Nanoscale Details of Liquid Drops on 1D Patterned Surfaces Revealed by Etching[1]

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The behavior of liquid drops on patterned and rough surfaces is a topic of both scientific importance and practical manufacturing impact. Generally, the interaction has been monitored with macroscopic measurements (apparent contact angles and drop dimensions)[2]. Molecular dynamics calculations are limited to unrealistically small volume drops by computational restrictions, but show details of the fluid interaction with pattern features[3]. The drop configuration is often described by either a Wenzel state (fluid penetrates grooves) or a Cassie-Baxter state (fluid contacts top of grooves only)[2]. To bridge this gap, we report measurements with an etching solution (KOH:H_2O, 0.16mol/L) deposited on a developed photoresist surface and investigations of the etch profile into the PR at different times.

A 170-nm linewidth, 500-nm period, 1D nanopatterned photoresist structure fabricated by interferometric lithography was used. Bottom antireflective coating (BARC icon-16) and positive photoresist (SPR-505) were spun on bare silicon wafer. After interferometric lithography and developing (Fig. 1a,b), the as-developed surface was exposed to a 4 μL KOH:H_2O drop. Both perpendicular and parallel contact angle for deionized water and KOH solution were measured and compared. The wetting state and etching rate were observed through SEMs of the etched structures (Fig. 1c,d).

Fig. 1 shows that the KOH drop only contacts the top PR surface as shown by the roughness of the etched structures; the side of photoresist is unaffected and proves that the fluid does not penetrate the grooves (Cassie-Baxter state). For an increased etching time, along the centerline of the drop perpendicular to the photoresist walls the etching proceeds to completion but stops abruptly with a space of one or two pattern periods (Fig. 2) indicating that the drop is pinned at the edge of a wall by tensile forces. We also have measured the thickness variation of the photoresist as a function of time (Fig. 3). The etch rate is highly nonlinear with time indicating that there is a surface layer with more etch resistance than the bulk of the photoresist.

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[2] D. Xia, L.M. Johnson and G.P. Lopez, *Adv. Matls*. **24**, 1287 (2012).
[3] A. Shahraz, A. Borhan, K.A. Fichthorn, *Langmuir* **29**, 11632 (2013)

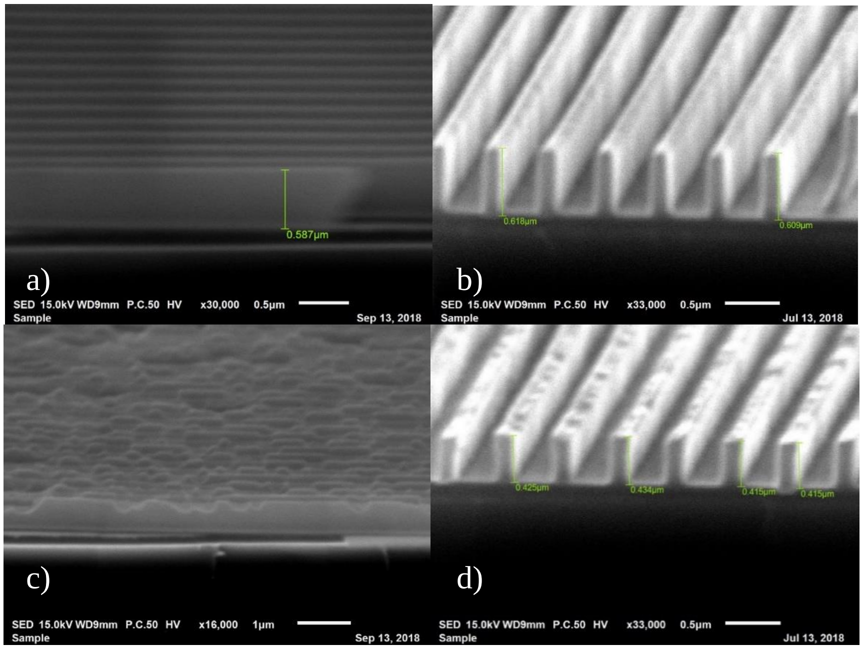

Fig. 1. a), Side view of grating walls before KOH etching. b), Cross-section view of grating walls before KOH etching; c), Side view of etched grating; d), Cross-section view of etched grating. Note the top surface roughness which supports our conclusion that the droplet is in the Cassie Baxter state.

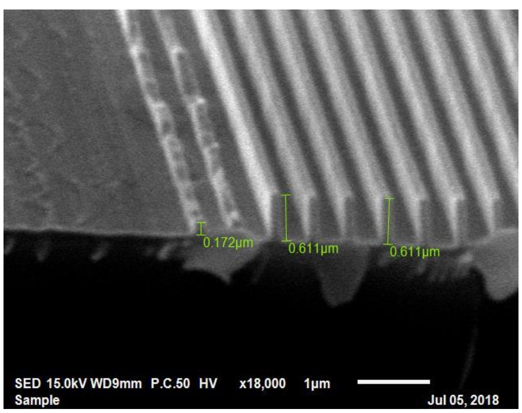

Fig. 2. Image taken at centerline of drop. The abrupt edge of the etching demonstrates the pinning at the edge of a photoresist line.

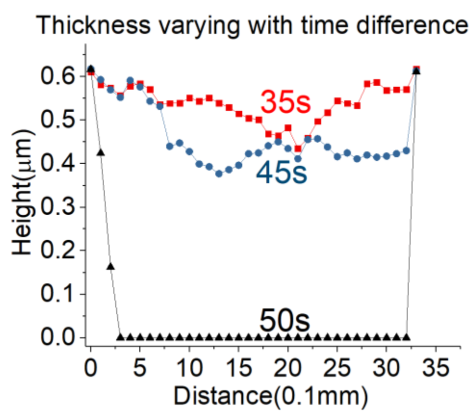

Fig. 3. Photoresist thickness vs. etching time along a centerline of the drop perpendicular to the grating lines.