

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 (μ CP)¹ for patterning self-assembled monolayers (SAMs)² of alkylsiloxanes on the surface of silicon dioxide. μ CP is a convenient technique for generating patterned SAMs of alkanethiolates on gold,^{3,4} but it has not been applied to Si/SiO₂ 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 μ CP can, nonetheless, be used to produce patterned SAMs of alkylsiloxanes on Si/SiO₂. Although these patterned SAMs provide only partial selectivity in the etching of SiO₂ in aqueous HF/NH₄F 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 SiO₂.

Figure 1 outlines the procedure.^{1,6} A PDMS stamp with parallel lines was used to pattern a SAM of octadecylsiloxane on Si/SiO₂. The patterned substrate was then immersed in a solution of Cl₃SiR or (EtO)₃SiR (R = -(CH₂)₃NH₂, -(CH₂)₃-SH, -(CH₂)₃Br, -(CH₂)₃NCO, -(CH₂)₂(CF₂)₅CF₃, or -(CH₂)₁₅-CH=CH₂) in hexane (~0.4% w/w) for ~5 min to derivatize the remaining regions of Si/SiO₂ with siloxanes terminated in a different functional group. Subsequent treatment of a patterned SAM containing vinyl-terminated regions with an aqueous solution of KMnO₄ and KIO₄ 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 μ CP with a flat PDMS

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(6) Substrates were cleaned by heating at 70 °C for ~30 min in Piranha solution (a mixture 7:3 (v/v) of 98% H₂SO₄ and 30% H₂O₂), 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 μ CP 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/SiO₂ 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-Heptadecyltriethoxysilane was synthesized according to the published procedure. Other alkylsilanes were purchased from Aldrich or Hüls and were used without purification.

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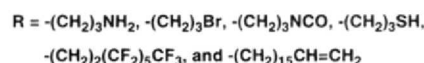
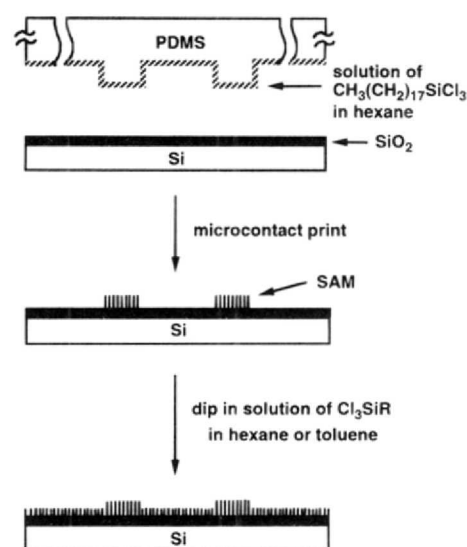


Figure 1. Schematic outline of the procedure for patterning alkylsiloxanes on the surface of Si/SiO₂. No order or structure is implied by the representations of the SAMs.

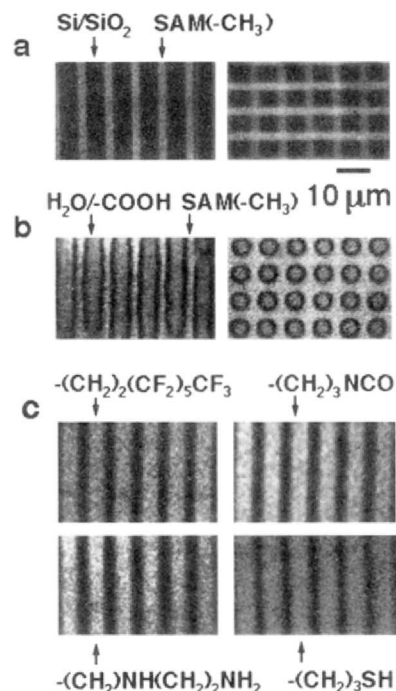


Figure 2. (a) SE micrographs of patterned SAMs of octadecylsiloxane on the surface of Si/SiO₂. (b) Condensation figures obtained by condensing water vapor on SAMs that have complementary patterns of methyl- and carboxylic acid-terminated regions. The rough edges are artifacts from surface tension in 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.

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/SiO₂ did not protect the surface against etching in aqueous HF/NH₄F

Table 1. Comparison between SAMs Formed by Immersion and Printing

	contact angle (deg)				thickness ^a (Å)
	H ₂ O		J-91 prepolymer		
	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 μ CP ^a	107	83	73	56	21.3

^a SAMs were formed on Si wafers with native oxide. Dipping time was \sim 5 min. For μ CP, a flat PDMS stamp was used, and the stamp was in contact with the surface for \sim 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.

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 SiO₂ were etched completely in 4 min. The pattern of SiO₂ 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 SiO₂ (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/SiO₂.¹⁴

Patterned SAMs comprising alkylsiloxanes on Si/SiO₂ and glass¹⁵ are complementary to those of alkanethiolates on gold, silver, and copper. In the past, patterning siloxane monolayers on the surface of Si/SiO₂ required UV photolithography.¹⁶ While this technique generates patterns effectively, it provides

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(12) Silicon wafers (<100> orientation) covered with 0.2- μ m-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 \sim 1 cm) for \sim 20 min. The bare regions of silicon dioxide uncovered by polymers were etched in a NH₄F-buffered aqueous HF solution (250 mL of H₂O, 165.5 g of NH₄F, and 40 mL of 48% HF). Similar results were also observed when hexadecane liquid was used instead of prepolymer of PMMA or PU.

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(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 SiO₂, 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.

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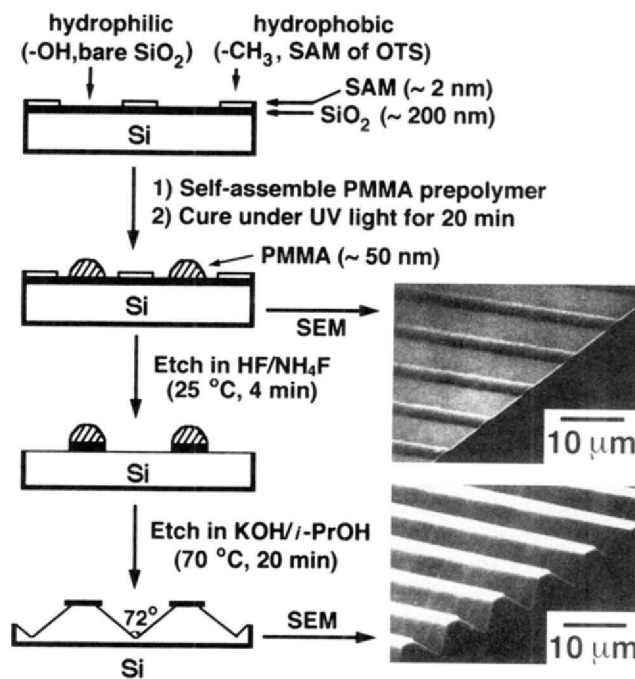


Figure 3. Procedure used to fabricate microstructures in silicon. A prepolymer of PMMA or PU was allowed to self-assemble on the hydrophilic regions (that is, bare SiO₂) and cured under a UV light source. The polymeric structures were effective resists for etching of the exposed regions of SiO₂ in an aqueous solution of HF (buffered by NH₄F). The resulting pattern of SiO₂ (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 SiO₂ mask remained on the surface after silicon etching.

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 resolution (<50 nm) is not critical.

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