

HYDROPHOBIC NON-FOULING SURFACES FOR DROPLET BASED MICROFLUIDIC BIOANALYTICAL SYSTEMS

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Abstract

This paper presents the principle, fabricated structure, characterization and results obtained for a new class of surfaces—“hydrophobic non-fouling surfaces”—for droplet-based microfluidics. Building on the theory of wetting of rough surfaces, we have developed novel surfaces which are chemically hydrophilic, i.e., the droplet is in contact with a non-fouling hydrophilic material but exhibits hydrophobic properties (high contact angle) as a result of thermodynamically stabilized air traps beneath the droplet.

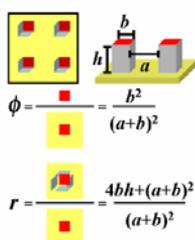
Keywords: non-fouling surfaces, bio-fouling, droplet microfluidics

1. Introduction

Superhydrophobic surfaces [1, 2] —with low resistance to flow— seem promising candidates for any low energy scheme for manipulating fluids. Past studies have confirmed that hydrophobic interactions are involved in protein adsorption [4, 5]. Proteins being ubiquitous components of bioassays, the use of super-hydrophobic surfaces in microfluidic bioanalysis systems presents a challenge. Also, most non-fouling materials are hydrophilic [4].

2. Principle and Design

We designed a rough surface realized by pillars of controlled geometry in a silicon wafer.



$$\phi = \frac{b^2}{(a+b)^2}$$

$$r = \frac{4bh + (a+b)^2}{(a+b)^2}$$

Figure 1: The texture parameters ϕ and r are expressed in terms of the design parameters a (gap length), b (pillar size) and h (pillar height).

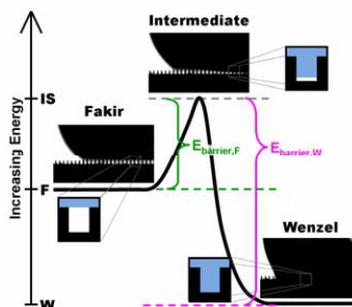


Figure 2: Photographs of droplets in Fakir and Wenzel states along with their energy levels. Substrate is designed to make Fakir state metastable.

The roughness is characterized by r , the ratio of rough to planar surface area (Fig. 1). As seen in Fig. 2, a droplet can sit on the pillar tops with air pockets trapped beneath, in the “Fakir” state [5] or in the Wenzel state where it is conformal with the topography. In the Fakir state, the base of the droplet contacts a composite surface of pillar tops and air—creating a contact angle θ_F given as: $\cos \theta_F = \phi(\cos \theta_i + 1) - 1$. Here θ_i is the intrinsic contact angle of the pillar tops. A Fakir droplet on a surface does not spontaneously transit to Wenzel state because of the presence of an energy barrier— analogous to the activation energy of a chemical reaction. We observed that the contact angle depends only on ϕ and θ_i : it is independent of the coating on the sidewall. But the energy barrier depends only on the coating of the sidewalls—it is independent of the θ_i of the pillar tops.

3. Experimental

Therefore, we proposed novel composite micro-textured surfaces with a hydrophobic material, alkanethiol coated gold, on the troughs and side walls of the pillars and a hydrophilic non-fouling material polyethylene glycol (PEG), on the pillar tops (Fig. 3).

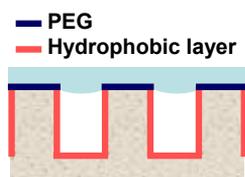


Figure 3: Schematic diagram of liquid deposited on the surface. The top surface is hydrophilic non-fouling polyethylene glycol (PEG). The trough and side-walls are hydrophobic. Although the liquid-vapor surface may be curved, the large size of the droplet relative to the spacing between pillars allows the profile to be approximated as spanning straight across surfaces in the derivation.

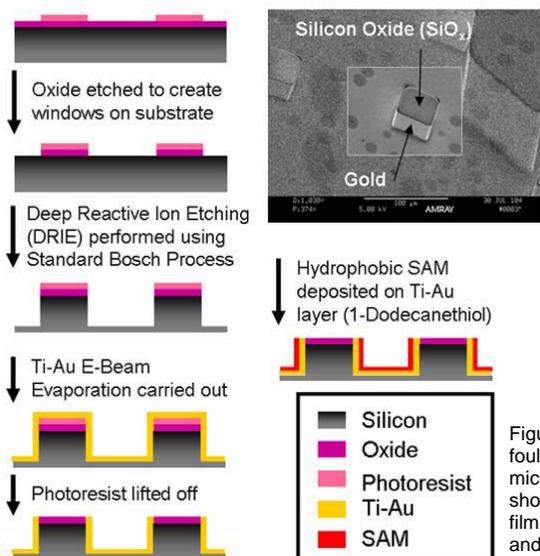


Figure 4: Fabrication steps for the non fouling hydrophobic surface. In the SEM micrograph, the non-conducting oxide shows up dark while conducting metal film (Ti-Au) on the sidewalls of the pillars and on the trough shows up bright.

The fabrication process is detailed in Fig. 4. A self assembled monolayer of dodecanethiol on gold was used for the hydrophobic coating. A droplet was then placed on this surface and the contact angle measured using a goniometer. The light filtering through the air traps established that the droplet rested in the Fakir state, as expected, contacting only the hydrophilic oxide layer on the pillar tops, with the high contact angle as seen in Fig. 5. The measurements were repeated over several test surfaces—with a range of pillar widths and gaps—as summed up in Fig. 6.

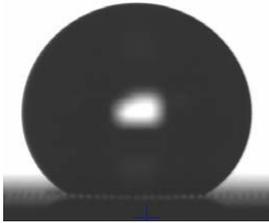


Figure 5: Even though the pillar tops are hydrophilic with $\theta_c=32^\circ$, the droplet (of volume $7.68 \mu\text{l}$) is in the Fakir state with $\theta_c = 137^\circ$ as evident from the light seen below the droplet.

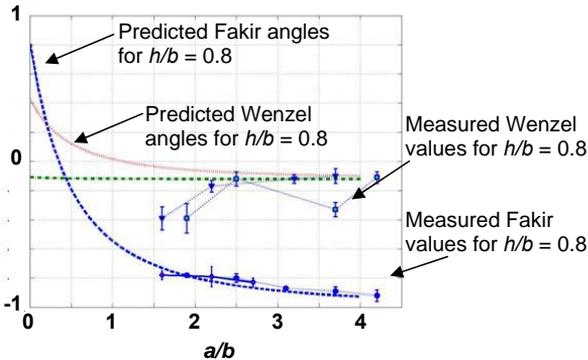


Figure 6: Measured contact angle values for Wenzel and Fakir are plotted along with the predicted angles based on the measured pillar dimension b and spacing a . Predicted values for (blue) Fakir, (pink) Wenzel with $h/b = 0.8$ and (green) Wenzel with $h/b = 1.9$ are plotted. The measured values for Fakir state closely match the predicted values while the measured Wenzel values expectedly deviate more.

4. Conclusion

The first phase of the project was thus successfully completed: the “proof-of-concept” results demonstrated “hydrophobic” surfaces where droplets contact only the “hydrophilic” region. Quantification of fouling, the ongoing second phase, entails using radio-labeled protein adsorption on well characterized PEG layer deposited on the oxide.

References

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