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Sliding acceleration of water droplets on a surface coated with fluoroalkylsilane and octadecyltrimethoxysilane

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Abstract

Both fluoroalkylsilane (FAS) and octadecyltrimethoxysilane (ODS) were coated on oxidized silicon wafers using soaking and CVD method. Smooth coatings with *Ra* values of less than 1 nm were attained. The slope of the sliding acceleration against the inverse of the droplet mass showed an inflection point. That point shifted to the direction of smaller droplets with decreasing FAS ratio to ODS. The water droplets' length was increased when the sliding velocity was increased. Fluoroalkylsilane addition to ODS increases the interaction between water and the hydrophobic surface. Results showed that the sliding acceleration of a water droplet depends strongly on the surface ratio of these silanes.

Keywords: Hydrophobic; Silanes; Sliding angle; Velocity; Acceleration; Wetting; Silicon; Water; Coating

1. Introduction

Technology for hydrophobic coatings has been important for suppressing chemical reactions and bonding formation between water and solid surfaces. Such coatings have been used in various industries for protection against wetting, snow and ice adherence, rusting, and to reduce friction [1–5].

The contact angle of water has been commonly used as a criterion for evaluating the static hydrophobicity of a surface, but it is inadequate for evaluating dynamic hydrophobicity: the sliding behavior of water droplets. Recently, recognition of the importance of dynamic hydrophobicity is growing in various industries such as the glass, automobile, and electronics industries [6]. To date, the sliding angle (the angle at which a droplet of water of a certain weight begins to slide down an inclined plate) or contact angle hysteresis is commonly employed as a criterion for assessing the dynamic hydrophobicity of a solid surface [7–10]. However, these values do not include information on the sliding acceleration or velocity. Furthermore, a hydrophobic surface with a low sliding angle does not always exhibit high sliding acceleration or velocity for a water droplet [6,11]. Information on how fast the droplet can be removed from the surface at a certain tilt angle is becoming more important than that related to the lowest tilt angle at which the droplet slides down. However, a fundamental

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understanding of the factors, along with their contribution to the overall sliding acceleration or velocity, remains elusive [9,11–14].

Recently, we investigated sliding acceleration of a water droplet on an oxide surface treated with octadecyltrichlorosilane (ODS) by changing the droplet mass [15]. The slope of the sliding acceleration against the droplet mass changed at 20 mg, suggesting that the dominant sliding mode switches from slipping to rolling. Moreover, we have directly observed stick-slip motion of water droplets during sliding on a silicon surface treated by fluoroalkylsilane (FAS) [16]. That elongation corresponded inversely to the change of sliding acceleration. The tilt angle and droplet mass affected this phenomenon. These studies suggested that the surface chemical composition is an important factor for sliding acceleration of water droplets. This study specifically treated silicon surfaces using both FAS and ODS. Sliding acceleration or velocity of water droplets on the surfaces was evaluated by changing the FAS/ODS ratio.

2. Experimental section

A Si(100) wafer (Aki Corp., Miyagi, Japan) was cut into 3×5 cm and cleaned with acetone and 10% HF solution for removing a heterogeneous oxide layer from the surface [17]. Vacuum ultraviolet (VUV) light was irradiated ($\lambda = 172$ nm with a power density of around 7 mW cm^{-2}, UEM20-172; Ushio Inc.) to the cleaned wafers for 10 min in air to form a homogeneous oxide layer on the substrate surface [18]. The substrate surfaces became completely hydrophilic with a water-contact angle less than 5°.

Heptadecafluorodecyltrimethoxysilane ($CF_3(CF_2)_7CH_2$-$CH_2Si(OCH_3)_3$, hereafter denoted as FAS, TSL8233; GE Toshiba Silicones, Tokyo, Japan), was dissolved into 70 ml of *Fluorinert77* (C_nF_m, mainly $n = 8$; 3M Inc., MI, USA) without any dehydration; the concentration was fixed as 5 mM. The cleaned wafers were soaked in this liquid for 0 min, 2 min, 20 min, 60 min, and 24 h at room temperature in ambient air. We employed a commercial glass bottle with screw cap for this soaking. After soaking, samples were rinsed several times using flowing solvents (acetone and toluene) with high solubility for FAS. All these samples, except for the sample soaked in FAS solution for 24 h, were set into a 65 cm^3 petri dish together with approximately 0.02 cm^3 of *octadecyltrimethoxysilane* ($CH_3(CH_2)_{17}Si(OCH_3)_3$, hereafter called ODS; Aldrich Chemical Co. Inc., Milwaukee, WI, USA) under dry N_2 atmosphere. The petri dish was heated without special sealing in an oven for 1 h at 150 °C under dry N_2 atmosphere. The ODS vaporized in the vessel and reacted with remaining surface OH groups that were not reacted with former FAS treatment. After coating, samples were rinsed with acetone and toluene, then dried at 70 °C. In this study, prepared samples are denoted as A, B, C, D, and E with respect to the soaking time in FAS liquid 0 min, 2 min, 20 min, 60 min and 24 h: sample A is ODS only; sample E is FAS only; and samples B, C, and D are mixtures of ODS and FAS.

Surface roughness was evaluated using atomic force microscopy (AFM, MMAFM-2; Veeco Instruments, CA, USA). The chemical composition of the sample surface was evaluated using X-ray photoelectron spectroscopy (XPS, JPS-9010MX; JEOL, Tokyo, Japan). The binding energy scales were referenced to 284.5 eV, as determined by locations of peaks on the C *1s* spectra of hydrocarbon (CH_x) for correcting the deviation [19,20]. The sessile drop method, using a commercial contact angle meter (CA-V; Kyowa Interface Science Co. Ltd., Saitama, Japan) was used to measure the contact angles. The water and oleic acid droplets used for measurement were 4 mg. The water contact angle was measured at five different points for each sample, whereas the oleic acid contact angle was measured at one point for each sample. The critical surface energies of the samples were determined simply by using "Zisman plots" with droplets of *n*-alkane such as *hexane*, *octane*, *decane*, *dodecane*, *tetradecane* and *hexadecane* (C_6H_{14}, C_8H_{18}, $C_{10}H_{22}$, $C_{12}H_{26}$, $C_{14}H_{30}$, $C_{16}H_{34}$, All were provided by Wako Pure chemical Co., Tokyo Japan). Sliding angles of water droplets were measured using a commercial sliding angle measurement system (SA-20; Kyowa Interface Science Co. Ltd.). The water droplet weight for this measurement was 30 mg. The temperature of atmosphere and water during wettability evaluation was around 20 °C.

Sliding acceleration of the water droplet was evaluated from direct observation. The sample was tilted at 35°. A water droplet of a certain weight was placed on the needle tip of a hypodermic syringe and gently placed on the inclined sample surface. The measurement was triggered when the needle tip of syringe was removed from the droplet. Sequential photographs of the sliding motion of the water droplets on the surface were taken every 4 ms with a high-speed digital camera system (HAS200R; Seika Corp., Tokyo, see Fig. 1). Droplets weighed 22–45 mg. Sliding acceleration was estimated by measuring the sliding distance of the front edge of a contact line between the

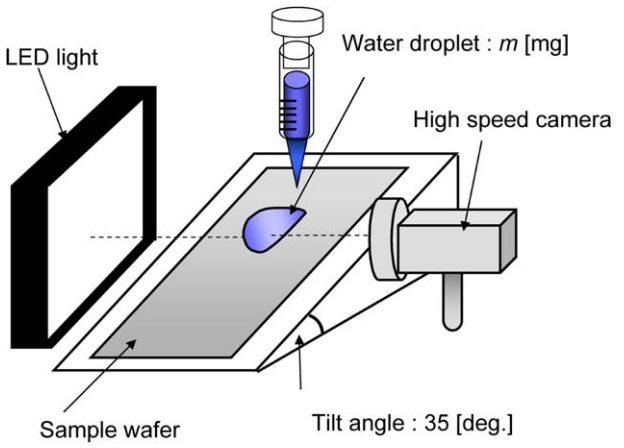

Fig. 1. Schematic illustration of the sliding behavior measurement.