Wettability Study of Multiply-Alkylated Cyclopentanes (MACs) on Silicon Substrates

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Extended Abstract

In order to investigate the influence of surface microtextures on the wettability, Multiply-alkylated cyclopentane, a novel hydrocarbon mobile lubricant, was deposited on silicon surface treated by different cleaning and etching processes. Using an atomic force microscope, measurement on the silicon surface was made to fully characterize the surface. Contact angles of water on these surfaces were measured using a DSA100 contact angle meter. The result indicates the wettability of the hydroxylated silicon wafer and the silicon wafer with a monohydride-terminated surface is better than the cleaned silicon wafer, which are mainly caused by topological structure changes of the surface. Furthermore, the nano-adhesion property was also measured. The different behavior in adhesion forces is due to the differing surfaces of the silicon wafers.

Keywords: Etching; hydroxylated; monohydride-terminated; adhesion

1. INTRODUCTION

Multiply-alkylated cyclopentanes (MACs), a novel hydrocarbon mobile lubricant, are a mixture of the di- and tri-substituted (2-octylodecyl) cyclopentane. They have excellent viscosity properties, thermal stability and low volatility for use as lubricant and is presently gaining wide acceptance on actual space application [1, 2]. MACs may also have the potential as lubrication in the micro-electromechanical systems (MEMS) application. While MACs have been observed to dewet bearing steel surfaces [3] and it was wondered if this represented a long-term life threat. Controlling the wettability is quite important in the study of nano-adhesion and nano-friction. Since silicon has been the most widely used material in the MEMS [4], this paper studied the wettability of MACs on silicon wafers treated by different cleaning and etching processes. The nano-adhesion property was also measured.

2. EXPERIMENT DETAILS

2.1. Materials

P-doped single-side polished single-crystal silicon (1 0 0) wafers (obtained from GRINM Semiconductor Materials Co. Ltd., Beijing) about 0.5mm 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 [5]. The solvent n-hexane (purity >98%) was used as received.

2.2. Substrates and film preparation

The silicon wafers were first ultrasonicated sequentially in acetone, ethanol and acetone each for 5 min and then rinsed with adequate ultra-pure water and dried by N_2. The 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 ℃ for 30 min. Other cleaned silicon wafers were immersed in 40% deaerated 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 deaerated ultra-pure water and dried by N_2. Then we got three kinds of substrates: the cleaned silicon wafers; the hydroxylated silicon wafers and the H-Si(100).

The solution of MACs in hexane with a concentration of 0.05% (w/v) was spun cast onto the aforementioned three kinds of silicon substrates at a speed of 3000 rpm, thus monolayer films were formed.

2.3 Characterization of the films

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 atomic force microscope (AFM) (Nanoscope IIIa, Digital Instrument), using tapping scanning mode. The nano-adhesive behavior of the films was characterized with an AFM controlled by CSPM4000 electronics, using the contact mode. Commercially available rectangle Si_3N_4 cantilever with a normal force constant, 6N/m and a Si_3N_4 tip with a radius of less than 10nm (Budgetsensors Instruments Inc) was employed. To avoid influence of molecules which may transfer to the tip on the AFM/FFM experiment, the tip was scanned on a cleaved mica surface to remove these physical adsorbed molecules. The force distance curves were recorded and the pull off force reckoned as the adhesive force, which was given by

$$F=KcZp$$

Where Kc is the force constant of cantilever and Zp is the vertical displacement of the piezotube, i.e., the deflection of the cantilever [6, 7]. In data processing, a test of ten measurements was made for each sample. All the tests were conducted at room temperature and a relative humidity of *45%*.

3. RESULTS AND DISCUSSION

3.1. Wettability

Contact angles of MACs films on three kinds of silicon substrates were measured, as shown in Table 1. The contact angle of the cleaned silicon wafer increased very little. It may indicate that MACs were unwetted on cleaned silicon wafer and there were little MACs adsorbed on it. The contact angles of the hydroxylated silicon wafer and the H-Si(100) increased by about 20° after coated with MACs. This result indicates that MACs were adsorbed on the substrates and made them more hydrophobic, which may be resulted from the apolar —(CH_2)n—CH_3 (hydrophobic) groups.

3.2. Surface topological structure

The topological structures of the samples were observed by AFM, as shown in Fig. 1, the thicknesses of which are 2.5±0.3 nm. It can be clearly seen that the cleaned silicon wafers are unwetted and there are little MACs adsorbed on it, which is consistent with the result of contact angle measurement. The

Table 1 List of the contact angles of the samples used in this article

Substrates	Without MACs (°)	With MACs (°)
Cleaned silicon wafer	46.8	51.8
hydroxylated silicon wafer	2	25.9
H-Si(100)	74.9	94.1

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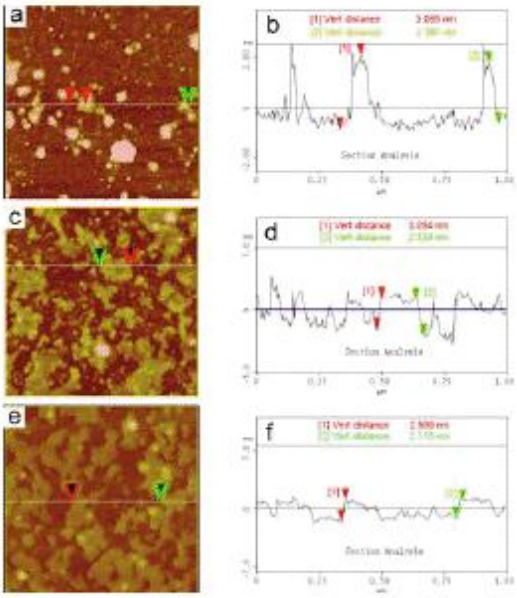

Fig. 1 AFM images of MAC films. (a) Cleaned silicon wafer with MACs. (b) Line section analysis of (a). (c) Hydroxylated silicon wafer with s. (d) Line section analysis of (c). (e) H-Si(100) with MACs. (f) Line section analysis of (e)

wettability of the hydroxylated silicon wafer and the H-Si(100) is better. It is well known that the wettability of solid surface is decided both by topological structure and chemical structure [8, 9]. MACs, which have no functional groups, are physically adsorbed on the substrates. This indicates that the wettability changes of the samples are mainly caused by topological structure changes of the surface.

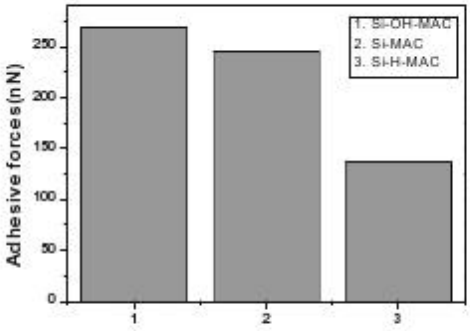

Fig. 2 Adhesive forces of hydroxylated silicon wafer with MACs (1), Cleaned silicon wafer with MACs (2) and H-Si(100) with MACs (3)

3.3. Adhesion

The adhesive forces measured from the pull-off point on each sample are presented in Fig. 2. It shows that the adhesion force for the hydroxylated silicon wafer with MACs is the largest in the three. This may be induced by the partly exposed hydroxylated silicon wafer, which can increase the capillary force and further increase the adhesion force. It also can be seen that the adhesion force for the H-Si(100) with MACs is the smallest. This may be resulted from the partly exposed monohydride-terminated surface, which can decrease the adhesion force. This may also explain why the adhesion force for the cleaned silicon wafer with MACs is between the above two samples. We may conclude that the difference in adhesion forces is due to the differing surfaces of the silicon wafers. The result of the adhesion force is consistent with the contact angles measurements.

4. CONCLUSION

In this paper, we studied the wettability of MACs on silicon wafers treated by different cleaning and etching processes. The wettability of the hydroxylated silicon wafer and the H-Si(100) is better than the leaned silicon wafer, which are mainly caused by topological structure changes of the surface. The different behavior in adhesion forces is due to the differing surfaces of the silicon wafers. In the future, we will further our research in this aspect and mainly focus on the study of the influence of surface microtextures on the wettability of MACs for the practical application as lubrication for MEMS.

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