text{ZrO}_2$ /PDA multilayer films.

On the other hand, the LbL procedure is generally performed in aqueous solution that is able to dissolve the charged materials. In 1997, Wang et al. (1997) developed a method to fabricate SAMFs in ethanol solution. It is found that the interlayer interaction is the hydrogen



**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 5** Construction of multilayers through surface reaction of hydroxyl-terminated monolayers with other groups

bonding between polyacrylic acid (PAA) and polyvinyl pyrrolidone (PVP). Thus, LbL can be expanded to the non-aqueous solution system.

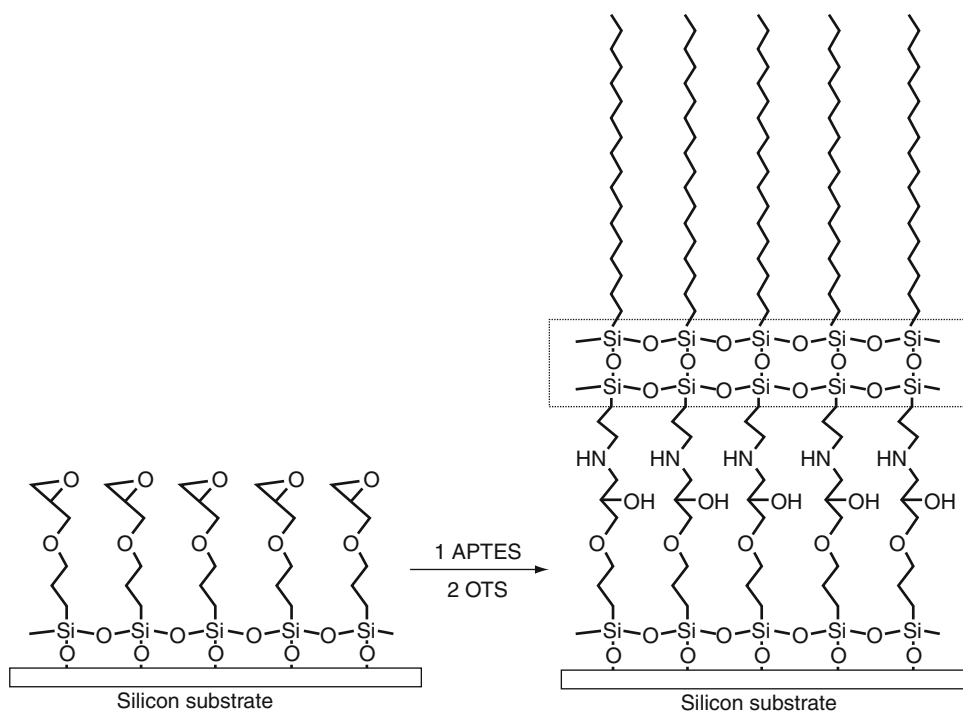
According to various interlayer interactions such as electrostatic force, hydrogen bonding, and covalent bonding, various SAMFs can be prepared successfully.

### Key Application

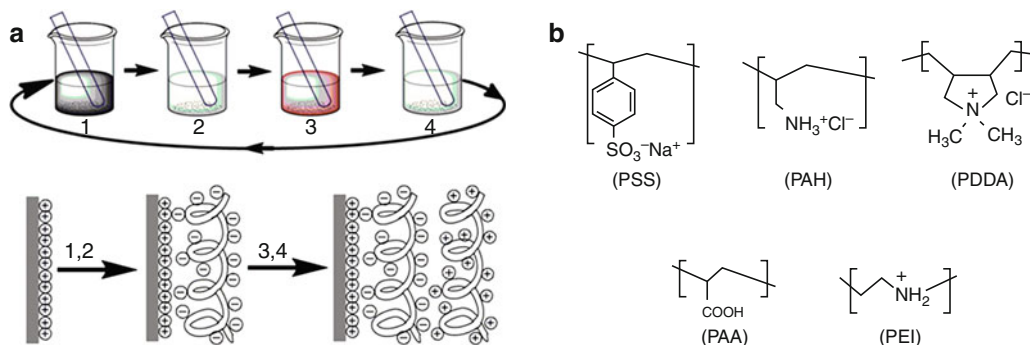
Lubricating film for micro-/nano-electromechanical systems (MEMS/NEMS)

Development of MEMS/NEMS has given rise to attempts to use ultrathin organic layers, such as SAFs, as lubricating coatings. MEMS/NEMS are featured by a diminishing gap between mating surfaces. For modern and future applications, this gap should be kept on a nanoscale level. However, owing to the miniaturization

of devices, serious stiction and friction problems occur. Treatment of surfaces by means of various coatings to reduce the stiction and friction is definitely desirable. SAFs are ideal candidates for lubricating film in MEMS/NEMS, not only for the dimension matching but also for its simple preparation process (Tsukruk 2001). Taking the well-studied OTS-SAMs as an example, SAFs suitable for lubricating film should meet some requirements; a strong interfacial binding (Si–O–M, M is the atom of the substrate) is needed to enhance the stability of the film, a long alkyl chain [–(CH<sub>2</sub>)<sub>17</sub>–] related to the load-carrying capacity is preferred. Moreover, the hydrophobic tail group (–CH<sub>3</sub>) determining the adhesion/friction force is also necessary. It was found that OTS-SAMs possessed much lower friction coefficient and greater load-carrying capacity as compared with APTES-SAMs.



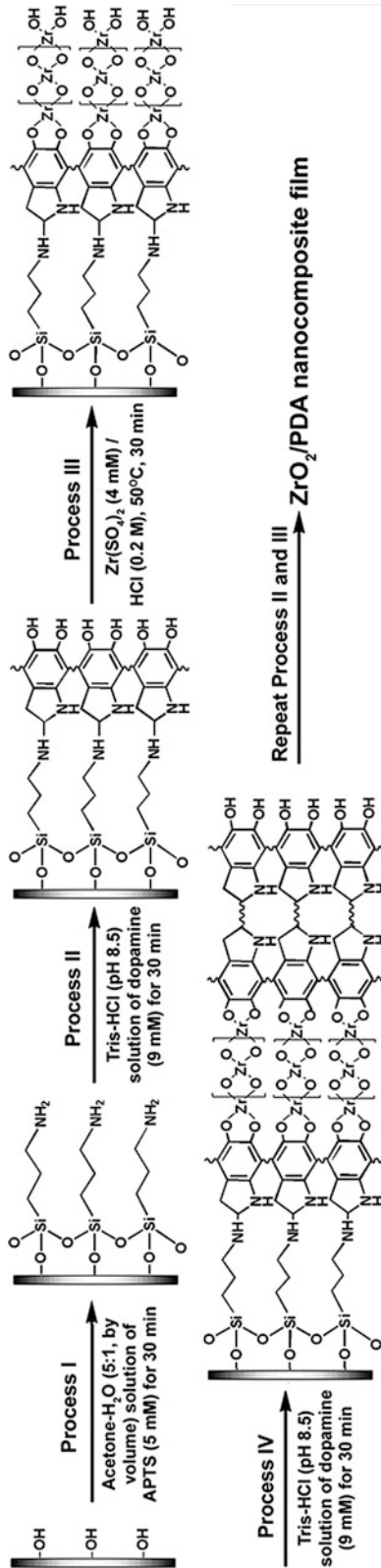
**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 6** Grafting of APTES onto the GPTMS-SAMs via epoxy ring opening and further modification with OTS to construct self-assembled multilayer film



**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 7** The schematic view for the process of ELBL (a); chemical structures of the typical polyelectrolytes used in ELBL (b)

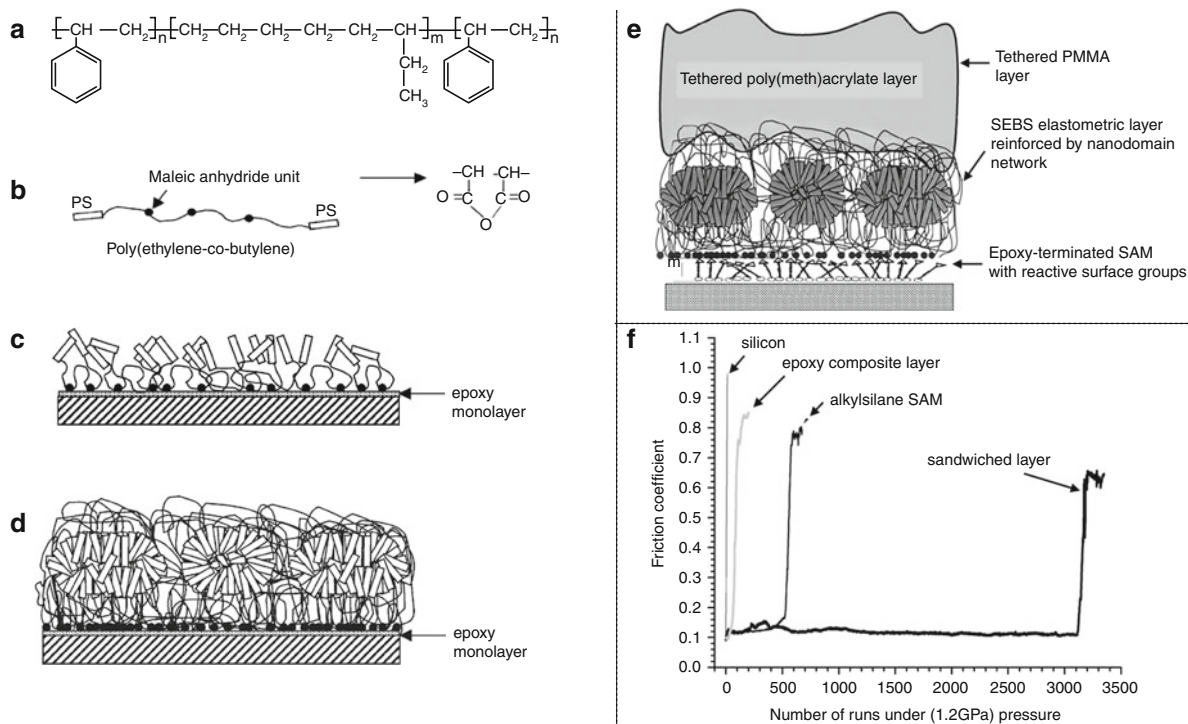
A lot of effort has gone into improving the tribological performance of SAFs by constructing various SAMFs. Especially, the interchain interaction within SAMFs is enhanced and the load-carrying capacity is expected to be improved

(Song et al. 2008). For example, a series of dual-layer SAMFs has been constructed and the interchain hydrogen bonding is thought to be responsible for the lengthened anti-wear life at a high applied load of 0.3 N (Song et al. 2008).



Solid-Like Lubricating Films, Self-Assembled Films, Fig. 8 A schematic view for constructing  $ZrO_2$ /PDA SAMF





**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 9** Chemical (a) and schematic (b) structure of SEBE; SEBS layer with disordered structures and a thickness <math>< 2.5\text{ nm}</math> (c); SEBS layer with nanodomain morphology and a thickness <math>< 2.5\text{ nm}</math> (d); Architecture of sandwiched trilayer (e); Friction coefficient versus the number of reciprocal sliding runs for different samples (f)

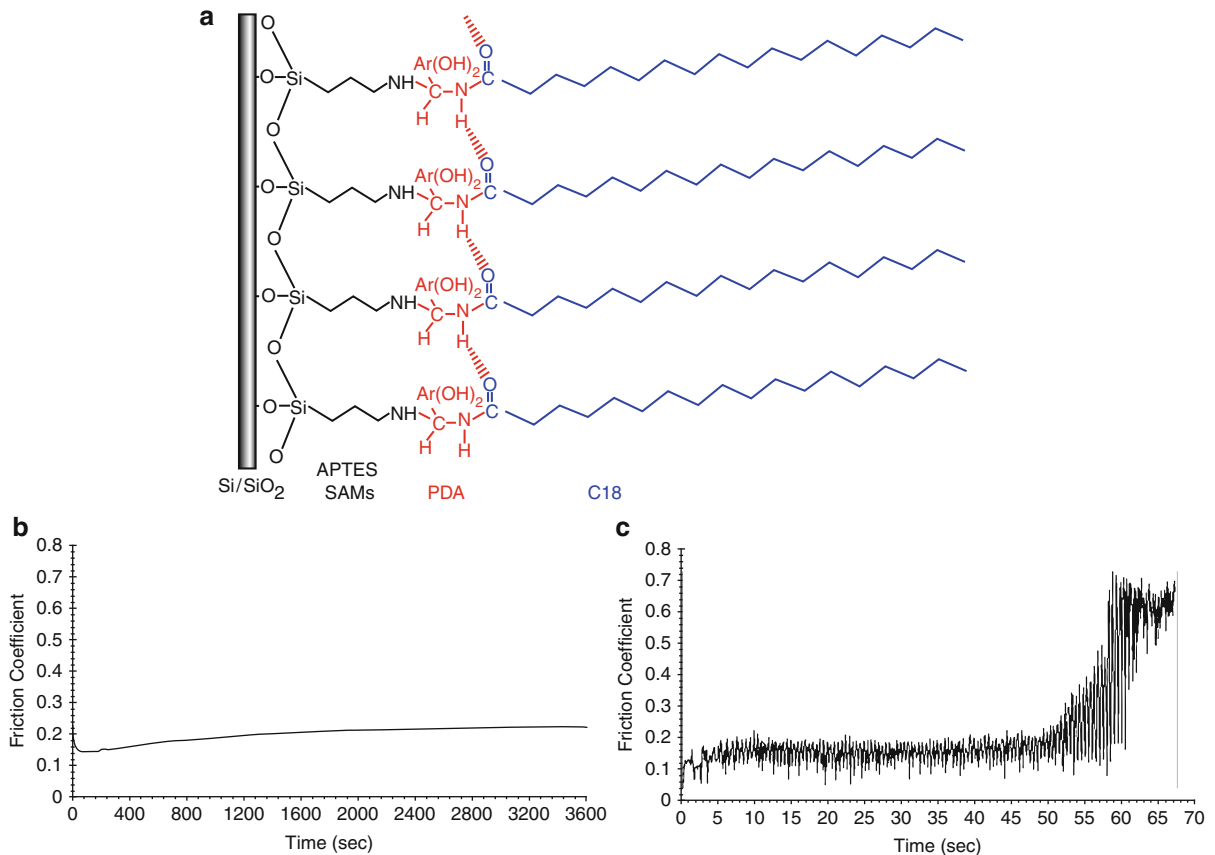
The polymer-based SAFs with cross-linking network structures can sustain high compression and shear stress. For example, a copolymer of poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (coded as SEBS, Fig. 9a, b) functionalized with 2% maleic anhydride into the hydrocarbon chains was assembled onto the surface of epoxy-terminated monolayer (Fig. 9c, d, Luzinov et al. 2001). The as-fabricated films possess low friction coefficient, modest adhesion, low stiction, and good wear stability as well. To further improve the wear resistance, a SAF with trilayer sandwiched architecture has been constructed (Fig. 9e, Sidorenko et al. 2002). As expected, the anti-wear life is much longer than that of the epoxy composite layer (Fig. 9f).

Most recently, inspired by the structures of SAMs, a tri-layer film composed of an APTES underlayer (behaving as the head group in SAMs), a PDA interlayer (as the alkyl chain in SAMs), and stearoyl chloride (as the tail

group in SAMs) was prepared. The carrying-capacity of this tri-layer film was further boosted as compared with the corresponding dual-layer SAMFs without PDA interlayer (Fig. 10, Ou et al. 2009).

As discussed above, various SAFs with properties of low friction and good wear resistance have been investigated extensively as lubricating coatings for MEMS/NEMS. These fundamental works have generated the basic understanding of microtribology. To develop practical lubricating SAFs in MEMS/NEMS, however, there are still challenges to be overcome. For example, to date, most of the lubricating SAFs studied have been constructed on a smooth silicon substrate, whereas the actual surface in MEMS/NEMS is much more complicated and multifarious. Therefore, more versatile assembling processes and systems should be developed and more work is needed.





**Solid-Like Lubricating Films, Self-Assembled Films, Fig. 10** A schematic view for the formation and combination bonding of the three-layer film on silicon wafer (a); The macrotribological behaviors of the tri-layer SAMFs (b) and the dual-layer SAMFs without PDA interlayer (c)

## Cross-References

- ▶ [Anti-Adhesion/Stiction Surface Design, Fabrication, and Applications](#)
- ▶ [Asperities](#)
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- ▶ [Bonding at Surfaces/Interfaces](#)
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- ▶ [X-Ray Photoelectron Spectroscopy \(XPS\)](#)

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## Solid-Liquid Bi-phase Lubricating Coatings

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### Synonyms

[Adhesion and lubricious coatings](#); [Adsorption](#); [Boundary lubrication by lubricious coatings](#); [Friction and coatings](#); [Lubrication through coatings](#); [Lubricious diamond-like carbon coatings](#); [Wear of coatings](#)

### Definition

In spite of the low chemical activity and “inertness” of DLC coatings, it has become clear in recent years that some DLC coatings react with additives and form various tribochemical products and films. However, these interactions are weaker, the tribofilms are thinner, and they are less wear resistant in comparison to steels. At the same time, the importance of the various physical effects of the fluid (oil) and the well-known, wear-protective, and low-friction nature of the DLC coatings themselves with regard to tribological behavior are almost totally unclear. In other words, the roles of the different “components” in the boundary lubrication of DLC coatings, i.e., the contribution of the additives, the base oils, and the DLC coating itself are not fully understood. Therefore, in this work an attempt to elucidate some of the aspects of these questions

related to the physical properties of base oils, the adsorption of oil films and their strength, the DLC coatings and avoiding the chemical effects of the oils or additives is presented. Results show a dramatic improvement with the use of a base oil – particularly when it has high viscosity – on DLC coatings’ wear and durability, but just the contrary – a friction increase – when compared with non-lubricated DLC contacts. Based on some specific quasi-static experiments it is also suggested that base oil films might adsorb at the DLC surface and protect it against wear.

## Scientific Fundamentals

### Introduction

Modern mechanical systems need to operate under demanding working conditions, such as high loads, high speeds, high temperatures, and adverse environments. Furthermore, in milder conditions better results are expected today than in the past. Sometimes reduced production costs are also required, for example, by reducing the amount of surface finish. Under lubricated conditions, which represent the vast majority of all mechanical systems, this suggests that lubrication is changing from the hydrodynamic to the mixed or boundary regime, where direct contacts between surfaces are dominant. In addition, many systems regularly operate under conditions of poor lubrication, due to starved lubrication or the nature of the loading conditions. The successful operation of tribological contacts and thus the whole system is therefore dependent on the properties of the surfaces and the ability to form wear-protective and low-shear, tribochemical, boundary-interface films.

Around the world there are various attempts to solve these problems, including the development of better oil additives, new wear-reducing and low-friction coatings, multi-layered and “smart” nano-structured coatings, chameleon surfaces, and textured surfaces. The boundary lubrication of DLC coatings is among the efforts toward addressing these problems (Matthews et al. 1998; Erdemir and Donnet 2006; Velkavrh et al. 2008; Kalin et al. 2008; Neville et al. 2007). DLC coatings are known for their high hardness, low-friction properties, good wear resistance, and, typically, poor wetting and “inertness” (i.e., a low surface energy) (Sanchez-Lopez et al. 2003; Kalin et al. 2009). Inertness, which is an important property for low oxidation, corrosion, and adhesion prevention, is also a drawback for successful boundary lubrication, where interactions and tribochemical reactions between the surface and the lubricants are required to ensure low friction and low wear. Namely, oil additives that are currently