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Microcontact Printing of Octadecylsiloxane on the Surface of Silicon Dioxide and Its Application in Microfabrication

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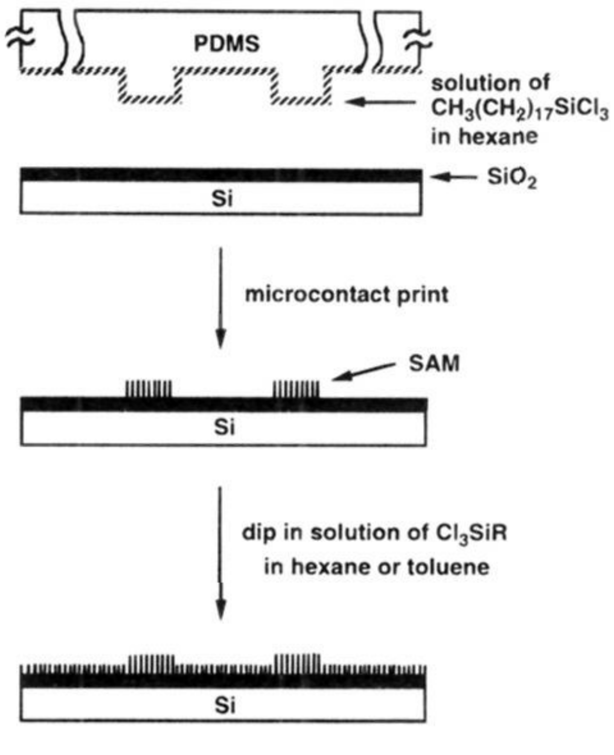
This paper describes the use of microcontact printing (μCP)[1] for patterning self-assembled monolayers (SAMs)[2] of alkylsiloxanes on the surface of silicon dioxide. μCP is a convenient technique for generating patterned SAMs of alkanethiolates on gold,[3,4] but it has not been applied to Si/SiO_2 and glass. The SAMs of alkyltrichlorosilanes on the hydroxyl-terminated surfaces are less ordered than those of alkanethiolates on gold, and they form more slowly.[5] Here we demonstrate that μCP can, nonetheless, be used to produce patterned SAMs of alkylsiloxanes on Si/SiO_2. Although these patterned SAMs provide only partial selectivity in the etching of SiO_2 in aqueous HF/NH_4F solution, they are useful in other ways. In particular, we show that poly(methyl methacrylate) (PMMA) or polyurethane (PU) selectively organized on the hydrophilic regions of the patterned surface is an effective resist that allows selective etching of the unprotected SiO_2.

Figure 1 outlines the procedure.[1,6] A PDMS stamp with parallel lines was used to pattern a SAM of octadecylsiloxane on Si/SiO_2. The patterned substrate was then immersed in a solution of Cl_3SiR or $(EtO)_3SiR$ (R = $-(CH_2)_3NH_2$, $-(CH_2)_3SH$, $-(CH_2)_3Br$, $-(CH_2)_3NCO$, $-(CH_2)_2(CF_2)_5CF_3$, or $-(CH_2)_{15}CH{=}CH_2$) in hexane (~0.4% w/w) for ~5 min to derivatize the remaining regions of Si/SiO_2 with siloxanes terminated in a different functional group. Subsequent treatment of a patterned SAM containing vinyl-terminated regions with an aqueous solution of $KMnO_4$ and KIO_4 converted the olefins to carboxylic acids.[7] We characterized these patterned surfaces by XPS, SEM, SIMS, and optical microscopy of condensation figures (CFs)[8] (Figure 2). SEM suggests that the edge resolution of these lines is lower than that observed for alkanethiolates on gold (~200 vs ~50 nm).[9]

Comparison of the properties of nonpatterned SAMs of octadecylsiloxane that were generated by μCP with a flat PDMS stamp and by immersion in solution (Table 1) suggested that the former SAMs were more uniform, although the thicknesses of the SAMs prepared by these two methods were comparable.

Although the patterned SAM of octadecylsiloxane on Si/SiO_2 did not protect the surface against etching in aqueous HF/NH_4F



R = $-(CH_2)_3NH_2$, $-(CH_2)_3Br$, $-(CH_2)_3NCO$, $-(CH_2)_3SH$, $-(CH_2)_2(CF_2)_5CF_3$, and $-(CH_2)_{15}CH{=}CH_2$

Figure 1. Schematic outline of the procedure for patterning alkylsiloxanes on the surface of Si/SiO_2. No order or structure is implied by the representations of the SAMs.

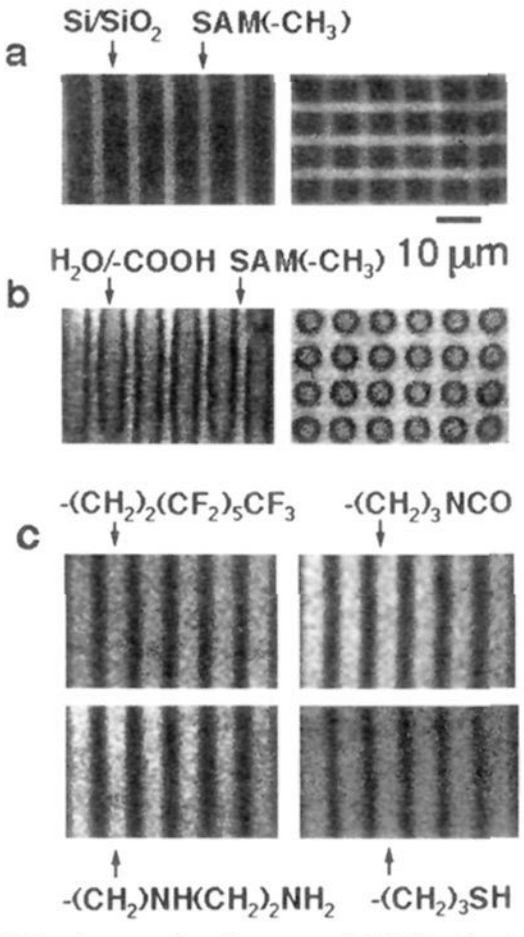


Figure 2. (a) SE micrographs of patterned SAMs of octadecylsiloxane on the surface of Si/SiO_2. (b) Condensation figures obtained by condensing water vapor on SAMs that have complementary patterns of methyl- and carboxylic acid-terminated regions. The rough edges are artifacts from surface tension in the liquid, not defects in the pattern. (c) SIMS ion maps of surfaces patterned with SAMs terminated in different functional groups. In all cases, the surface was printed with lines of octadecylsiloxane and then filled in with a second siloxane. The elements imaged are (clockwise, from upper left) fluorine, nitrogen, sulfur, and nitrogen. The scale applies to all images.

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(1) Wilbur, J. L.; Kumar, A.; Kim, E.; Whitesides, G. M. *Adv. Mater.* **1994**, *6*, 600−604.

(2) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437−463.

(3) Kumar, A.; Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498−1511.

(4) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274−3275.

(5) For recent studies, see: McGoven, M. E.; Kallury, K. M.; Thompson, M. *Langmuir* **1994**, *10*, 3607−3614. Parikh, A. N.; Allara, D. L.; Azouz, I. B.; Rondelez, F. *J. Phys. Chem.* **1994**, *98*, 7577−7590.

(6) Substrates were cleaned by heating at 70 °C for ~30 min in Piranha solution (a mixture 7:3 (v/v) of 98% H_2SO_4 and 30% H_2O_2), thoroughly rinsed with deionized water, and used immediately. ***Caution****: Piranha solution is an extremely strong oxidant and should be handled with care!* Samples used for XPS, SEM, and SIMS were prepared on silicon wafers covered with native silicon dioxide. The "ink" used in μCP was a ~0.2% (w/w) solution of octadecyltrichlorosilane (OTS) in hexane; similar results were obtained using toluene as the solvent. The stamp was left in contact with the Si/SiO_2 for ~5 s in printing. The stamp was rinsed with hexane and ethanol after each printing. When washed carefully between uses, one stamp has been used for more than 100 impressions without loss in the quality of the patterns. 16-Heptadecenyltriethoxysilane was synthesized according to the published procedure. Other alkylsilanes were purchased from Aldrich or Hüls and were used without purification.

(7) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074−1078.

(8) Lopez, G. P.; Biebuyck, H. A.; Friesbie, D. C.; Whitesides, G. M. *Science* **1993**, *260*, 647−649.

(9) Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581−4587.

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Table 1. Comparison between SAMs Formed by Immersion and Printing

	contact angle (deg)				
	H_2O		J-91 prepolymer		thickness[a] (Å)
	θ_a	θ_r	θ_a	θ_r	
native SiO_2	wet	wet	18	10	
thermal SiO_2	<20	<20	28	15	
SAM by dipping[a]	93	50	47	22	20.5
SAM by μCP[a]	107	83	73	56	21.3

[a] SAMs were formed on Si wafers with native oxide. Dipping time was ~5 min. For μCP, a flat PDMS stamp was used, and the stamp was in contact with the surface for ~5 s. The thickness was measured using ellipsometry, and values given here are the averages of five measurements. Contact angle values are the averages of three measurements.

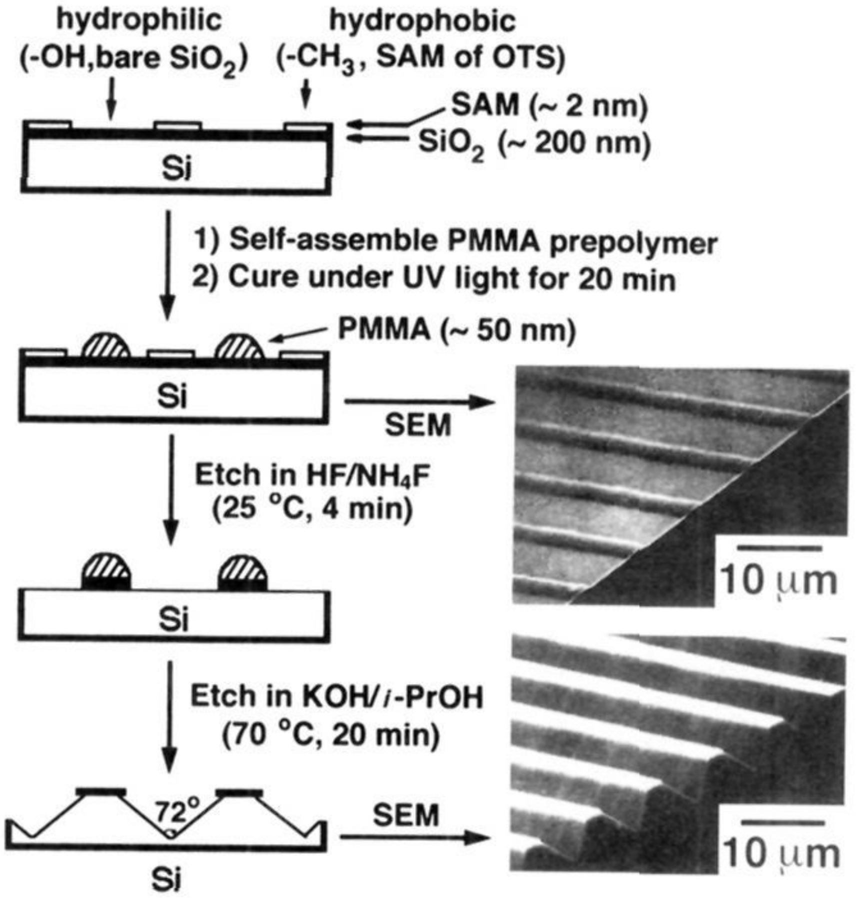

Figure 3. Procedure used to fabricate microstructures in silicon. A prepolymer of PMMA or PU was allowed to self-assemble on the hydrophilic regions (that is, bare SiO_2) and cured under a UV light source. The polymeric structures were effective resists for etching of the exposed regions of SiO_2 in an aqueous solution of HF (buffered by NH_4F). The resulting pattern of SiO_2 (PMMA or PU was soluble in the strongly alkaline solution used for silicon etching) was used as a mask for the anisotropic etching of the underlying Si in KOH/*i*-PrOH. The samples were tilted before the SEM photographs were taken. The SiO_2 mask remained on the surface after silicon etching.

solution, PMMA or PU that was assembled selectively on the hydrophilic regions of the patterned surface provided good protection (Figure 3).[10-12] The unprotected areas of SiO_2 were etched completely in 4 min. The pattern of SiO_2 formed in this step served as a mask for the anisotropic etching of the underlying silicon in KOH/*i*-PrOH.[10,13] In these experiments, the liquid prepolymers did not completely wet the surface of thermally-formed SiO_2 (Table 1), and the lines of polymeric liquids that were left on the hydrophilic regions from the dewetting minimized their free energy by retracting. As a result, the final width of these lines was smaller than the width of the lines of bare Si/SiO_2.[14]

Patterned SAMs comprising alkylsiloxanes on Si/SiO_2 and glass[15] are complementary to those of alkanethiolates on gold, silver, and copper. In the past, patterning siloxane monolayers on the surface of Si/SiO_2 required UV photolithography.[16] While this technique generates patterns effectively, it provides little control over the surface chemistry of the UV-damaged regions and cannot, in general, be used on nonplanar surfaces. Microcontact printing can be performed on both planar and nonplanar surfaces and does not require routine access to a photolithography facility for each pattern formation.[17] We believe this technique will prove valuable for many other applications—for example, studies of protein absorption and cell attachment—where high edge resolution (<50 nm) is not critical.

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(10) Kim, E.; Kumar, A.; Whitesides, G. M. *J. Electrochem. Soc.* **1995**, *142*, 628–633.

(11) Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790–2793.

(12) Silicon wafers (⟨100⟩ orientation) covered with 0.2-μm-thick thermal silicon dioxide (MEMC) were cleaned and used for experiments involving etching. After the surface was patterned with octadecylsiloxane, a drop of prepolymer of PMMA (SK-9, Edmund Scientific) or PU (J-91, Edmund Scientific; NOA81, Norland Products Inc.) was placed on the patterned area. The assembled prepolymer was cured under a mercury lamp (medium pressure; the distance between the sample and the lamp was ~1 cm) for ~20 min. The bare regions of silicon dioxide uncovered by polymers were etched in a NH_4F-buffered aqueous HF solution (250 mL of H_2O, 165.5 g of NH_4F, and 40 mL of 48% HF). Similar results were also observed when hexadecane liquid was used instead of prepolymer of PMMA or PU.

(13) Peterson, K. E. *Proc. IEEE* **1982**, *70*, 400–424.

(14) The reduction in width of the assembled polymer was observed *in situ* by optical microscopy. When silicon wafers with native oxide were used, the final width of the cured polymeric lines was approximately equal to the width of the lines of bare SiO_2, because the native oxide is more hydrophilic than the thermally-formed oxide (Table 1). We also used gold surfaces that were covered by hydroxyl-terminated alkanethiolate, and the width of the cured polymer lines was approximately equal to the width of the lines of hydroxyl-terminated SAM.

(15) We have also observed condensation figures (as well as the diffraction patterns of these CFs) on patterned SAMs comprising methyl- and carboxylic acid-terminated siloxanes on glass slides.

(16) Calvert, J. M.; Dulcy, C. S.; Peckerar, M. C.; Schnur, J. M.; Georger, J. H., Jr.; Calabrese, G. S.; Sricharoenchaikit, P. *Solid State Technol.* **1991**, October, 77–82.

(17) Jackman, R.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *269*, 664–666.