Modified Surface Wetting using Optical Lithographic Techniques

Sam Lowrey, Jacob Johnston and Richard Blaikie
MacDiarmid Institute for Advanced Materials and Nanotechnology;
Department of Physics, University of Otago, New Zealand
Correspondence: sam.lowrey@otago.ac.nz

1. Introduction

Condensation control on heat exchangers (HXs) can yield tremendous heat transfer enhancements of up to 5-7x. Condensing HXs are used in heating, ventilating and air conditioning systems which account for ≈17% of total global energy consumption.

Superhydrophobic (SHPB) surfaces can promote dropwise over filmwise condensation thus increasing liquid mobility, reducing thermal resistance and raising heat transfer rates, offering a plethora of applications from self-cleaning surfaces to enhanced condensation in HXs and anti-icing on aircraft.

State-of-the-art hierarchical SHPB structures are inspired by the lotus leaf's surface structure, employing randomly distributed nanoscale features but lack scalability. Hierarchical structures with ordered nanoscale features may offer a new means for further increasing droplet mobility and uniformity of droplet nucleation and further reduction in nucleation density during condensation processes.

Optical lithography (OL) allows precise control over nanoscale structural geometry, is a relatively low cost micro/nanofabrication technique and allows fast fabrication compared with other common micro/nanopatterning methods.

Here we present a survey of structures fabricated using OL means and their resultant wetting characteristics along with two novel hierarchical structures, one of which has greater order in its nanoscale features, and utilise low cost materials such as a 3M command strip which provides a substrate having an array millimetric scale pillars, see **Fig. 2**).

Figure 1. The lotus leaf exhibits superhydrophobicity, a wetting property arising from its micro/nanostructural surface consisting of random arrays of microscale bumps with superimposed nanoscale hairs (see **Fig. 2 G**).

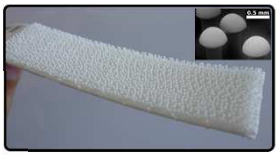


Figure 2. 3M command strip. Inset: scanning electron microscope image of several individual pillars. **Inset:** increased magnification showing pillar structure.

2. Background

LITHOGRAPHIC TECHNIQUES

Lloyd's mirror interference lithography (LMIL, Fig. 3a) is a well established microfabrication technique. Solid-immersion LMIL (SILMIL, Figs. 3b and c) allows greater resolution then other interference lithography (IL) methods as it places the system in the ultra high numerical aperture (UHNA) regime [1]. The trade-off is reduction in the depth of focus (DOF) which is theoretically infinite for other IL methods [2]. The use of a resonant underlayer (RU) can significantly enhance the DOF for SILMIL. Here we fabricate microstructures using LMIL and nanostructures using SILMIL and combine these two techniques to produce hierarchical structures. A relatively low cost 405 nm exposure source is used with these lithographic techniques.

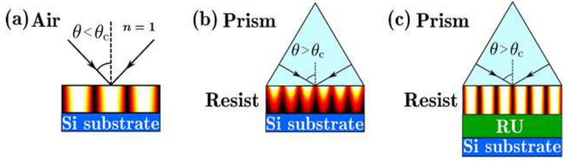
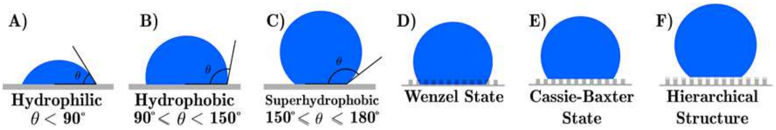


Figure 3. a) Lloyd's mirror interference lithography configuration. b) and c) Solid-immersion LMIL: b) low aspect ratio and c) high aspect ratio configurations, both in the UHNA regime. RU=Resonant Underlayer; Si=Silicon.

SURFACE WETTING



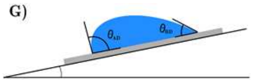


Figure 4. criteria used to characterise surface wetting can include the static contact angle '*θ*' (with range shown in **A-C**) and contact angle hysteresis, the difference between advancing/receding contact angles (see **G**). **D-F)** show wetting states that arise from topographic structure. State **D**) reduces droplet mobility; state **E** promotes droplet mobility. **F)** depicts a hierarchical structure.

3. Hierarchical Structures

Figure 5. (a) SEM image of a micro/nanostructure. Microscale pitch ~1 µm; nanoscale pitch ~116 nm. The structure was fabricated using LMIL, followed by SILMIL.

The resultant structure had a relatively small microscale height of around 200-300 nm and a nanoscale height of around 100 nm.

The exposure field was relatively large being around 1x1 cm^2. This is crucial in order to have contact between a relatively small droplet and sample. This method can be scaled up through simple modification of our optical setup.

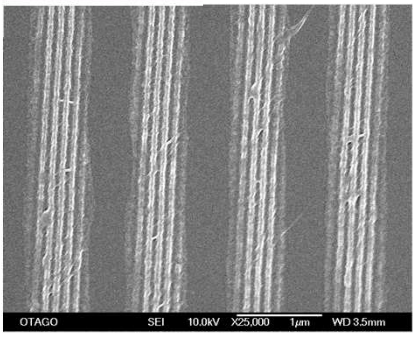
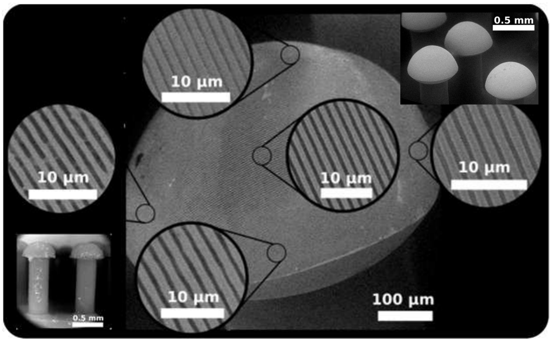


Figure 6. (a) SEM image of a milli/microstructure. Microscale pitch ~2 µm. Millscale pitch ~ 1-2 mm. The structure was fabricated using LMIL. The milli-pillar and micro-line heights were ~ 1.2 mm and 1.1 µm, respectively.

A 1-2 nm layer of platinum helped to increase photoresist adhesion with the polypropylene sample (3M command strip [Fig. 2]) resulting >80% grating coverage on milliscale surfaces. Exposure field was relatively large being around 1x1 cm^2.

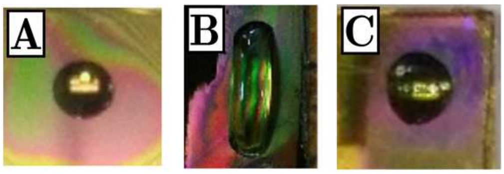
Insets: top-right, image showing upper pillar structure. **Bottom-left**, image showing pillar height.



4. Results and Discussion

STRUCTURE COVERAGE

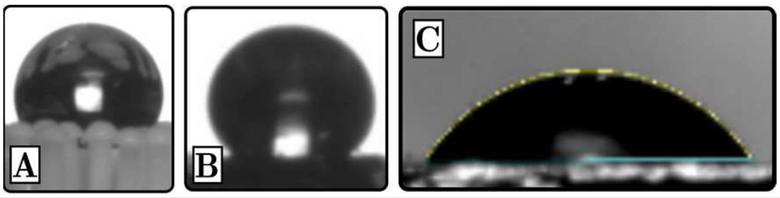
Figure 7. Plan-view photographic images of a droplet on various samples:
(A) plain photoresist (i.e. no topographic structure);
(B) grating structure with microscale lines (2 µm pitch) oriented in the vertical direction;
(C) pillar surface having a 2 µm pitch.



The droplet volume used in each test was 3 ± 0.1 µL. Fig. B demonstrates droplet elongation parallel to the grating lines. This is due to anisotropic in-plane wetting and was present in all microscale grating samples. This anisotropy was retained for droplet volumes in the range 1-10 µL, confirming good coverage of structure over a relatively large area. In Fig. C, the surface consists of pillars which should set up isotropic in-plane wetting. A small degree of anisotropy was present over the range of pillar samples tested but overall the coverage was considered to be reasonably isotropic over the exposure area and adequate for characterizing the wetting state of the samples.

The milliscale structure (**Fig. 8A**) was found to have strong hydrophobicity but had high contact angle hysteresis attributed to the pillars promoting a partial Wenzel state, resulting in droplet pinning. Note that the droplet volume was modified for the milliscale samples with a 7 ± 1 µL droplet volume used for all tests.

Figure 8. (A) Wetting state profile of a baked (at 200°C) control milliscale structure showing a transitional wetting state and a 110° contact angle. (B) Wetting state profile of the platinum coated 2 µm lines achieving a contact angle of 131°. (C) Wetting profile of the high aspect ratio 116 nm lines with contact angle of 60°.



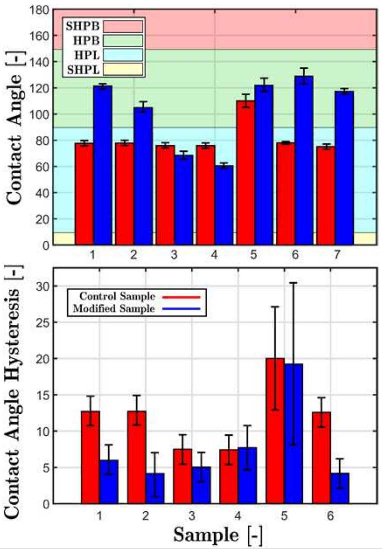
STANDARD WETTING CHARACTERISATION

Standard goniometry was used for wetting characterization of all samples and allowed measurements of both the static contact angle and the contact angle hysteresis of each sample.

Figure 9. contact angle (upper) and contact angle hysteresis (lower) for the various structures studied herein.

- **Sample 1:** 2 µm grating
- **Sample 2:** 2 µm pillars
- **Sample 3:** 116 nm grating, low aspect ratio
- **Sample 4:** 116 nm grating, high aspect ratio
- **Sample 5:** Hierarchical milli/microstructure
- **Sample 6:** Hierarchical micro/nanostructure
- **Sample 7:** Millistructure (pillars)

The hysteresis of sample 7 was not measured.



The samples show a wide contact angle range of 60°-123° where the largest increase in hydrophobicity was in the case of the hierarchical milli/microstructure. Interestingly, hydrophilicity was increased in the case of the both the low and high aspect ratio, 116 nm lines. This is attributed to potential altered surface chemistry of the photoresist by liquids specific to the SILMIL fabrication steps.

The contact angle hysteresis (CAH) shows a range of 4°-19°. The 2 µm lines and pillars contribute to the greatest reduction in CAH and in the case of the micro/nanostructure, the CAH has been reduced to 4°, meaning this structure the best configuration of CAH and contact angle for condensing HX applications.

5. Conclusions

THIS WORK HAS SHOWN

- Good coverage of micro/nanoscale structures can be achieved over relatively large areas using only optical lithographic techniques with these structures exhibiting uniform wetting characteristics for droplet volumes of up to 10 µL.
- A wide range of wetting, from hydrophilic to strongly hydrophobic, can be achieved with structures fabricated using only optical lithography.
- Contact angle hysteresis can be lowered in the presence of structures produced using optical lithography for enhanced droplet mobility.
- Relatively low cost materials and fabrication methods have been used to develop a novel milli/microscale hierarchical structure and a novel micro/nanoscale hierarchical structure. These structures have shown modified wetting characteristics compared with that of just a surface consisting of the base milli-, micro-, and nanoscale structures.

Future Direction

- Improve micro/nanoscale hierarchical structures by combining SILMIL with etching to generate larger microscale height.
- Move to chirped hierarchical structures having hydrophobic gradient for spontaneous droplet motion.
- Develop and investigate three-level hierarchical structures that merge the two structures presented herein.
- Combine these low cost optical lithographic techniques with other microfabrication techniques to achieve superhydrophobic wetting.

References

1. Lowrey, S. and Blaikie, R. 2015. Solid immersion optical lithography: tuning the prism/sample interface for improved ultra high-NA, high aspect ratio resist patterns over large exposure fields. In *SPIE Advanced Lithography* (pp. 94231W-94231W). International Society for Optics and Photonics.