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Topography Printing to Locally Control Wettability

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Control over surface hydrophobicity is of crucial importance in tribology, functional coatings, drug delivery, and microfluidic systems.[1−3] Chemical modification of surfaces with self-assembled monolayers,[4] small molecules,[5] polymer brushes,[6] or physically changing the surface morphology,[7] or combinations of both,[8,9] have been used to generate a surface of controlled wettability. However, no strategy exists for the fabrication of substrates with local control over wettability by "printing" topographically structured surfaces. Here, we present a soft-lithographic method based on transferring PDMS patterns onto planar or topographically patterned substrates. The advantages of this procedure are substrate tolerance, that is, the method can be applied on Si wafers, glass, gold, but also on "soft" surfaces, such as polymers and photoresists, and spatial control over the wettability of nonplanar surfaces. As demonstrated below, the creation of a two-tier hydrophilic−hydrophobic structure provides a simple and effective method for the selective wetting of the inside of lithographically prepared channels. This is of crucial importance in new microelectronic fabrication processes, such as ink-jet printing, where ink diffusion due to "overfilling" dramatically decreases the printing resolution.

The procedure to transfer print hydrophobic surfaces (Figure 1a) is inspired by recently developed (decal) transfer printing techniques,[10−14] but the activation and transfer step is based on a silicate-forming reaction between NaOH and the surface SiO_x layer.

First, a patterned PDMS stamp was oxidized (30 s) in an O_2 plasma to render the surface hydrophilic. The hydrophilic PDMS stamp was then immersed in 10 mM $NaOH_{(aq)}$ for 1 h, and after drying under N_2, it was brought into contact with a clean Si wafer or a hydrophilic, topographically patterned photoresist layer. This assembly was cured for 1 h at 65 °C, and then the PDMS stamp was peeled off, leaving a PDMS pattern transferred onto the areas of contact. The transfer of PDMS is due to cohesive mechanical failure (CMF) since the alkali fusion reaction of SiO_2-containing materials leads to the formation of silicate species on the stamp surface, which cross-link with Si/SiO_2 surfaces and hydroxyl groups on oxidized polymer substrates (see also Supporting Information, SI). Figure 1b−d shows a series of optical and scanning electronic microscopic (SEM) images of PDMS patterns transferred onto Si wafers. Depending on the design of the PDMS stamp, the feature size of transferred PDMS could be varied from 200 nm to 100 μm, without obvious differences in reproduction quality.

Surfaces patterned at the (sub)micron level with hydrophobic (PDMS) features will exhibit significantly increased contact angles.[15,16] Figure 2a and b shows optical and AFM images of the topography printed PDMS patterns on Si/SiO_2 surfaces and their corresponding advancing contact angles, clearly demonstrating that even superhydrophobic surfaces can be generated. The height of the features transferred in the topography printing step is strongly influenced by the NaOH concentration. Only trace amounts are transferred at concentrations below 0.1 mM, whereas 1−100 mM solutions lead to accurately reproduced, 100−300 nm high, PDMS features over several square centimeters (Figures S2 and S3). The thickness of the features printed directly influences the contact angles of the resulting surfaces.

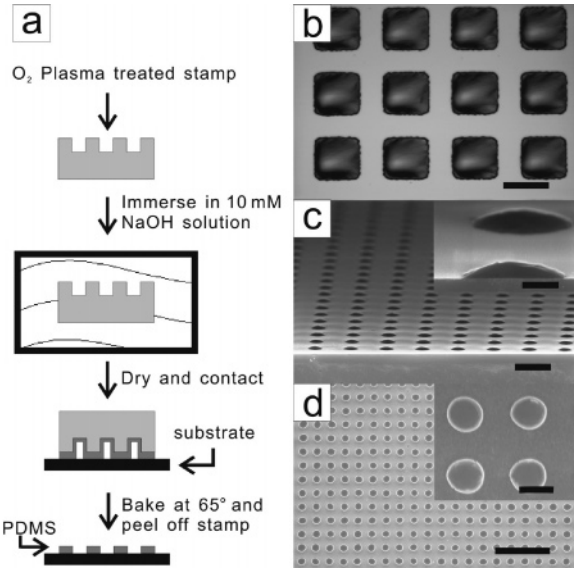

Figure 1. (a) Schematic illustration of PDMS transfer procedures; (b) optical microscopic image of PDMS squares (scale bar = 70 μm); (c) SEM image of PDMS dots (scale bar = 4 μm), inset is its zoom-in image (scale bar = 500 nm); (d) SEM image of PDMS dots (scale bar = 2 μm), inset is a zoom-in SEM image (scale bar = 250 nm).

By using hierarchically patterned stamps with 2 μm dots arranged in 150 μm squares, it is possible to produce areas with altered wettability in any pattern, without changing the topography printing conditions. The contact area and therefore the cohesive failure mechanism for every printed feature is unchanged. Figures 2c and d demonstrates the formation of substrates modified with patterns of micron-sized PDMS dots. These results demonstrate that topography printing can easily be used to pattern surfaces into any design, requiring effectively only optimal transfer of the 2 μm dots.

Our key result here is the formation of hydrophobic patterns *on top of* lithographically prepared patterns in the photoresist for locally controlling the wettability, without the need for further lithography or chemical deposition steps. Such a technique is very important, for example, in display fabrication where polymers are ink-jet-printed onto prepatterned surfaces. The spilling of ink onto the banks of the photoresist presents a formidable impediment for the large-scale application of ink-jet printing of polymer electronic devices. Ideally, the bottom of the wells should be hydrophilic, while the top of the photoresist structures should be hydrophobic to prevent any wetting beyond the lithographically prepared features. As shown in Figure 3a, a PDMS pattern was transferred on the top of the oxidized SU8 microchannels. Figure 3b,c shows the SU8 pattern before and after transfer printing 1.7 μm PDMS lines with a 4 μm

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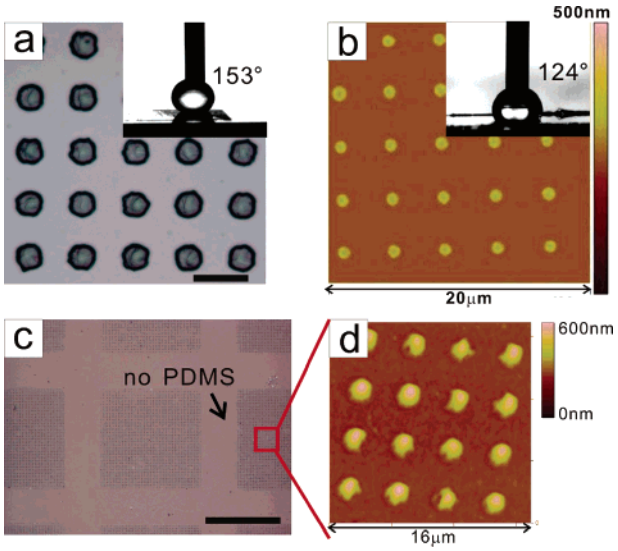

Figure 2. (a) Optical microscopic image of PDMS dots (scale bar = 70 μm); the inset is its corresponding advancing contact angle image. (b) AFM topography of the PDMS pattern; the inset is the corresponding advancing contact angle image. (c) Optical microscopic image of hierarchically patterned PDMS (scale bar = 150 μm) and (d) AFM image of printed area.

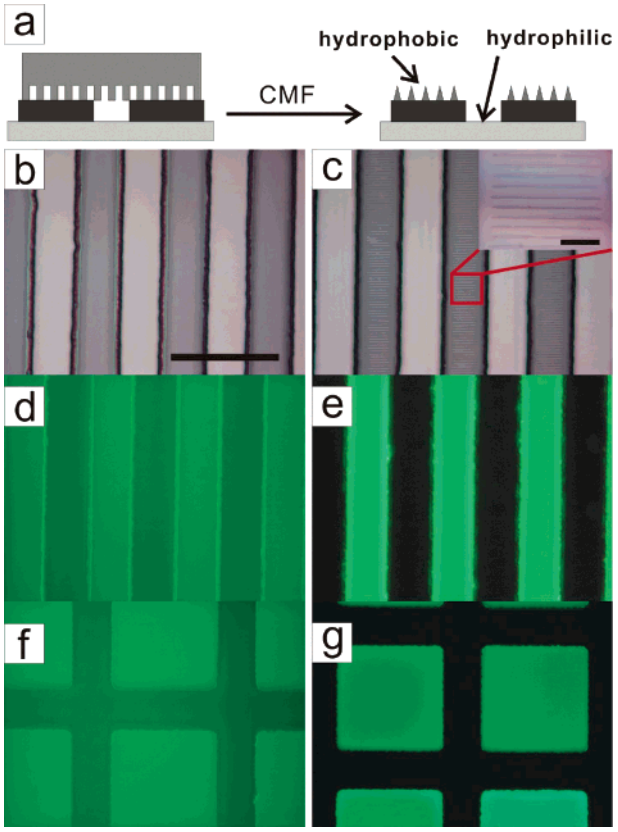

Figure 3. (a) Scheme of transferring PDMS pattern onto structured SU8 photoresist; (b) SU8 lines made by photolithography (scale bar = 150 μm, applicable to c−g); (c) printed PDMS on (a); the inset shows the zoom-in image on the PDMS pattern area (scale bar = 15 μm); (d) fluorescent solution treated (b) (previously treated with O_2 plasma); (e) fluorescent solution treated (c); (f) fluorescent solution treated SU8 microwells (previously treated with O_2 plasma); (g) fluorescent solution treated SU8 microwells with additional PDMS patterns.

period perpendicular to the direction of SU8 lines. Since only the resist banks are in contact with the PDMS stamp, the trenches remain unpatterned and hence hydrophilic. The ability of controlling the wetting of microchannels by this two-layer structure was demonstrated by dip-coating the sample with a fluorescent solution (Oregon Green 488, Molecular Probes) and imaging with a fluorescent microscope. As shown in Figure 3d, without the additional PDMS pattern, the fluorescent solution wet the entire surface. In contrast, Figure 3e shows that the fluorescent solution only wet hydrophilic trenches of the two-layer sample and dewet on SU8 with additional PDMS structure. Similar results can be found in SU8 microwells in which the top was patterned with PDMS, leaving the wells unpatterned. Again, the fluorescent solution wet the entire surface of SU8 treated with O_2 plasma but only wet the hydrophilic well bottom of the two-layer sample.

In conclusion, this paper reports a new PDMS stamping-based patterning strategy which exploits the printing of topographical features (instead of molecules) to locally control surface wettability. We have shown the flexibility of the approach by printing a range of features on different substrates. By controlling the aspect ratios of the features, the contact angle of the resulting patterns can be increased to make (super)hydrophobic surfaces. The printing of various PDMS geometries also allowed us to locally change the wettability of topographically structured surfaces. The flexibility of our method is further demonstrated by creating PDMS architectures on a patterned SU8 photoresist, leading to differential wetting and dewetting properties in microchannels/microwells and on the PDMS transferred area, respectively.

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Supporting Information Available: Experimental details, mechanism of binding reaction between PDMS and substrate, and optical microscope images of PDMS patterns on various substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Rajan, T. P. D.; Pillai, R. M.; Pai, B. C. *J. Mater. Sci.* **1998**, *33*, 3491.

(2) Vlachou, M.; Hani, N.; Efentakis, M.; Tarantili P. A.; Andreopoulos, A. G. *J. Biomater. Appl.* **2000**, *15*, 65.

(3) Delamarche, E.; Juncker, D.; Schmid, H. *Adv. Mater.* **2005**, *17*, 2911.

(4) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.

(5) Wu, X.; Shi, G. *Nanotechnology* **2005**, *16*, 2056.

(6) Zhou, F.; Huck, W. T. S. *Chem. Commun.* **2005**, 5999.

(7) Jin, M.; Feng, X.; Feng, L.; Sun, T.; Zhai, J.; Li, T.; Jiang, L. *Adv. Mater.* **2005**, *17*, 1977.

(8) Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 357.

(9) Guo, Z.; Zhou, F.; Hao, J.; Liu, W. *J. Am. Chem. Soc.* **2005**, *127*, 15670.

(10) Childs, W. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 13583.

(11) Childs, W. R.; Nuzzo, R. G. *Adv. Mater.* **2004**, *16*, 1323.

(12) Park, K. S.; Seo, E. K.; Do, Y. R.; Kim, K.; Sung, M. M. *J. Am. Chem. Soc.* **2006**, *128*, 858.

(13) Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Someya, T.; Gershenson, M.; Rogers, J. A. *Science* **2004**, *303*, 1644.

(14) Khang, D. Y.; Jiang, H.; Huang, Y.; Rogers, J. A. *Science* **2006**, *311*, 208.

(15) Pantankar, N. A. *Langmuir* **2003**, *19*, 1249.

(16) Burton, Z.; Bhushan, B. *Nano Lett.* **2005**, *5*, 1607.

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