Surface Patterning

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Selective Surface Patterning with an Electric Discharge in the Fabrication of Microfluidic Structures**

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Surfaces with micro- and nanoscale patterns are attracting wide interest for their potential use in, for example, sensors, data storage, displays, optoelectronics, biomimetics, and micro- and nanofluidics. An attractive method to manipulate substrate properties easily and with good controllability is selective surface modification with self-assembled monolayers (SAMs). Selective modification of SAMs is possible through selective placement, for example, by microcontact printing (μCP)[1] and dip-pen nanolithography (DPN),[2] or by selective removal of the monolayer constituents, for example, by energetic beams (photons, electrons, atoms, ions)[3–6] or scanning probe lithography (SPL).[7] μCP is a rapid and simple technique but, even though successfully applied to curved substrates,[8] as a contact stamping method it does not tolerate textured surfaces. DPN and SPL are high-resolution techniques but neither can handle high-relief structures. In addition, these techniques are slow in scanning large areas and require expensive equipment. Bombardment with energetic beams is relatively fast and better suited for textured surfaces. However, these methods tend to need masks, complex setups, special equipment, or a vacuum environment.

Herein, we report the exploitation of an electric discharge for selective surface modification of a hydrophobic trichloro(octadecyl)silane (ODS) SAM on a Si–SiO_2 surface. Electric discharge is widely utilized in the micromachining of metal, glass, and semiconductor substrates. Microelectro discharge machining and micro hollow-cathode discharges, for instance, have been used in the production of microholes and microchannels with typical dimensions in the range of 50–100 μm,[9–11] as well as in deposition applications.[10,12] In addition, discharge-created plasmas are frequently used in surface modification.[13,14] Our work represents the first application of microscale electric discharge under ambient conditions to the selective removal of a SAM on silicon dioxide. The patterns created on ODS-modified black and micropillar-structured silicon (Figure 1) were found to perform well in microfluidic applications.

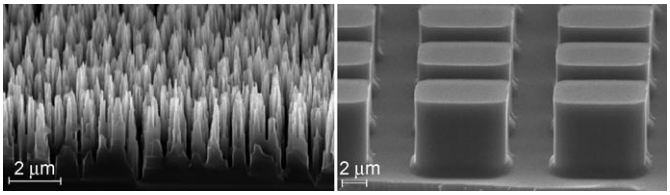

Figure 1. Scanning electron microscopy (SEM) images of black silicon (left) and silicon micropillars (right).

Piranha-oxidized (general pretreatment) silicon chips were coated with an ODS SAM, which was subsequently removed from desired areas with an electric discharge: a platinum wire set at a high voltage was brought close to a grounded silicon chip and scanned over the surface to produce the desired patterns (Figure 2). While optimizing

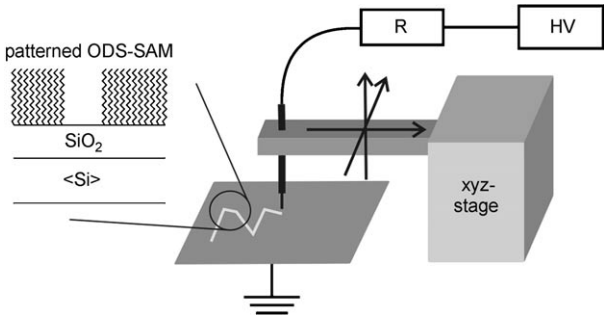

Figure 2. Setup for electric discharge patterning. See text and Experimental Section for details. R = resistor, HV = high-voltage supply.

the patterning parameters, we observed the following relationships: 1) the shorter the distance between the tip and the chip, the smaller the line width; 2) the smaller the current, the smaller the line width; and 3) the faster the writing speed, the

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smaller the line width. A minimum line width of 50 μm was achieved by using a 1-μA current with positive tip voltage, a distance of 20 μm, and a writing speed of 5 mm s^{-1}. The computer-controlled motorized stage provides an easy and rapid method to write any pattern desired with a single sweep of the discharge under atmospheric pressure on planar, curved, and textured surfaces. With a 1 mm s^{-1} writing speed, the patterning time of the underlined word "MICRO" was 40 s (Figure 3) and that of a 2 cm channel was 20 s.

Figure 3. Photograph of a patterned ODS micropillar chip. Water flows spontaneously from the droplet on the left into the hydrophilic "MICRO" pattern.

Figure 4 presents a hydrophilic surface-guided microchannel 70 μm in width, patterned by electric discharge on an ODS SAM-coated micropillar silicon chip. An aqueous

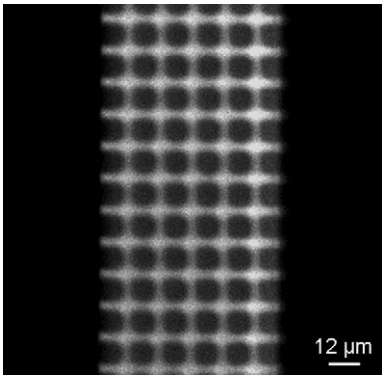

Figure 4. Fluorescence microscopy image showing aqueous fluorescein solution applied to a micropillar chip; the patterned area acts as a surface-guided hydrophilic channel (width 70 μm).

fluorescein solution introduced to one end of the pattern flowed by capillary forces[15,16] throughout the discharge-treated area, thus acting as a hydrophilic microchannel in which the patterned surface chemistry guided the flow. By using the electric discharge method, several channels of different width, length, and shape can be patterned on one chip without the need for designing and fabricating masks.

The removal of the ODS SAM by electric discharge patterning was studied with water contact angle measurements, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). High water contact angle values confirmed the hydrophobic nature of the ODS-coated surface, and low values—corresponding to that of a piranha-treated surface—the hydrophilic nature of the discharge-treated surface (Table 1). The water contact angle hysteresis (the difference between advancing and receding contact angles) of a discharge-treated surface corresponds to that of a piranha-treated surface, which implies the same kind of surface heterogeneity for these two surfaces.

Table 1: Advancing and receding water contact angles on piranha-treated and surface-modified planar Si–SiO_2 chips. The contact angles of the surrounding areas remained unchanged.

Chip surface	Water contact angle [°] Advancing	Receding
piranha-treated	16 ± 4	4 ± 4
ODS SAM	116 ± 2	89 ± 2
discharge-treated ODS SAM	13 ± 1	4 ± 1
OCS SAM	80 ± 1	56 ± 1
discharge-treated OCS SAM	17 ± 3	4 ± 2

The FTIR spectrum of the ODS-coated surface showed intense CH_2 (2922 and 2853 cm^{-1}) and CH_3 (2964 and 2880 cm^{-1}) stretching vibrations (Figure 5). Very weak CH

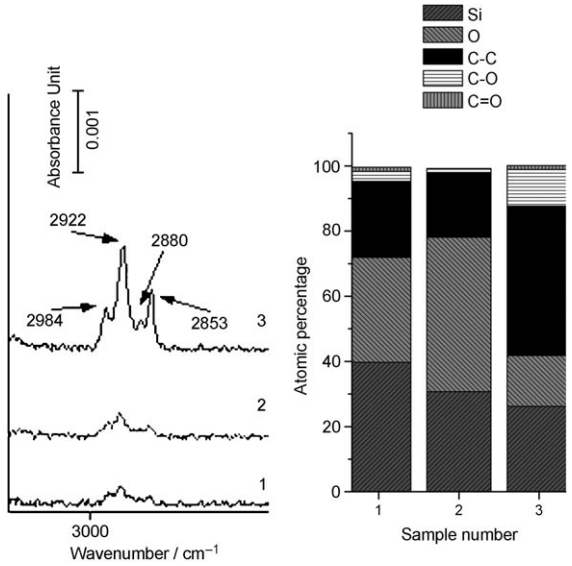

Figure 5. FTIR spectra and XPS results from 1) piranha-treated, 2) discharge-treated, and 3) ODS SAM surfaces. See the text and the Supporting Information for details.

stretching, most likely originating from airborne hydrocarbon contamination, was observed on the discharge- and piranha-treated surfaces. The X-ray photoelectron spectrum of the ODS-coated surface clearly showed a higher carbon content than that of the discharge- and piranha-treated surfaces (Figure 5), which supports the results obtained by FTIR spectroscopy. Importantly, the X-ray photoelectron spectra of the piranha- and discharge-treated surfaces showed only residual amounts of compounds including C–O or C=O bonds, which excluded the possibility that the oxidation products of ODS could account for the hydrophilicity of the discharge-treated surface (see the Supporting Information). The FTIR and XPS results thus indicated that the ODS SAM was removed by the discharge.

The AFM image of a planar uncoated silicon chip, scanned over the edge of a discharge-treated area, shows no visible imprint of the discharge (Figure 6A). For a planar

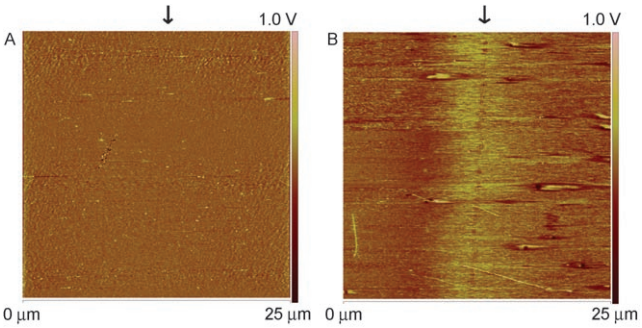

Figure 6. AFM lateral-force images ($25 \times 25\ \mu m^2$) from planar uncoated discharge-treated (A) and planar ODS-coated discharge-treated (B) silicon chips. The edges of the discharge-treated areas appear in the middle of the images (marked with arrows); the left sides are discharge-treated and the right sides are untreated original silicon dioxide (A) or ODS SAM (B) surfaces.

ODS SAM-coated chip, in contrast, the edge of the discharge-treated area is visible (Figure 6B). On the discharge-treated side (Figure 6B, left), the friction between the AFM tip and the surface corresponds to that of the uncoated silicon chip (Figure 6A). On the edge of the ODS SAM side, the increased friction is seen as a lighter area (Figure 6B).

The results clearly demonstrate that an electric discharge effectively removes the ODS SAM to reveal the underlying hydrophilic silicon dioxide surface without causing noticeable change to the surface texture (see the Supporting Information). Moreover, the discharge-treated areas were successfully modified further with (3-aminopropyl)triethoxysilane (APS) or trichloro-7-octenylsilane (OCS), which requires a hydroxylated oxide surface (see the Supporting Information).[17] In other words, the exposed areas can be coated with a new SAM of different chemical character. As the discharge does not cause any physical damage to the silicon surface, it is possible to restore the original SAM by refilling the patterned areas with the same monolayer constituent (see the Supporting Information). The way is then opened for repeated patterning of the same chip. The applicability of the electric discharge patterning to other SAMs was demonstrated with an OCS-modified silicon surface (Table 1).

We applied the electric-discharge-patterned ODS silicon chips to fast drug analyses by mass spectrometry. In the first application, a micropillar chip with a conical tip[18] was coated with ODS, and a hydrophilic surface-guided microchannel (width ca. 200 μm) was patterned on it by removing ODS with an electric discharge. A droplet of polar analyte solution was introduced to the entrance of the channel, and the micropillar array enabled a spontaneous fluid flow with capillary forces along the hydrophilic channel toward the conical tip. The high voltage applied to the chip created a high electric field at the tip, and the analyte (verapamil) was ionized by electrospray and transferred for mass spectrometric analysis (Figure 7 and the Supporting Information). Several electrospray ionization

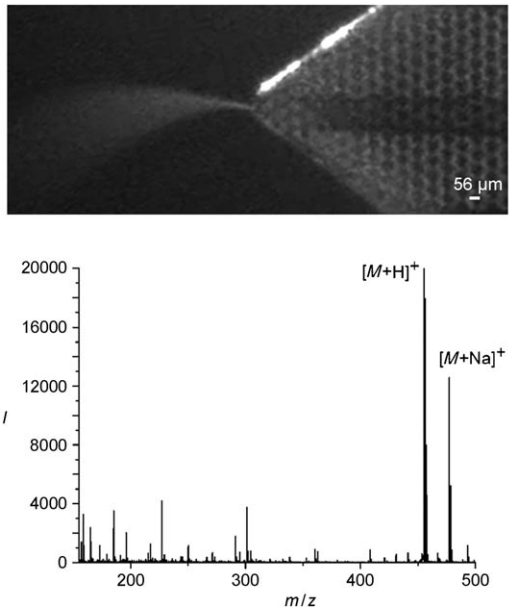

Figure 7. A patterned ODS micropillar chip was used in the analysis of verapamil by electrospray ionization mass spectrometry. The polar analyte solution was guided by the hydrophilic channel (width ca. 200 μm) to the tip of the chip and analyzed by a mass spectrometer (top). Bottom: the resulting spectrum of 10 μM verapamil.

tips can be readily fabricated on a single chip to provide fast array-based high-throughput analyses.

In the second application, small hydrophilic sample spots (diameter $< 100\ \mu m$) were patterned with electric discharge on an ODS-coated black silicon chip for the purpose of concentrating aqueous samples for desorption/ionization on silicon mass spectrometry (DIOS-MS) analyses. Black silicon enables efficient absorption of laser energy and is therefore utilized in DIOS-MS.[19] By concentrating aqueous samples on small hydrophilic spots, we expected to increase the analyte signal by decreasing the unpredictable spreading of the sample solution on the surface, which is often associated with desorption/ionization mass spectrometry.[20] The DIOS mass spectra demonstrated a significant increase in the analyte (verapamil) signal intensity from the patterned chips as compared to the intensity from nonpatterned hydrophilic chips (treated with piranha solution) and from nonpatterned hydrophobic chips (treated with HF solution; Figure 8 and the Supporting Information). The patterned black silicon and micropillar silicon surfaces serve not only as a demonstration of the applicability of the patterning method to textured surfaces, but also as intriguing examples of using patterned surface chemistry for improved or facilitated microfluidic applications.

In conclusion, we have developed a rapid and facile method based on electric discharge to pattern organic SAMs on silicon. The method allows the patterning of areas of arbitrary size and shape under atmospheric conditions without the need for a mask. Electric discharge patterning is applicable to both planar and textured surfaces, the latter demonstrated by the black silicon and micropillar silicon chips utilized in mass spectrometric analysis. The technique is

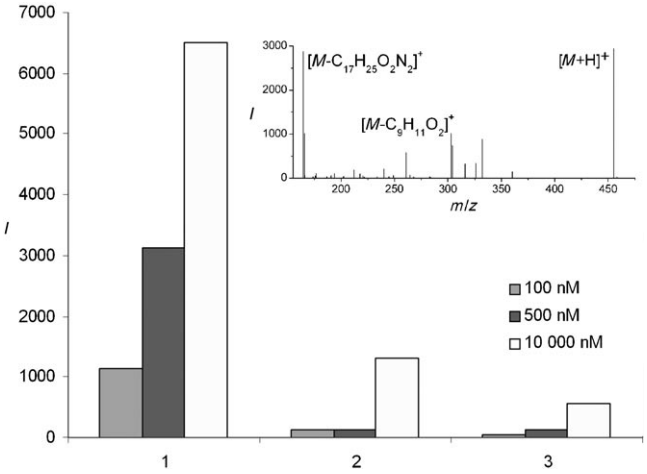

Figure 8. Effect of sample concentration using electric-discharge-patterned black silicon chips for DIOS-MS in the detection of verapamil. The analyte signal (combined intensities of $[M+H]^+$ at m/z 455 and two abundant fragments at m/z 303 and 165) is presented for three concentrations of aqueous verapamil solution, from 1) a patterned ODS chip, 2) a hydrophilic reference chip, and 3) a hydrophobic reference chip. Inset: mass spectrum of the verapamil solution (10000 nM) from the patterned (1) chip.

amenable to parallelization, as multiple patterning tips can be connected to a high voltage and used for the production of multiple patterns simultaneously. As such, patterned SAMs on silicon can be used as etching masks and in microfluidics. Further modifications of patterned areas could enable spatially controlled attachment of biomolecules, solid-phase combinatorial chemistry, and on-chip sample pretreatment for various lab-on-a-chip applications.

Experimental Section

Micropillar silicon (pillar diameter ca. 9 μm, pillar height 10 μm) and black silicon (needle height ca. 2 μm, needle width ca. 100 nm) were fabricated by deep reactive-ion etching to cover a whole p-type (100) silicon wafer of resistivity 2.56–3.94 Ωcm.[19] The wafers were cut into 1×1 cm^2 chips and cleaned and oxidized with 25% hydrogen fluoride and piranha (95–97% sulfuric acid/30% hydrogen peroxide, 3:1) solutions. For SAM formation, the chips were immersed in a 3% (v/v) solution of ODS or OCS in toluene under an argon atmosphere. After 1 h at room temperature, the chips were removed from the solution and rinsed with toluene, cured at 120 °C, and washed with toluene and methanol in an ultrasonic bath. Backfilling of the discharge-treated areas with APS, OCS, or ODS was carried out in the same manner.

The patterning tip (a 50-μm-diameter platinum wire) was connected to a high-voltage supply through a resistor and brought close to the grounded silicon chip. The current was kept constant at the desired value between 0.1 and 3 μA, and the voltage was from 500 V to 2 kV depending on the current. Both positive and negative voltages were applied. The tip was scanned over the surface at a distance of 20–1000 μm using a computer-controlled *xyz* stage with a writing speed of 0.25–5 mm s^{-1}. Large hydrophilic areas were created by a dense scan with steps of 70–100 μm.

The Supporting Information contains details of all analysis methods, analytical results not presented in the text (FTIR and XPS results, contact angle values, and SEM images), discussion on the mechanism of SAM removal and on the backfilling of the patterned chips, the fabrication of the ionization chips, and mass spectrometry measurements.

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