

# Wettability and Nanotribological Property of Multiply Alkylated Cyclopentanes (MACs) on Silicon Substrates

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*The geometrical microstructure together with the chemical composition of the surface governs the wettability of solid surfaces, which is very important in the study of nanoadhesion and nanofriction properties of surfaces. Multiply alkylated cyclopentane (MAC), a novel hydrocarbon mobile lubricant, was deposited on silicon by a dip-coating method. In order to investigate the influence of the surface microstructures on the wettability of MACs, silicon substrates were treated by different cleaning and etching processes. Measurements of an atomic force microscope and a contact angle meter indicate that the wettabilities of MACs on the hydroxylated silicon and the hydrogenated silicon are better than the wettability on the cleaned silicon, and that superiority is mainly caused by topological structure changes of the surface. Furthermore, the nanoadhesion and nanofriction properties were investigated. The different behaviors in adhesion and friction forces are due to the different surface energies of these silicon substrates.*

## KEY WORDS

Etching; Hydroxylated; Hydrogenated; Nanoadhesion Force; Nanofriction Force

## INTRODUCTION

Microelectromechanical systems (MEMSs) have obtained rapid development in the past decades due to their superior performance and low unit cost (Spearing (1)). However, large surface area-to-volume ratio causes serious adhesive and frictional problems for MEMS operations (Bhushan, et al. (2)). One method to alleviate the problems of adhesion and friction is to coat the surface micromachining, involving the fabrication of micromechanical structures with thin films (Howe (3); Muller (4); Petersen (5)). It is well known that self-assembled monolayers (SAMs) are good lubricants for MEMS (Bhushan (6);

Bhushan and Liu (7); Liu and Bhushan (8)). However, because of low molecular flexibility and mobility, SAMs exhibit low carrying load capacity and poor durability (Ruehe, et al. (9); Patton, et al. (10); Rye, et al. (11)). Besides SAMs, perfluoropolyether (PFPE) films, which have excellent viscosity, thermal stability, and low volatility, are also considered as potential candidate lubricants for microelectromechanical/nanoelectromechanical systems (MEMS/NEMS) (Sundararajan and Bhushan (12)). Yet they are susceptible to catalytic degradation on metal surfaces and tend to cause metal fluoride corrosion (Jones, et al. (13); Paciorek and Kratzer (14); Kasai (15); Helmick, et al. (16); Mori and Morales (17)). Better lubricants for MEMS with longer durability and better tribological performance are needed.

Multiply alkylated cyclopentanes (MACs), which are novel hydrocarbon mobile lubricants, are composed of one cyclopentane ring with from two to five alkyl groups substituted on the ring. They are synthesized by reacting dicyclopentadiene with alcohols of various chain lengths, producing a lubricant with a selectable range of physical properties (Venier and Casserly (18); Ma, et al. (19), (20)). Currently, the MAC is a mixture of the di- and trisubstituted (2-octyldodecyl) cyclopentanes. MACs have excellent viscosity properties, thermal stability, and low volatility for use as lubricant and are presently gaining wide acceptance on actual space application (Venier and Casserly (21); Dube, et al. (22)). Furthermore, MACs can be readily fortified with application-specific additives and offer good thermo-oxidative stability and chemical compatibility (Akin and Shea (23)). MACs' unique properties make them well suited to the demands of MEMS application. However, as far as we know, use of MACs to achieve excellent tribological properties for MEMS application has not been reported. The surface tension of one commercially available MAC fluid is approximately 30 dyn/cm at room temperature. They offer better film strength, coat moving parts, reduce oil creep, and protect loaded components, yet it may be too high for the successful operation of MEMS. MACs have been observed to de-wet bearing steel surfaces (Pochard, et al. (24)) and we wondered if this represented a long-term threat to bearing life. So we intended to study the wettability of MACs on different surfaces to obtain better adhesion and friction properties for MEMS operations.

Wettability is one of the most important properties of solid surfaces and has attracted much attention since the time of Young in 1805 (Young (25)). It is governed by both chemical composition and topological characteristic of the surface. Controlling wettability is quite important in the study of nanoadhesion and nanofriction properties. Since silicon has been the most widely used material in MEMS (Spearing (1)), it may have the largest potential in the application of lubrication for MEMS. In this article, we studied the wettability of MACs on silicon substrates treated by different cleaning and etching processes. The nanoadhesion and nanofriction properties were also measured by an atomic force microscope, which has been widely used in the fields of materials science and nanotribology because of its high spatial resolution, high force measurement sensitivity, simplicity of operation, and ability to image a wide range of materials under a variety of conditions (Sarid, et al. (26); Binnig, et al. (27); Tsukruk and Bliznyuk (28); Quate (29)).

## EXPERIMENT DETAILS

### Materials

P-doped single-side polished single-crystal silicon (100) wafers (obtained from GRINM Semiconductor Materials Co. Ltd., Beijing, China) that were about 0.5 mm thick were used as the substrate. MACs were synthesized by reacting dicyclopentadiene with alcohols of various chain lengths to produce a lubricant with a selectable range of physical properties (Venier and Casserly (18)). The solvent *n*-hexane (purity > 98%) was used as received.

### Substrates and Film Preparation

Firstly, the silicon wafers were ultrasonicated sequentially in acetone, ethanol, and acetone each for 5 min and then rinsed with adequate ultrapure water and dried by nitrogen ( $N_2$ ). Then some cleaned silicon wafers were hydroxylated by immersing in a piranha solution, a mixture of 7:3 (v/v) 98%  $H_2SO_4$  and 30%  $H_2O_2$  at 90°C for 30 min. Also, some cleaned silicon wafers were immersed in 40% de-aerated aqueous  $NH_4F$  solution for 5-7 min to obtain a monohydride-terminated surface; that is, H-Si (100). Wafers were then rinsed with adequate de-aerated ultrapure water and dried by  $N_2$ . In this way, we obtained three kinds of substrates: cleaned silicon, hydroxylated silicon, and hydrogenated silicon.

The solution of MACs was firstly prepared in hexane with concentration of 0.05% (w/v). Then the aforementioned three kinds of silicon substrates were slowly dipped into and withdrawn from a tank containing the solution with a uniform velocity of 50  $\mu m/s$  and were immersed in the solution for up to 120 s in order to obtain a uniform coating. Each silicon substrate with MACs film was allowed to air-dry in a clean room prior to our conducting measurements as described below.

### Characterization of the Films

Thermogravimetric analysis was conducted in nitrogen with a Perkin-Elmer 7 series apparatus at a scanning rate of 10°C/min to study the volatility of MACs. The thickness of the films was measured on a Gaertner L116-E ellipsometer, which was equipped with a He-Ne laser (632.8 nm) set at an incident angle of 50°. A

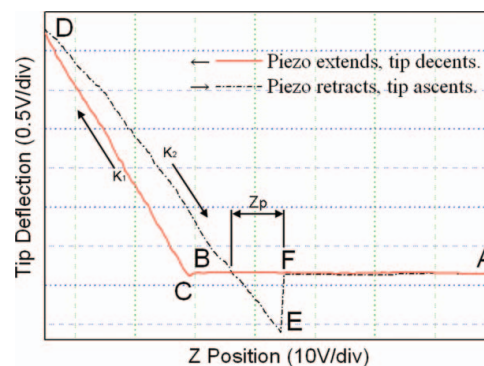


Fig. 1—Typical force-distance curves for all substrates tested.

real refractive index of 1.48 was assumed for all the films. Ten replicate measurements were carried out for each specimen, and the thickness was recorded to an accuracy of 0.3 nm. The static contact angles for ultrapure water on the samples were measured with a DSA100 contact-angle meter. At least five replicate measurements were carried out for each specimen, and the measurement error was below 2°. The film morphologies were examined with an SPM (Nanoscope IIIa, Digital Instrument) atomic force microscope (AFM), using tapping scanning mode. The standard Nanoscope IIIa software was used to analyze all of the images.

The nanoadhesive behavior of the films was characterized with an AFM/FFM controlled by CSPM4000 electronics, using the contact mode. A commercially available rectangle  $Si_3N_4$  cantilever with a normal force constant = 6 N/m and a  $Si_3N_4$  tip with a radius of less than 10 nm (Budgetsensors Instruments Inc.) was employed. For all measurements, the same cantilever was successfully used in this comparative study. Furthermore, to avoid influence of molecules that may have transferred to the tip during the experiment, the tip was scanned on a cleaved mica surface to remove these physically adsorbed molecules. The force-distance curves were recorded, and the pull-off force (Fig. 1) was reckoned as the adhesive force, which was given by

$$F = K_c Z_p, \quad [1]$$

where  $K_c (= K_2/K_1)$  is the force constant of cantilever, and  $Z_p$  is the vertical displacement of the piezo tube; i.e., the deflection of the cantilever (Xiao and Qian (30); Tsukruk and Bliznyuk (31)). In data processing, a test of ten measurements was made for each sample; repeated measurements were within 5% of the average value for each series.

The nanofriction force is a lateral force exerted on a tip during scanning and can be measured using the twist of the tip-cantilever assembly. To obtain friction data, the tip was scanned back and forth in the *x* direction in contact with the sample at a constant load while the lateral deflection of the lever was measured. The difference in the lateral deflection or friction signals between back- and-forth motions is proportional to the friction force. Friction forces were continuously measured with various external loads. The load was increased (or decreased) linearly in each successive scan line, and typically normal loads ranged from 0 to 60 nN. Friction force measurement was performed at a rate

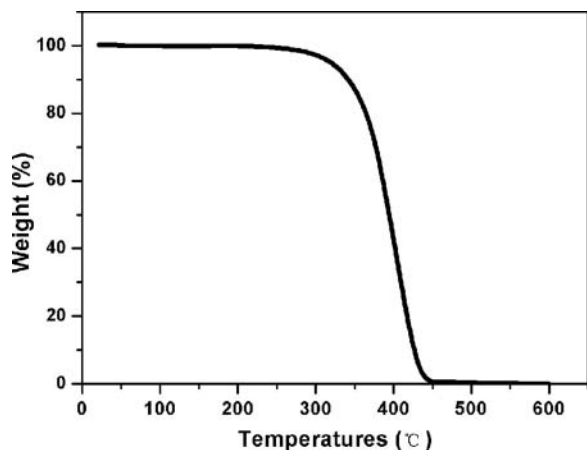


Fig. 2—TGA curve of multiply alkylated cyclopentanes (MACs).

of 1 Hz along the scan axis with a scan size of  $1\ \mu\text{m} \times 1\ \mu\text{m}$  (viz. sliding velocity of  $2\ \mu\text{m/s}$ ). The scan axis was perpendicular to the longitudinal direction of the cantilever. The sets of data were displayed graphically in a friction image. All the tests were conducted at room temperature and a relative humidity of 45%.

## RESULTS AND DISCUSSION

### Characterization of MACs

Thermal stability of MACs was examined by TGA between 20 and  $600^\circ\text{C}$ . As shown in Fig. 2, MACs have very high decomposition temperature and very low vapor loss, which are equivalent to those of a commercial MAC base fluid (2001A) (Dube, et al. (22)). There is little weight loss below  $300^\circ\text{C}$ .

### Wettability

Contact angles for ultrapure water on three kinds of silicon substrates with and without MACs were measured, as shown in Table 1. The contact angle of the cleaned silicon increased very little after it was coated with MACs. That finding may indicate that MACs were unwetted on the cleaned silicon and that there were few MACs adsorbed on it. The contact angles of the hydroxylated silicon and the hydrogenated silicon increased by about  $20^\circ$  after coating with MACs. This result indicates that the MACs were adsorbed on the substrates, making them more hydrophobic, and that outcome may be due to the apolar  $-(\text{CH}_2)_n-\text{CH}_3$  (hydrophobic) groups.

### Surface Topological Structure

The topological structures of the samples were observed by AFM, as shown in Fig. 3, the thicknesses of which are

TABLE 1—CONTACT ANGLES FOR ULTRAPURE WATER ON THREE KINDS OF SILICON SUBSTRATES WITH AND WITHOUT MACs

Substrates	Without MACs ( $^\circ$ )	With MACs ( $^\circ$ )
Cleaned silicon	46.8	51.8
Hydroxylated silicon	2	25.9
Hydrogenated silicon	74.9	94.1

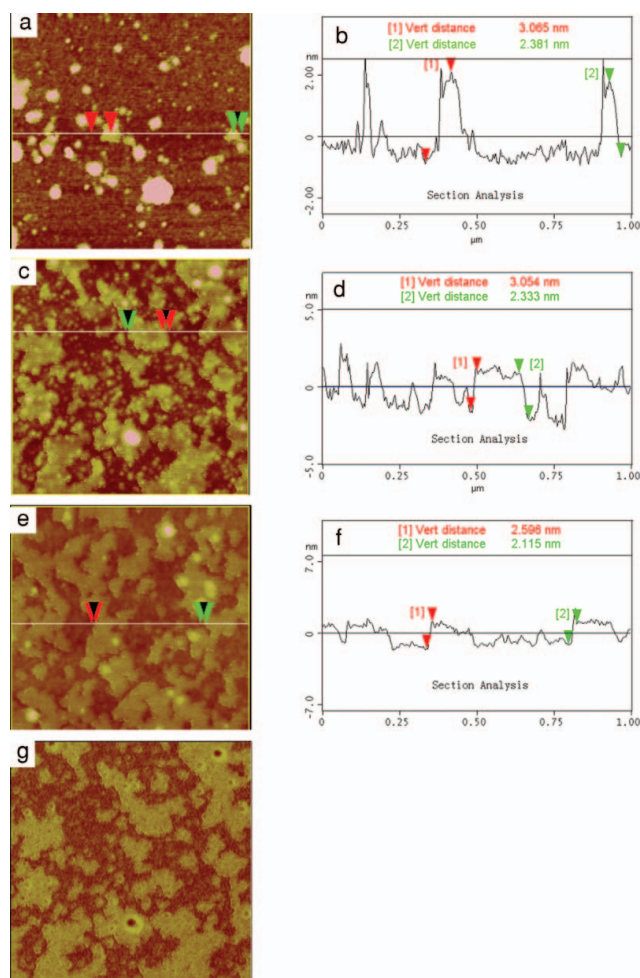


Fig. 3—AFM images of MACs films: (a) MACs on the cleaned silicon; (b) line section analysis of (a); (c) MACs on the hydroxylated silicon; (d) line section analysis of (c); (e) MACs on the hydrogenated silicon; (f) line section analysis of (e); (g) phase map for (c).

$2.5 \pm 0.3\ \text{nm}$ . The topological structure of the samples obtained from the topographic maps is in accordance with that obtained from the phase maps. Typically, the phase map of MACs on the hydroxylated silicon is given here (Fig. 3g). It can be clearly seen that the cleaned silicon is unwetted and that there are few MACs adsorbed on it, and that outcome is consistent with the result of contact angle measurement. The wettability of MACs on the hydroxylated silicon and the hydrogenated silicon is better. It is well known that the wettability of a solid surface is determined by both topological structure of the surface and chemical structure of the molecules on the surface (Wenzel (32); Cassie and Baxter (33)). As for the liquid phase, its wetting power is altered either by the use of liquids of different polarity or by the introduction of surface-active solutes. MACs, which have no functional groups, are physically adsorbed on the substrates. This may indicate that the wettability changes of the samples are mainly caused by topological structure changes of the surface.

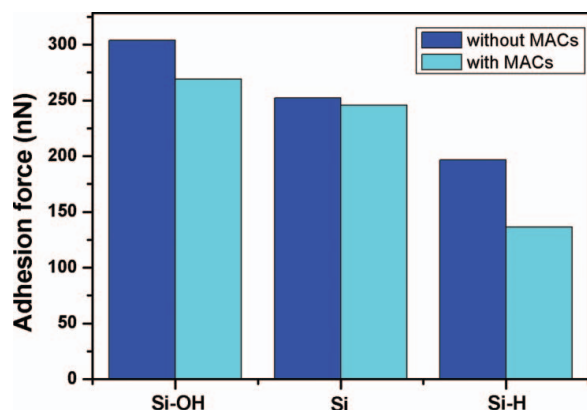


Fig. 4—Adhesion forces of hydroxylated silicon with and without MACs, cleaned silicon with and without MACs, and hydrogenated silicon with and without MACs.

### Nanoadhesion and Nanofriction Forces

Results of studies show that the adhesion force depends strongly on whether the substrate is hydrophilic or hydrophobic (Binggeli and Mate (34); Eastman and Zhu (35); Sedin and Rowlen (36)). In an ambient environment, the surface of the samples would be covered by a thin water film. The capillary force due to the wettability of water to the substrate would strongly influence the interaction between the tip and the surface.

The nanoadhesion forces measured from the pull-off point on each sample are presented in Fig. 4. It can be clearly seen that the adhesion force of each substrate is smaller after coating with MACs. It indicates that MACs can improve the nanoadhesion. The adhesion force of the hydroxylated silicon, which is hydrophilic and easily adsorbed a thin water film with high capillary forces and surface energy, is the largest. It also shows that the adhesion force for MACs on the hydroxylated silicon is the largest during the three silicon substrates with MACs. This may be induced by the partly exposed hydroxylated silicon, which has high capillary force and surface energy and could further increase the adhesion force. It also can be seen that the adhesion force

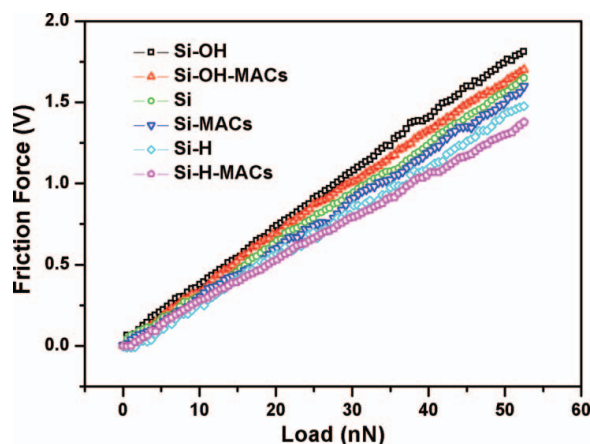


Fig. 5—The plot of friction force versus load curves for the surface of the three kinds of silicon substrates (the hydroxylated silicon, the cleaned silicon, and the hydrogenated silicon) with and without MACs.

for MACs on the hydrogenated silicon is the smallest. This may be due to the partly exposed monohydride-terminated surface, which is more hydrophobic, has low surface energy, and can decrease the adhesion force. This may also explain why the adhesion force for MACs on the cleaned silicon is between the two aforementioned samples with MACs. The changing trend of the observed adhesion forces is consistent with that of the contact angles measurement. We may conclude that the difference in adhesion forces of MACs on silicon substrates is due to the different surface energy of the silicon.

Figure 5 presents the plot of friction force versus load curves for the surface of the three kinds of silicon substrates with and without MACs. The friction force given here is in the form of a voltage signal, which should be proportional to the real friction force (Brewer, et al. (37); Zhang and Archer (38)). Therefore, the friction forces on various film surfaces can be compared. It can be seen that MACs on the hydrogenated silicon exhibited the lowest friction coefficient and that MACs on the hydroxylated silicon showed the highest during the three substrates with MACs. The observed friction coefficients reveal a trend that is similar to those obtained for the adhesion forces. As in adhesion, surface energy and molecular deformation are key factors that need to be considered when determining frictional values (Lee, et al. (39)). This is likely to result from the different interfacial energies of the samples, on which MACs are not well wetted, since MACs are physically adsorbed on the substrates. Thus, the results highly suggest that MACs on the hydrogenated silicon with low surface energy can greatly reduce the adhesion and friction forces.

### CONCLUSIONS

In this article, the wettability of MACs on silicon substrates that were treated by different cleaning and etching processes was studied. As the results showed, the wettabilities of MACs on the hydroxylated silicon and the hydrogenated silicon are better than the wettability on the cleaned silicon, and that outcome is mainly caused by topological structure changes of the surface. The different behaviors in adhesion and friction forces are due to the different surface energies of the silicon substrates.

To our knowledge, this is the first report of the wettability of MACs on silicon substrates that were treated by different cleaning and etching processes, which is very important in the study of nanoadhesion and nanofriction properties. In the future, we will further our research in this matter and mainly focus our studying of the influence of surface microtextures on the wettability of MACs for the practical application of lubrication for MEMSs.

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