Directional self-cleaning surface design for ink jetting devices

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Abstract

Functional surfaces with self-cleaning property are highly desirable in many applications in the printing industry. One of the challenges in fluid ink jet systems is ink wetting and drooling onto the printhead front face. The contamination of the printhead front face leads to missing drops, wrong-sized drops, mis-directionality, and satellite drops resulting in degraded print quality. In this study, we report the creation of textured surfaces on Si wafer by photolithography, followed by chemical modification, that leads to superoleophobic, directional self-cleaning surfaces. We systematically investigate its wetting and adhesion properties with water, hexadecane and Xerox solid ink using static and dynamic contact angle measurement techniques. The textured surfaces are made of micro grooves which demonstrate interesting anisotropic wetting behavior. In the direction parallel to the grooves, low surface tension testing liquids show very low sliding angle (i.e. directional self-cleaning) which is a key enabler for the self-cleaning effect and maintenance free printhead.

Introduction

Digital color printers and presses are complex electromechanical devices that put marks on papers. Traditional approaches to design and optimize these devices have primarily been focused on the electrical and mechanical properties. Print surfaces with custom-made surface properties are critical and are usually after thoughts. We believe that designer surfaces with controlled wetting or de-wetting properties or adhesion properties would be the performance differentiator for future engines. Features, such as easy-clean, self-clean in certain components, or fusing without any offset would be considered as a breakthrough.

Over the recent decades, inspired by nature and motivated by its amazing self-cleaning effect on Lotus leaves, researchers have created superhydrophobic surfaces by various approaches [1, 2]. These efforts usually involve the combination of surface roughness and surface chemistry. However, most man-made contaminants are organic in nature, to be anti-contaminating against organic materials, highly oleophobic rather than hydrophobic surfaces are needed. More specifically surfaces with superoleophobicity are a lot more valuable and practical than surfaces that are superhydrophobic [3]. Most Xerox imaging materials are organic matters with low surface tension and we are interested in studying the interactions of superoleophobic surfaces with these materials with the aim of improving future print processes and printing systems.

One of the challenges in fluid ink jet systems is ink wetting and drooling onto the printhead front face. The contamination of the printhead front face leads to missing drops, wrong-sized drops, mis-directionality, and satellite drops resulting in degraded print quality. In some cases, the contaminated printhead can be cleaned with a maintenance unit which, however, introduces system complexity, cost, and reliability issues. Printhead with self cleaning front face design will eliminate ink contamination. In this work, we fabricated a superoleophobic model surface by photolithography and demonstrate its directional self-cleaning property.

Experimental

A model superoleophobic surface was created by photolithography by first spin-coating photoresist SPR700 on a Si wafer, followed by exposure of the resist through a mask, and then developed, etched, striped off the remaining resist and piranha clean the surface. The resulting textured surfaces then was modified by tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) via molecular vapor deposition of on a MVD100 reactor from Applied Microstructures.

Contact angle and sliding angle measurements were performed on a goniometer model OCA20 from Dataphysics. The drop size of the test liquid is controlled to be ~ 5 μL. The advancing/receding contact angles are measured using sessile drop method by adding/removing liquid to/from the existing droplet at a very small rate (0.15μl/sec). The sliding angles are measured using the tilting base unit accessory to the Dataphysics goniometer. After dispensing a 10 μL droplet, the stage is tilted about one degree per second to a maximum of 90°. The sliding angle was defined as the angle where the test liquid droplet starts to move. For imaging material, Xerox solid ink pellets of ~1 mm in diameter were heated at elevated temperature for both contact and sliding angle measurements. The accuracy of these measurements is ±2°.

Results and Discussion

Microscopy and Property of the Model Fluorinated Textured Surface

The textured surfaces are made of micro grooves by photolithography.

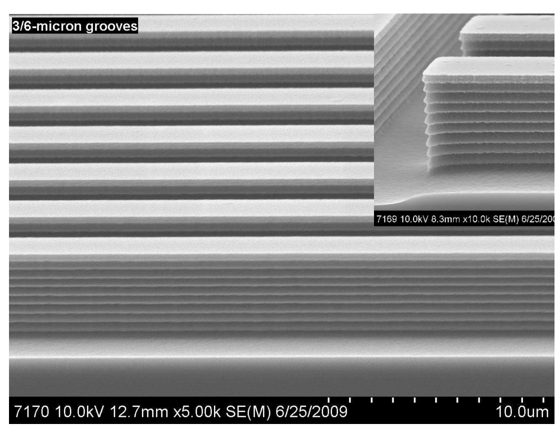

***Figure 1**. SEM micrograph of the textured groove structure on Si wafer created by photolithography, inset shows the re-entrant structure created by Bosch etching process.*

Figure 1 shows a SEM micrograph of a textured surface consisting of grooves ~ 3 μm in width and ~ 4 μm in height with a pitch distance of ~ 6 μm on Si wafer. The surface was chemically modified by a fluorosilane coating (FOTS) using the molecular vapor deposition technique. Figure 1 inset shows the detailed wavy structure of the side wall created by the Bosch etching process. The re-entrant structure at the top of the groove structure is geometrically critical to achieving surface superoleophobicity [3, 4]. Figure 2 shows a pillar structure with the same geometrical parameters and same surface treatment.

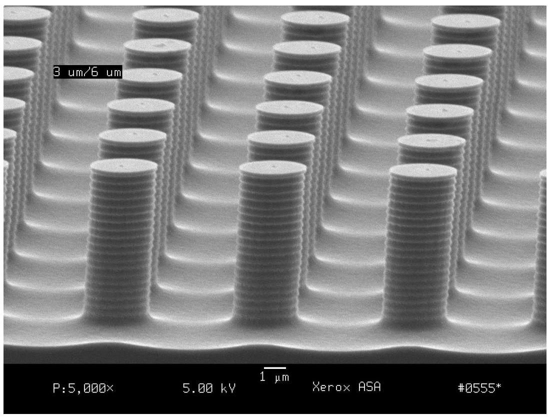

***Figure 2**. SEM micrograph of the textured pillar structure on Si wafer created by photolithography*

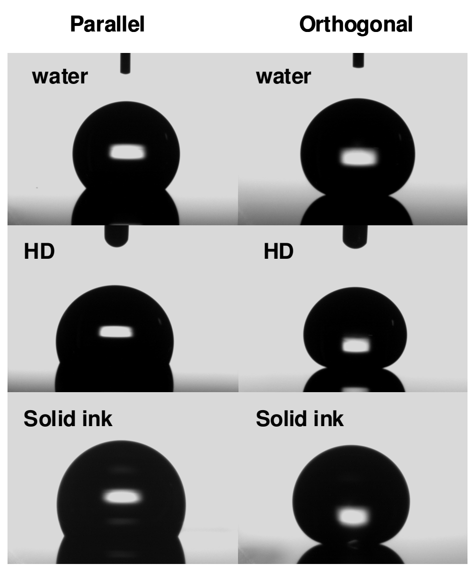

***Figure 3**. Anisotropic wetting on the textured groove structure from parallel (left) to orthogonal (right) direction with water, hexadecane (HD) and the Xerox solid ink*

The surface property of the textured groove structure was studied by contact angle measurements using water, hexadecane (HD) and Xerox solid ink as test liquids. The contact angle data for the textured surface are depicted in Figure 3 and compared with the surface with pillar structure in Table 1.

Anisotropic wettings are obtained on this textured groove structure (Figure 3). The water contact angles are at 131.3° and 153.8° when measured from the parallel and the orthogonal directions of the groove, respectively. The water contact angle for a comparable pillar structure was ~ 156° [4]. For hexadecane (HD), contact angles on the groove structure are 113.2° and 161.8° from the parallel and the orthogonal directions, respectively. The hexadecane contact angle for a comparable pillar structure was ~ 158° [4]. Similarly, the contact angles for the Xerox solid ink at elevated temperature are at 119.7° and 156.3° in the direction of parallel and orthogonal to the groove structure, respectively. The results indicate that the groove structure is both superoleophobic and superhydrophobic in the orthogonal direction. The surface properties are identical to the comparable pillar structure. Both oleophobicity and hydrophobicity reduce somewhat in the parallel direction.

Table 1. Summary of contact angle and sliding angle data for various testing liquids on different surfaces

Surface	Test liquid	Static CA	Advancing/ Receding CA	Sliding angle
Grooves Parallel	Water	131.3°	137.5°/122.6°	7.5°
	HD	113.2°	118.9°/99.6°	4.1°
	Solid ink	119.7°	-	24.7°
Grooves Orthogonal	Water	153.8°	158.5°/119.3°	23.3°
	HD	161.8	164.2°/97.9°	34.4°
	Solid ink	156.3°	-	>90°
Pillars	Water	156.2°	161.0°/142.6°	10.1°
	HD	157.9°	165.0°/120.9°	9.8°
	Solid ink	154.9°	-	33°- 58°
Smooth FOTS	Water	107.3°	116.3°/95.6°	14°
	HD	73.3°	74.2°/65.2°	9°
	Solid ink	78.5°	-	~15°

When a droplet moves on a surface, the contact line advances (or wets) into a fresh surface area and recedes (or de-wets) from a wetted surface area over the energy barriers due to defects, such as physical roughness and chemical inhomogeneousness. The defects and energy barriers give rise to (solid-water-air) contact line pinning and contact angle hysteresis which is the contact angle difference between the advancing and receding contact angles. During advancing, the droplet with a contact angle much larger than that on smooth FOTS surface and top of the grooves and pillars can easily wets the top of the grooves and pillars. The re-entrant structure shown in Figure 1 inset effectively locks even the low surface tension liquid like hexadecane wetting just the first few of waves which minimizes the energy barrier during advancing. This applies for all the three textured surfaces, groove parallel, groove orthogonal, and pillar structure. The advancing angles are tracking closely to their static contact angles. During receding, the contact line pinned at the inner edge and outer edge of the grooves and pillars. For the droplets moving on pillars and perpendicular to the grooves, the discontinuous contact line probably also enhances its pinning effect. This contact line pinning result in much larger contact angle hysteresis in the pillar textured surface and groove textured surface in the orthogonal direction.

Sliding angles for 10 μL of water and hexadecane droplets (7.5° and 4.1°, respectively) are small, even smaller than the pillar structure, in the parallel direction. This is despite of the smaller static contact angles in the parallel direction. The sliding behavior depends on the movement of the contact line [5] and how the drops move (sliding off or rolling off) toward the sliding direction. A continuous short contact line may be preferable for a surface where droplets are sliding off; while a discontinuous and irregular contact line could be better for a surface where droplets are literally rolling off. The sliding angle results are consistent with contact angle hysteresis. For instance, in the direction parallel to groove, the hysteresis is smaller so does the sliding angle.

Evidence for the Cassie-Baxter State

Two states are commonly used to describe the liquid-solid interface on rough surfaces: the Cassie-Baxter state and the Wenzel state. The static contact angles for a droplet at the Cassie-Baxter state (θ_{CB}) and the Wenzel state (θ_W) are given by equations (1) and (2) [6,7], respectively.

$$\cos\theta_{CB} = R_f\, f \cos\theta_Y + f - 1 \qquad (1)$$

$$\cos\theta_W = r\cos\theta_Y \qquad (2)$$

where f is the area fraction of projected wet area, R_f is the roughness ratio on the wet area and $R_f\, f$ is solid area fraction, r is the roughness ratio, and θ_Y is the contact angle of the liquid droplet on a flat surface.

The re-entrant structure shown in Figure 1 inset maintains the low surface tension liquids including the molten ink in the Cassie state, meaning that the testing liquids "sit" on a composite surface consisting of mostly air and a solid with significantly decreased contact area. The re-entrant structure provides a surface topography that prevents the low surface tension testing liquids entering the Wenzel state (wetting state: liquid fills up the grooves on the rough surface and the drop is pinned, characterized by high contact angle, high contact angle hysteresis and high sliding angle or pinned). Although contact angles for both states are significantly increased for both the Wenzel and Cassie states, the Cassie state is desirable due to its low sliding angle and low adhesion between the ink and textured surface.

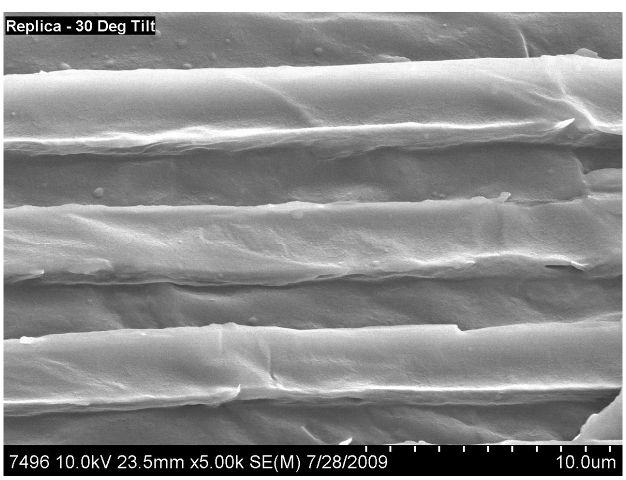

***Figure 4**. SEM micrograph of the solidified solid ink-substrate interface showing little penetration of the molten ink into the groove valley.*

The liquid-solid interface has been directly studied by putting the Xerox molten solid ink on the textured superoleophobic surface in a heated chamber and carefully taking off the ink drop when it solidifies at room temperature. The SEM micrograph of the interface is given in Figure 4. The result clearly shows that the ink drop does penetrate into the groove, but never touches the bottom of the groove. If the ink is fully penetrated to the bottom of the groove, the depth of the solid ink imprint should be ~ 4 μm, rather than ~ 1 μm. This observation is consistent with the contact and sliding angle measurements. Specifically the high contact angle and low sliding angle suggest that the testing liquid drops are in the Cassie-Baxter state and primarily "sits' on air in the groove structure.

Concluding Remarks

Superoleophobic groove structure with anisotropic wetting behavior has been fabricated on Silicon wafer by photolithography, followed by chemical modification. The extremely low sliding angle in the parallel direction suggests that this groove structured surface may offer directional self cleaning property for certain industry applications.

References

[1] P. Roach, N. J. Shirtcliffe and M. I. "Newton, Progress in superhydrophobic surface development," Soft Matter, 4, 224 (2008).
[2] X. Zhang, S. Feng, J. Niu, Y. Jiang and Z. Wang, "Superhydrophobic surfaces: from structural control to functional application," Journal of Materials Chemistry, 18, 621 (2008).
[3] A. Tuteja, W. Choi, G. H. McKinley, R. E. Cohen and M. F. Rubner, "Design parameters for superhydrophobicity and superoleophobicity," MRS Bulletin, 33, 752, (2008); and references therein.
[4] K.Y. Law, H. Zhao, and V. Sambhy, Effects of surface texture and chemistry on surface hydrophobicity and oleophobicity, NSTI - Nanotech 2009, Vol. 3, pg. 177. (2009).
[5] Z. Yoshimitsu, A. Nakajima, T. Watanabe, and K. Hashimoto, "Effects of surface structure on the hydrophobicity and sliding behavior of water droplets," Langmuir, 18, 5818-5822 (2002).
[6] A. Marmur, "Wetting on hydrophobic rough surfaces: To be heterogeneous or not to be?" Langmuir, 19, 8343 (2003).
[7] S. Michielsen and H. J. Lee, "Design of a superhydrophobic surface using woven structures," Langmuir, 23, 6004 (2007).

Author Biography

Kock-Yee Law received his B.S. in chemistry from The Chinese University of Hong Kong (1974) and his Ph.D. in photo-organic chemistry from The University of Western Ontario (1978). He has been at Xerox Webster for over 29 years and he is currently a technical manager in the Xerox Innovation Group responsible for the development and delivery of Nanotechnology for the future.

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