

Tunable water-based lubrication behavior of alkyl- and fluoroalkyl-silanes

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In this paper, we report the tribological properties of self-assembled molecular (SAM) films of fluoroalkylsilanes and non-fluoroalkylsilanes, with different chain-lengths, adsorbed on Si substrate surfaces by covalent bonds. The SAM films were characterized using a universal ball-disk experimental tester in aqueous solutions. The substrate surface was examined by X-ray photoelectron spectroscopy (XPS), and the SAM films adsorbed on the Si surfaces were inspected by contact angle measurements and XPS. Lubrication studies revealed that several kinds of fluoroalkylsilanes had similar friction coefficients; the small differences were attributed to the chain flexibility. In contrast, differences in the aqueous lubrication properties of SAM films of non-fluoroalkylsilanes were clearly identified. It is suggested that substitution with fluorine atoms and the surface affinities of fluoroalkylsilanes contributed to redistribution of surface changes, causing variations in lubrication behaviors.

water-based lubrication, wettability, self-assembled molecular films

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Friction is a common phenomenon in engineering, and much energy is wasted because of serious friction or wear between moving parts. Much effort has been devoted to controlling energy dissipation during surface interactions. Also, micro/nano-electromechanical systems (MEMS/NEMS), the use of which has increased in recent decades, have many other tribological problems [1–4]. As the dimensions of a system decrease, the surface area/volume ratio increases. This could cause surface forces such as adhesion and friction to predominate over inertial forces [5]. Tribological limitations such as stiction, friction, and wear are major problems that limit the efficiency, power output, and reliability of these devices [6–8].

Although Si is the material most used in MEMS/NEMS components, the tribological performance of Si is very poor. Nanometer-thick organic self-assembled molecular (SAM) films are potential candidates as lubricants for improving the performance of MEMS and NEMS. Recently, much attention has been paid to self-assembled monolayers be-

cause they are easy to prepare, and they have excellent properties such as low thickness, stable physical and chemical properties, and good covalent bonding with substrates [9]. Moreover, the properties of SAM films can be extended by changing the lengths of the molecules, the type of terminal group, and the degree of cross-linking within the layer. In particular, fluorinated organic thin-films have been much studied because of their unique chemical stabilities and anti-adhesive properties [10–12]. Organosilane ultrathin films have been identified as promising boundary lubricants. This is because organosilane molecules interact strongly with substrates and their thicknesses are commensurate with the dimensions of the structures in these applications [13]. The introduction of fluorine could lead to enhanced intra- and inter-molecular steric interactions for bulky CF₃-terminated films, and the corresponding lateral steric interactions can plausibly occur over distances sufficiently long to permit the propagation of surface phonons [14]. These properties make them good candidates for use in micro/nano devices. Alkylsilane SAM films have therefore been extensively studied, and proposed as lubricants for MEMS [15–18]. It is

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known that roughness has a significant effect on the friction characteristics of solid surfaces [19–21]. Moreover, nanometer-thick films of organic self-assembled molecules, which have been used to modify the chemical nature of surfaces, have been shown to be good lubricants for improving the tribology of MEMS/NEMS devices [22].

Considering the hydrophobic properties of decorated surfaces and their interactions with water molecules, the aim of our present work is to study the tribological properties of SAM films, made using a series of alkylsilanes with different chain-lengths and fluorinated substituents on the surface of the Si wafers, under water lubrication conditions. This is different from our previous work [23,24], in which SAM films were investigated without any lubricants. The frictional characteristics of SAM films and their hydrophobicities can be studied with high reproducibility. The experimental results for perfluoroalkylsilane and non-perfluoroalkylsilane molecular films were compared in detail. The influences of the sliding velocity, the normal load, and the carbon-chain length of the alkylsilane molecular film on the friction coefficient were also evaluated. All the results showed that alkylsilane SAM films have great potential in technology and engineering applications.

1 Experimental

1.1 Materials

A single-crystal p-type Si (100) substrate (GRINM Semiconductor Materials Co., Ltd.) was used as received without further rinsing. Octyltrichlorosilane (denoted as C8, purity 97%) and decyltrichlorosilane (denoted as C10, purity 97%) were obtained from Acros Organics and Aldrich, respectively, and used without any further purification. 1H,1H,2H,2H-Perfluorooctyltrichlorosilane (denoted as C8F, purity 97%) and 1H,1H,2H,2H-perfluorodecyltrichlorosilane (denoted as C10F, purity 96%) were purchased from ABCR GmbH & Co. and Lancaster Synthesis, respectively. Chloroform, hydrofluoric acid, ammonia, vitriol, hydrogen peroxide, and toluene were bought from Beijing Jinxin Chemical Factory (AR grade). All solutions were prepared with Millipore (Milli-Q) water.

1.2 Substrate preparation

A single-crystal p-type Si (100) Si wafer polished on one side was cut into pieces of approximately 1.5 cm by 1.5 cm before cleaning and modification. The wafers were first cleaned by the following procedure: (1) ultrasonic degreasing in chloroform, acetone, and ethanol for 5 min each, followed each time by 10 min of supersonic rinsing in distilled water to remove any possible contaminants; (2) etching in hydrofluoric acid (40%) at room temperature for 30 s to remove the natural oxide layer; (3) cleaning and oxidizing by heating at 90°C in piranha solution (98% H₂SO₄:H₂O₂ =

7:3, v/v) for 30 min. The wafers were rinsed with water between each step. The cleaned wafers were immediately transferred to a cyclohexane (chromatographic purity) solution of octyltrichlorosilane (or another silane) with a volume ratio of 1:500 and incubated for 15 h to allow formation of molecular films. The wafers were then immersed in each of cyclohexane, acetone, and ethanol, and thoroughly supersonically rinsed to remove unbound silanes. The solvent was completely vaporized using high-purity nitrogen gas, to give a Si (100) substrate covered with the assembled molecules. Chemical adsorption of the Si–O covalent bond resulted in single-crystal Si wafer substrates modified by self-assembled alkylsilanes; this is shown schematically in Figure 1.

1.3 Apparatus and measurements

The bare Si wafer and the Si wafer decorated with molecular films of trichlorosilanes were characterized by X-ray photoelectron spectroscopy (XPS) to confirm the existence of SAM films on the Si substrates. The experiments were carried out using a PHI Quantera (ULVAC-PHI, Inc.) scanning X-ray microprobe. A monochromated Al K α line (1486.7 eV) was used as the excitation source. The binding energy was calibrated against the C1s peak of the carbon contaminant at 284.8 eV.

The contact angles of the surfaces with trichlorosilane molecular films were measured with a JC2000A (Shanghai, China; precision: $\pm 0.1^\circ$) under ambient conditions. Water droplets (2 μ L) were dripped carefully onto the surfaces of the molecular film and the Si wafer. The average contact angle was obtained by measuring three different positions of the same sample.

The thicknesses of the alkylsilane molecular films were measured using a Multiskop ellipsometer (Optrel GBR; $a = 532$ nm, angle of incidence = 70°). The thicknesses of the C8 and C10 alkylsilane molecular films were calculated using refractive indexes of 1.447 and 1.452, respectively; the results were 1.0 nm and 1.2 nm [25] (Table 2), which is consistent with the tilt from the surface normal expected in these systems. Each reported value is the average of at least

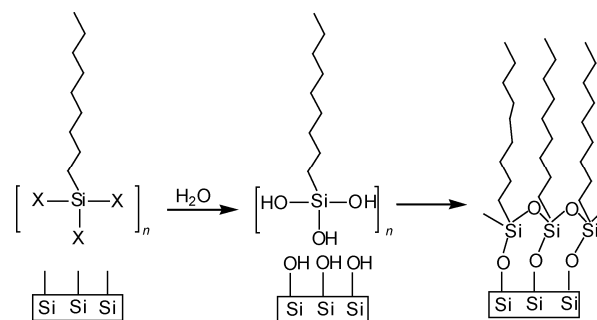


Figure 1 Schematic diagram of the mechanism of trichlorosilane assembly on a single-crystal Si wafer.

15 measurements obtained from the samples.

Tribological experiments were conducted in an ambient atmosphere in aqueous solutions at a temperature of about 28°C and a relative humidity of 35%. The amount of water used as a lubricant was 50 μL . A ball-on-disk universal microtribometer (UMT-2, CETR, rotary style) was used to evaluate the frictional properties of the prepared samples. An Si_3N_4 ball was fixed at the top of the pin on the tribometer's counterpart in these experiments. The diameter of the ball was about 4 mm, and its surface roughness (R_a) was approximately 14 nm. The normal load was used in the range 0.8–3 N. The friction force curves and the coefficient of friction versus time were measured and recorded simultaneously.

2 Results and discussions

Parallel XPS experiments were performed to characterize the Si wafer surface and the SAM films on the Si substrate, as shown in Figure 2. Table 1 summarizes details of the binding energies and chemical compositions. It can be seen that the cleaned Si wafer had prominent O1s and Si2p peaks, which indicated that hydroxyl groups were also present in the substrate. The low-intensity C1s (the binding energy is about 284 eV) peak in the XPS spectrum of the Si surface is probably caused by organic contaminants adsorbed from the atmosphere during specimen preparation for the XPS measurements. The photoemission intensity of the C1s peak from the organic contaminant is considerably lower than those of the alkylsilane-modified surfaces. As a result of the adsorption of alkylsilane molecules, the binding energy of the C1s peak (283 eV) in the C8/Si and C10/Si spectra is different from that of the peak arising from the carbon contaminant (284 eV). According to the standard test data for XPS, the C1s peak at about 283 eV is attributed to the carbon atoms of the methylene group in non-fluorinated alkylsilanes. The differences between the photoemission intensities and the binding energies of the bare Si surface and surfaces decorated with alkylsilane molecules confirm successful deposition of C8 and C10. The high atomic concentration of F1s (binding energy: 688 eV) in the spectra of C8F/Si and C10F/Si confirms the formation of C8F and C10F on the Si wafers.

The results of water contact angle measurements on the surfaces of bare Si and on Si modified with alkylsilane molecular films are shown in Figure 3. The images in Figure 3 show the static water contact angle with a water droplet (2 μL). The contact angles of Si, C8/Si, C10/Si, C8F/Si, and C10F/Si were 67°, 111°, 114°, 119°, and 128°, respectively. For ease of comparison, all the data on the water contact angle of the bare Si substrate and those of substrates decorated with alkylsilane molecular films are summarized in Table 2. Obviously, bare Si is relatively hydrophilic and modification by fluorinated and non-fluorinated silane

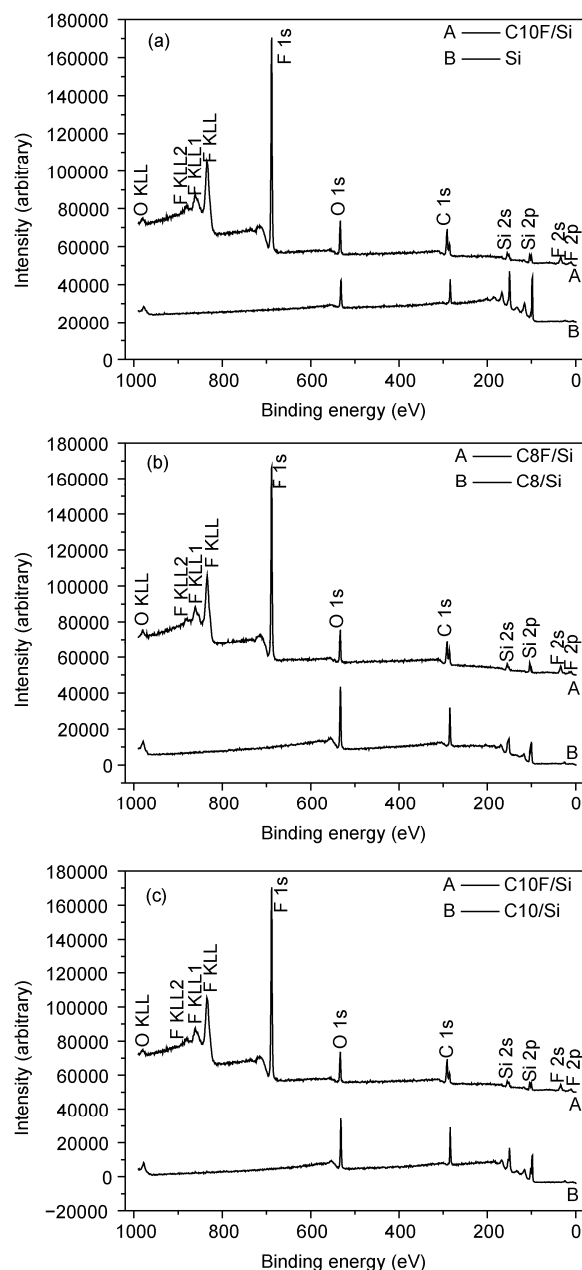


Figure 2 XPS spectra of bare Si and Si surfaces modified with fluoroalkyl- and non-fluoroalkyl-silane molecules: (a) bare Si and C10F/Si, (b) C8/Si and C8F/Si, and (c) C10/Si and C10F/Si. The C8F/Si and C10F/Si spectra were shifted up by 50 000 units in parallel.

Table 1 XPS binding energies (EB \pm 0.02 eV) of the different peak components^{a)}

	Si2p	C1s	O1s	F1s
	B.E.(eV)	B.E.(eV)	B.E.(eV)	B.E.(eV)
Si	98	284	557	
C8	98	283	555	
C10	98	283	553	
C8F	104	286	555	688
C10F	100	286	557	688

a) B.E: Binding energy.

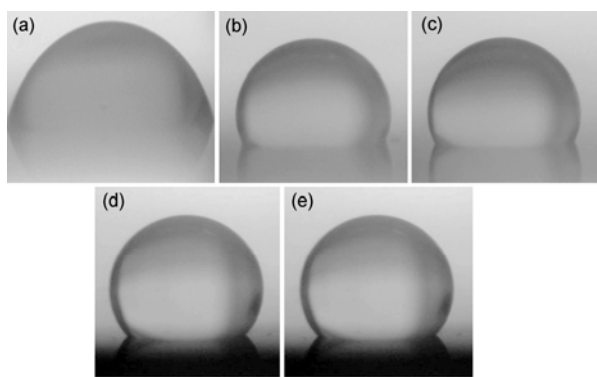


Figure 3 Images of water droplet (volume: 2 μL) on the surfaces of (a) bare Si, (b) C8/Si, (c) C10/Si, (d) C8F/Si, and (e) C10F/Si.

Table 2 Contact angles and thicknesses of the self-assembled molecular films

Samples	Contact angle	Thickness (nm)
Si	67°	
C8/Si	111°	1.0
C10/Si	114°	1.2
C8F/Si	119°	2.8
C10F/Si	128°	4.3

molecules could significantly improve the hydrophobicity of the bare Si substrate. The larger water contact angles of C8F and C10F adsorbed on the bare Si substrate compared with those of C8 and C10 adsorbed on the bare Si substrate may be caused by fluorination of the methyl and methylene groups, leading to lower surface energies of C8F and C10F. As a result, the electrical affinity increased significantly for perfluorinated substitution [26]. This means that the ability of fluorosilanes to accept electrons is stronger than that of non-fluorinated silanes. Furthermore, the substitution of fluorine atoms could enhance the Van der Waals interactions between the silane molecular chains, resulting in better ordering of the SAM films; this improves the hydrophobicity of the SAM films. A comparison of the water contact angles of C8F and C10F molecular films decorated on the Si substrate (Table 2) shows that the carbon-chain length has a slight effect on the static contact angles; in other words, the longer carbon-chain of C10F molecules results in excellent hydrophobicity because of the stronger interactions between the carbon chains of the C10F molecules than between those of the C8F molecules.

The thicknesses of the alkylsilane molecular films were investigated using a Multiskop ellipsometer. The thicknesses of the C8, C10, C8F, and C10F films are 1.0 nm, 1.2 nm, 2.8 nm, and 4.3 nm, as is shown in Table 2. It can be concluded from the data that the C8 and C10 molecular films are monolayers and the C8F and C10F are not monolayers, based on the lengths of the molecules. The monolayer film thicknesses of the C8 and C10 films were estimated based on the C–C bond length (0.154 nm) in saturated alkanes.

The calculated results for C8 and C10 were about 1.078 nm and 1.386 nm, respectively; these values correspond to our experimental results for non-fluorinated silane molecules. The formation of multilayer films of C8F and C10F on the substrates is attributed to hydrolysis of C8F and C10F; this means that two or three fluorinated alkylsilane molecules first cross-linked with each other, and then covalently bonded to the Si substrate. As is known, the fluorination of alkylsilanes increases the polarity of the Si–Cl bond as a result of their electrical affinities, and this makes hydrolysis of C8F and C10F molecules easier.

For further investigation of the tribological properties of the bare Si substrate and the surfaces modified with SAM films of fluorinated and non-fluorinated alkylsilanes with different chain-lengths, variations in the curves of friction coefficients versus time in the sliding-velocity range 3–120 mm/s were measured using water as a lubricant, as shown in Figure 4.

Repeated measurements on independently prepared samples produced similar results. The friction coefficients of the Si substrate and of the substrate modified by fluorinated and non-fluorinated alkylsilane increase with increasing sliding-velocity after the running period, although this effect is not obvious at low sliding-velocities; this is a result of enhancement of the shear force during the friction process. It can be seen from Figure 4(a) that the friction coefficients of bare Si under conditions of aqueous lubrication are much lower than that under dry conditions, which is about 0.7, as shown in our previous experiments [23]. In contrast to the results of the friction experiments performed in the dry state, it can be observed that all four alkylsilane SAM films sustain a higher sliding-velocity under conditions of aqueous lubrication. When the sliding velocity reached 200 mm/s, only C8/Si (Figure 4(b)) and C10/Si (Figure 4(c)) were destroyed after a sliding time of 200 s. These results could be attributed to lubrication by water. In these experiments, the amount of water used as a lubricant was 50 μL , and the water formed a thin film around the Si_3N_4 ball during the sliding process after the running period; this can be regarded as thin-film lubrication. It is also seen that the friction coefficients of Si modified with self-assembled alkylsilane molecules are lower than those of the bare Si at the same sliding velocity conditions, when the SAM films were not damaged. Comparing the friction coefficients of C8/Si and C10/Si in Figure 4(b) and (c) with those of C8F/Si or C10F/Si in Figure 4(d) and (e), it is shown that C8F/Si and C10F/Si are less sensitive to variations in the sliding velocity, and more durable at higher sliding-velocities because the SAM films of fluorine-substituted alkylsilanes are very stable and ordered. This result is the same as that in our previous work [23,24], and could be explained as follows. In aqueous solutions, perfluoro-carbon chains adopt a helical conformation and consequently possess larger cross-sections than those of simple hydrocarbon chains, resulting in a strong ability to endure

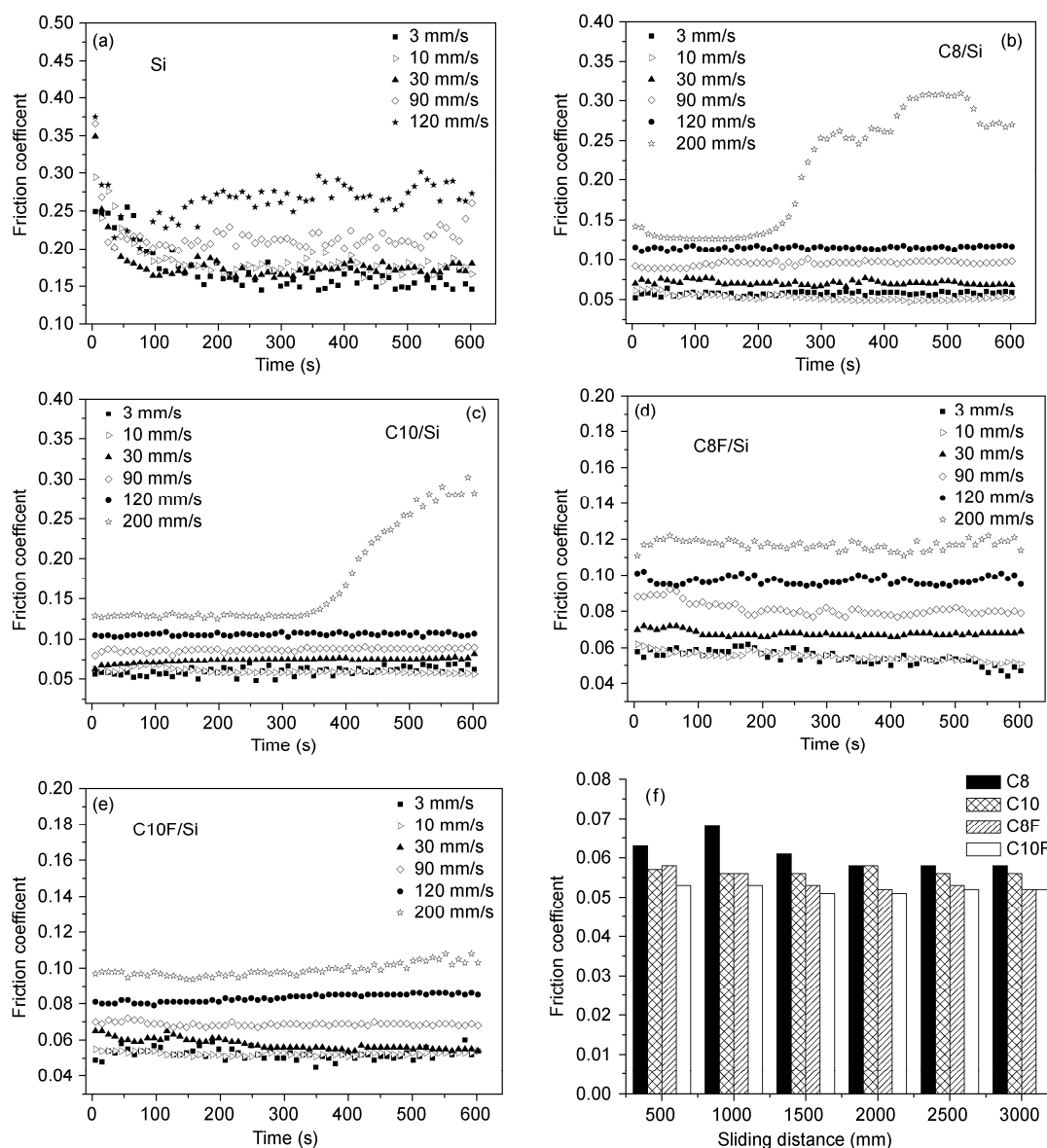


Figure 4 Variations in the friction coefficients over time at load of 80 g for a steel ball sliding against (a) Si, (b) C8/Si, (c) C10/Si, (d) C8F/Si, (e) C10F/Si, and (f) C8/Si, C10/Si, C8F/Si, C10F/Si at a sliding velocity of 10 mm/s, under water lubrication conditions.

high sliding-velocities, even though the perfluorocarbon chains are more rigid than hydrocarbon chains, and high resistance to oxidation and corrosion [27]. Another important phenomenon to note is that the differences between the friction coefficients of C8/Si and C10/Si and those of C8F/Si and C10F/Si, i.e., between hydrocarbon chains and perfluorocarbon chains, are much smaller than those we observed in the dry-state experiments. This may be caused by interactions between the water molecules and the carbon chains, which would reduce the differences between the conformations of the perfluorocarbon chains and the hydrocarbon chains. For ease of comparison, the friction coefficients of the C8/Si, C10/Si, C8F/Si, and C10F/Si surfaces at a sliding velocity of 10 mm/s are summarized in Figure 4(f). It can be seen that the friction coefficients de-

creased as the hydrophobicities of the alkylsilane SAM films increased. We therefore know that the wettability has an influence on the tribological properties of the surfaces, i.e., the more hydrophobic the surfaces are, the lower the friction coefficients are. A possible reason could be adhesion. As we mentioned above, the much more hydrophobic C8F and C10F have lower surface energies, as the contact angle measurements show, so the adhesion force between C8F/C10F and the steel ball should be less than that between C8/C10 and the steel ball [28], leading to lower friction. The carbon-chain lengths of the alkylsilane molecular films also have a slight effect on the friction coefficient. It has been shown that the adhesion force decreases with increasing chain-length [29], therefore the friction of C10F/Si is lower than that of C8F/Si.

As well as investigating the effects of sliding velocity on the friction coefficients, we also studied the influence of a normal load on the tribological properties of alkylsilane SAM films at a sliding velocity of 10 mm/s, as shown in Figure 5. It is clear that as the normal load increases, the friction coefficients increase accordingly. This is the same as the findings of our previous work [23]. The difference between the results for dry-state experiments and those with aqueous lubrication is that before the normal load reached 300 g, the four alkylsilane SAM films showed good pressure resistance because the thin water-film around the steel ball effectively reduces the friction coefficient. It was also confirmed that enhancing the hydrophobicity of the surface reduced the friction coefficient; this agrees with the results presented in Figure 5(f).

3 Conclusions

In summary, we successfully fabricated four kinds of alkylsilane SAM films on Si substrates and systematically studied their tribological properties, including the influence of sliding velocity and normal load under conditions of aqueous lubrication. With respect to wettability, the effects of the surface morphologies at the micro- and nano-scales and the variations in chemical composition at the surface, for fluorinated and non-fluorinated alkylsilanes, were discussed. We obtained relatively low friction coefficients for high sliding-velocities or normal loads using SAM films of fluorinated alkylsilanes on Si substrates. The conclusions drawn from these results will help us to design systems, using chemical methods, with improved frictional properties.

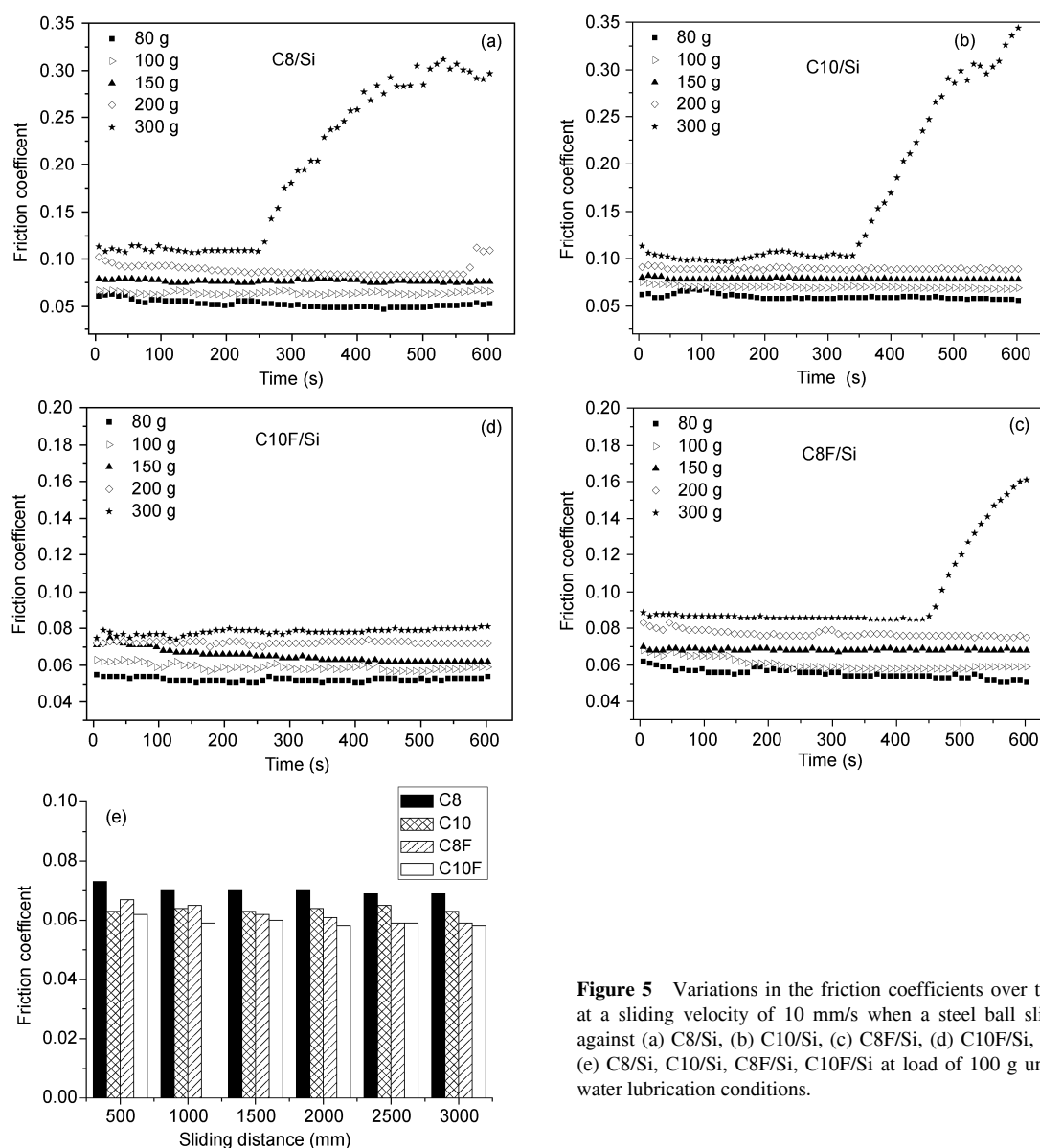


Figure 5 Variations in the friction coefficients over time at a sliding velocity of 10 mm/s when a steel ball slides against (a) C8/Si, (b) C10/Si, (c) C8F/Si, (d) C10F/Si, and (e) C8/Si, C10/Si, C8F/Si, C10F/Si at load of 100 g under water lubrication conditions.

Such low-friction systems have potential applications in MEMS/NEMS and microfluidic devices.

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