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Cryogenic Focused Ion Beam Milling for Studying Wetting Hysteresis Behavior

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Abstract: Wetting and spreading of a liquid on periodically patterned surfaces is a very important physical phenomenon. Hysteresis is observed when water droplets are deposited on micro patterned surfaces and affects droplet's motion such as rolling off [1]. Hysteresis is commonly defined by the difference between the advancing and receding contact angle [2]. However, the mechanism governing hysteresis is still not fully understood since contact angle cannot accurately define the interface between droplet and surface because of the Wenzel and Cassie states [3, 4]. Therefore, a clear illustration of the interface between liquid and surface becomes the key to fully understand the hysteresis. Cryo FIB-SEM technology is becoming a powerful tool for this research topic [5].

Materials & Methods: We prepared a periodically patterned Polymethyl-methacrylate (PMMA) surface using nanoimprinting technology. During the imprinting process, the mold with prefabricated nanostructures is pressed into polymer film under controlled elevated temperatures and pressures. In this work, the PDMS mold was imprinted onto PMMA on silicon wafer substrates at 180℃, 20 psi for 2.5 minutes on a nanoimprintor (NX-2600, Nanonex). To generate the superhydrophilic and superhydrophobic surfaces, oxygen plasma (PDC-32G, Harrickplasma) and Teflon coating (CVD) were used to treat the patterned PMMA surfaces.

To create the ice interfaces on the nanostructures, water droplets were generated using an air brush system (average droplet size: 6 - 150μm) and were directly sprayed on the patterned PMMA surfaces. During the spraying, the surface temperature was maintained at -10℃ on a cold plate, which was controlled by a constant temperature bath (RTE 221, Neslab). The sample was immediately transferred onto a cryogenically cooled stage at -145℃ and evacuated to approximately e-7 torr. The interfaces of frozen droplets and patterned PMMA surfaces were observed using the Carl Zeiss Auriga FIB/SEM system. The Leica VCT Cryo Stage was used to maintain the droplets at -145℃ during FIB milling and imaging. Areas of interest underneath frozen droplets were exposed using various FIB milling parameters.

Results: The images of the interfaces of droplets on the superhydrophilic and superhydrophobic surfaces are shown in Fig. 1. Both Wenzel and Cassie states were observed as shown in Fig. 1 B and C. A stick-slip behavior of wetting hysteresis was also noticed in cryo FIB/SEM images (Fig. 2 A and B). When contact line "sticks", the contact area remains constant with time and contact angle decreases linearly. Each stick is periodically followed by a "slip" where contact area suddenly decrease and contact angle suddenly increase similarly [6]. This information is very critical for a full understanding of surface wetting properties and wetting hysteresis. The imprinted PMMA provides a simple and cost effective way to create micro and nanoscale engineered surfaces which have wetting properties that can be easily modified. Cryo FIB techniques can be used to study these surfaces and dynamic processes.

Future work will include livetime cryo FIB-SEM observation of engineered surface interactions with water and other wetting agents using temperature control. Advances in nanoimprinting in polymer surfaces and other surface engineering processes in a range of feature sizes, structural designs, aspect ratios, and materials can be realized using cryoFIB techniques.

References:

[1] K. M. Smyth, Wetting Hysteresis and droplet roll off behavior on superhydrophobic surface, MIT master thesis, (2010)
[2] A. T. Paxson, K. K. Varanasi, Self-similarity of contact line depinning from textured surface, nature communications, **4** (2013), 1492
[3] S. Jung et al, Are superhydrophobic surfaces best for icephobicity, Langmuir, **27** (2011), 3059-3066
[4] A. B. D. Cassie, S. Baxter, Wettability of porous surfaces, Trans. Faraday Soc., **40** (1944), p. 546-551
[5] K. Rykaczewski et al, Direct imaging of complex nano- to microscale interface involving solid liquid, and gas phases, ACS NANO, **6** (2012), p. 9326-9334
[6] J. W. Krumpfer, T. J. McCarthy, Contact angle hysteresis: a different view and a trivial recipe for low hysteresis hydrophobic surfaces, Faraday Discuss, **146** (2010), 103-111

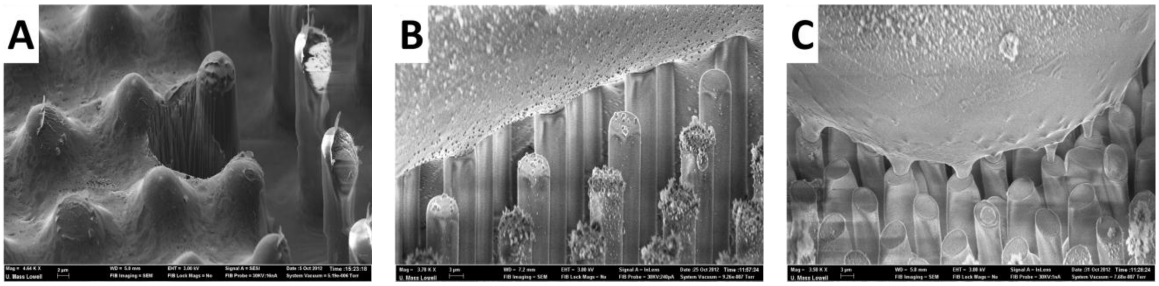

Fig. 1: Interfaces between frozen water and patterned PMMA surfaces: (A) superhydrophilic surface with full water spreading (scale bar is 2 μm); (B) superhydrophobic surface with water penetration (Wenzel State) (scale bar is 3 μm); (C) superhydrophobic surface without water wetting (Cassie State) (scale bar is 3 μm).

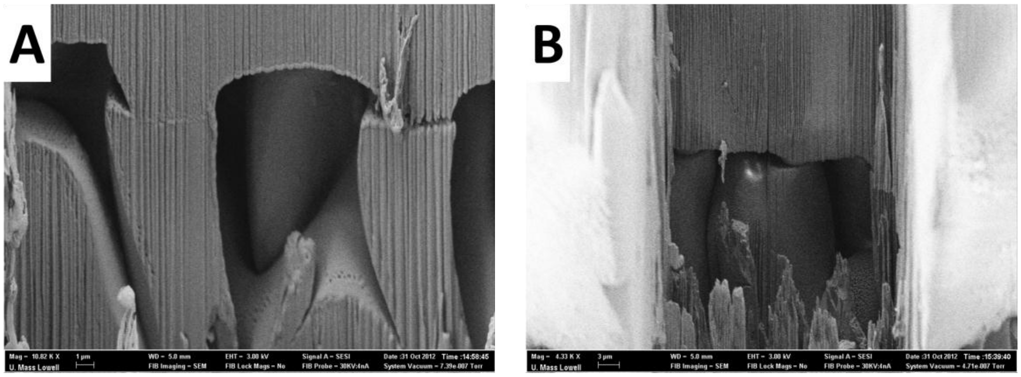

Fig. 2: Interfaces of wetting hysteresis (A) stick-slip behavior of contact line on micro-pillars array (scale bar is 1 μm); (B) center of droplet without receding (scale bar is 3 μm)