Electronic Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information (ESI)

Running droplet of interfacial chemical reaction flow

Xi Yao,[a] Hao Bai,[c] Jie Ju,[b] Ding Zhou,[a] Jing Li,[a] Hao Zhang,*[a] Bai Yang,[a] and Lei Jiang*[b]

[a]State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China

[b]Beijing National Laboratory for Molecular Science (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[c]National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

Fax: (+86) 10-8262-7566; Tel: (+86) 10-8262-1396

Correspondence and requests for materials should be addressed to H. Zhang (hao_zhang@jlu.edu.cn) and L. Jiang. (jianglei@iccas.ac.cn).

This file contains Mov. S1 to S8 with legends, experimental methods and Fig. S1 to S4 with legends.

Supplementary movies

Mov. S1 This is the original video clip of Fig. 1a. The silicon wafer was placed between the high speed video camera and a light source.

Mov. S2 This is the original video clip of Fig. 1c. The inward-spiral movement of a HF droplet (2 μL, 20wt%) demonstrates its potential application in open-system microfluidics, especially in cases when it shows complicated moving path of the droplets. Detailed fabrication procedure of the patterned surface is described in the Supplementary Information.

Mov. S3 Snaking motion of a HF droplet on a hydrophobic silicon wafer patterned with hydrophilic tracks. Together with the motion in Mov. S2, it demonstrates the "free-running" feature of HF droplet motion, which might be useful in the tasks which based on utilizing complicate surface morphology.

Mov. S4-6 The original video clips of Fig. 3a, 3b and 3c, respectively.

Mov. S7 The original video clips of Fig. S2, showing a HF droplet (10 μL) climbing on a vertically positioned silicon strip. The tip of the pipette was in a synchronous motion to the climbing droplet at the initial stage (0 to 3 cm) since the whole volume of the droplet was too large to be deposited at once.

Mov. S8 HF droplet motion at 398 K. The droplet was boiling while moving on a silicon strip, exerting tiny bubbles from the solid-liquid interface. The droplet was in a steady moving velocity of 280 mm/s, which nearly doubled the top speed of the motion under the boiling point (~160 mm/s).

Experimental methods

Materials and sample preparation: Hydrofluoric acid (HF, 40wt% of hydrogen fluoride in water solution) was purchased from Beihua Fine Chemicals Co., Ltd., Beijing, China. Deionized water (purified by Milli-Q System) was mixed with HF in different proportions to obtain HF solution with desired concentration. To prevent hostile HF vapor, HF was well-sealed in plastic tubes and stored in glove box for further use.

Commercially available silicon wafers were treated by oxygen plasma (DT-03 Low-temperature Plasma Cleaner, Suzhou Omiga Tech. Co., Ltd.) at 150 W with 100 sccm of air inflow for 3 min. This surface pre-treatment is aimed at removing surface contaminants. Oxygen plasma treatment is also helpful in achieving silicon surface with homogenous hydroxyl coverage and in turn, a uniform surface hydrophilicity. Moreover, we found that oxygen plasma is also capable of reactivating the as-etched (by HF) silicon surface. After oxygen plasma treatment, silicon substrates were capable to propel HF droplet motion again. Fig. S1 shows the XPS results before and after the oxygen plasma treatment to the etched surfaces, verifying that local oxide layer, i.e., hydroxyl was reinstalled on such surfaces. Fig. S4 demonstrates the recyclability of oxygen plasma treatment by measuring water contact angle (CA) on a silicon surface which was repeatedly etched by HF and then treated by oxygen plasma. After 4 cycles, the CA characterization became unreliable (Fig. S4), indicating that the surface had been randomly roughened with the amount of surface detects increased.

Fabrication of patterned surface: Silicon surfaces with hydrophilic-hydrophobic pattern were fabricated by combining the photo-lithography and chemical vapor deposition (CVD). The method was adopted from an earlier report.[1] Typically, silicon wafers were first treated by oxygen plasma as described above. Then two drops of positive photoresist (PR, BP212-37, purchased from Kempur Microelectronics, Inc.) were spin-coated on the silicon wafers (with spinning rate 3000 rpm for 1 min and the resulting resist film thickness being 2 μm), which were subsequently heated at 80°C for 0.5 h and irradiated by UV light for 1 min under the photo masks with desired patterns. After the degradation of the polymer photoresist in the exposed area, the wafers were carefully rinsed by ethanol until the pattern was clearly revealed, followed by rinsing with ample deionized water and drying by nitrogen flow. Then the dried wafers were treated by CVD with trichloro

(1H,1H,2H,2H-heptadecafluorodecyl) silane (purchased from TCI, Japan) in sealed container at 80˚C for 2 h. The grafted wafers were then rinsed subsequently by ethanol and deionized water.

High speed camera recording and CA measurements: The droplet motion in Fig. 1a was recorded by high speed video camera (Phantom v9.1, VRI, America) at the time resolution of 500 frames per second (f/s). The droplet motions on arbitrarily inclined silicon surfaces were recorded by high speed video camera (HCC1000 CCD, Germany). In Fig. 1a, the time resolution was 456.25 f/s; in Fig. 3a-c, the time resolution was 912.5 f/s for uphill motions at 15˚, 45˚ and 456.25 f/s at 90˚. All water contact angles were measured by OCA20 (DataPhysics, Germany). At least five points on a single surface were taken to obtain a mean value.

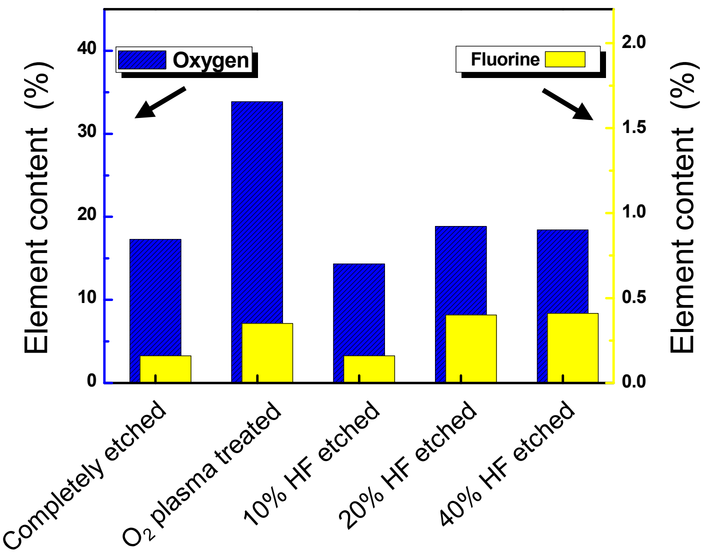

Fig. S1 The XPS results of the chemical composition of oxygen (blue) and fluorine (yellow) on silicon surfaces in different situations (colored online). The trace amount of fluorine content (< 0.5%) in all cases verified that fluorine termination is not a preferable result from the reaction. The oxygen content was 34% after oxygen plasma treatment while a half in other cases, indicating a critical content of hydrophilic group, beyond which the rear edge of the moving droplet depinned and the reaction was terminated.

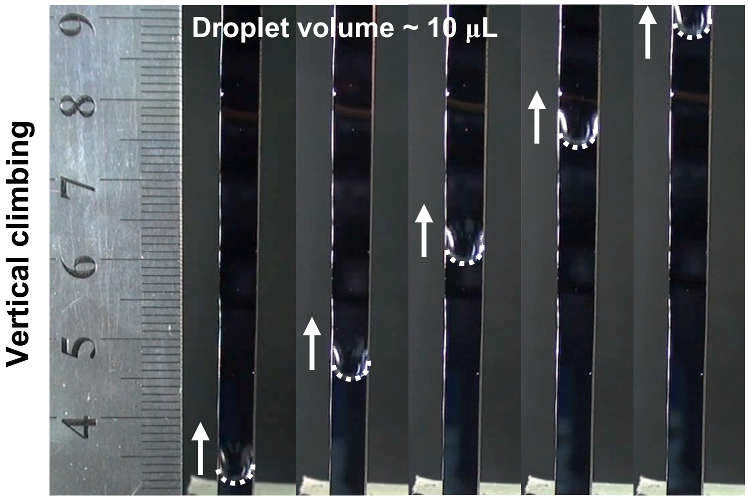

Fig. S2 Sequence of frames from the movie (see Mov. S7 in Supplementary Information) recording a 10-μL HF droplet (20wt%) climbing up on a vertically placed silicon strip (5 mm in width). The frames separated by 1 second were superimposed into one image. The lower edges of each droplet are indicated by white dots.

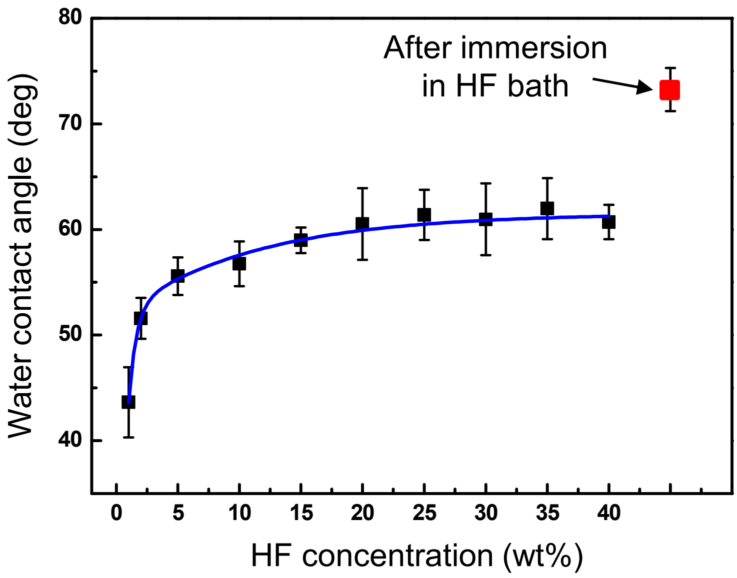

Fig. S3 The wettability of silicon surface after motions of HF droplets with different concentrations. The gradually increasing water contact angle indicates that as raising the reaction rate, the running droplet modifies the surface more and more completely. However, comparing to the red square taken from the silicon wafer treated by immersion in HF bath for 5 seconds, droplet motions for all concentrations are clearly far from reaching the saturated surface modification.[2]

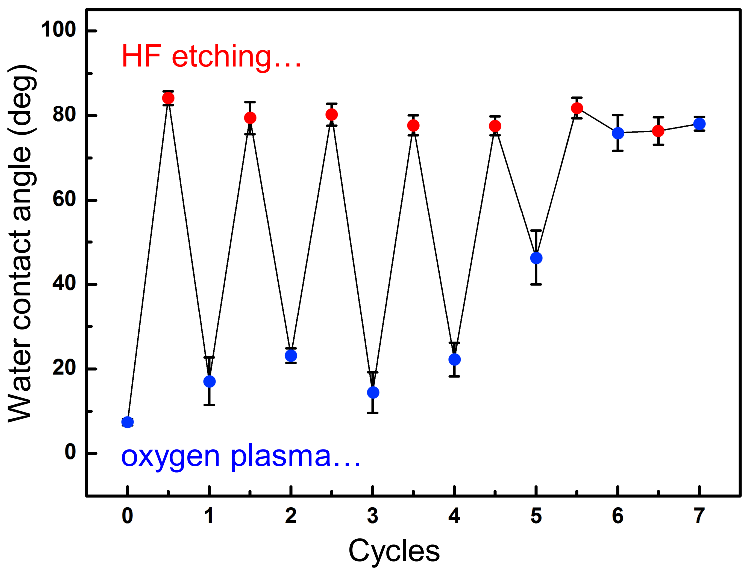

Fig. S4 Recyclability of silicon surface. The silicon surface had been effectively reactivated for four times before the surface became unstable for further characterization. Since each time of HF etching involves the peeling-off of several layers of silica atoms,[3] the surface roughness will gradually rise according to the silicon lattice structure and surface defects.

Reference

1 D. F. Zhu, X. A. Li, G. Zhang, X. Zhang, X. M. Zhang, T. Q. Wang, B. Yang, *Langmuir* 2010, **26**, 14276-14283.
2 U. Thiele, K. John and M. Bär, *Phys. Rev. Lett.*, 2004, **93**, 027802.
3 H. Bender, S. Verhaverbeke, M. M. Heyns, *J. Electrochemical Soc.* 1994, **141**, 3128-3136.