Soft-Lithographic Approach to Functionalization and Nanopatterning Oxide-Free Silicon

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§Supporting Information

ABSTRACT: We report a simple, reliable high-throughput method for patterning passivated silicon with reactive organic monolayers and demonstrate selective functionalization of the patterned substrates with both small molecules and proteins. The approach completely protects silicon from chemical oxidation, provides precise control over the shape and size of the patterned features in the 100 nm domain, and gives rapid, ready access to chemically discriminated patterns that can be further functionalized with both organic and biological molecules.

INTRODUCTION

The development of hybrid bioelectronic devices relies in large part on the integration of (bio)organic materials and inorganic semiconductors through a stable interface that permits efficient electron transport while protecting underlying substrates from oxidative degradation.1–4 Interfaces composed of ordered organic molecules covalently bound to inorganic semiconductors offer unique advantages in terms of stability and charge transfer over traditional conjugated polymers physisorbed on inorganic materials.5,6 Group IV semiconductors can be effectively protected with highly ordered SAMs composed of simple alkyl chains that act as impervious barriers to both organic and aqueous solutions.7 Several groups have reported that alkylation of Si–H substrates with both Grignard reagents and organo-lithium compounds results in complete functionalization of all exposed Si atoms with chemically stable Si–C bonds.8–14 Alternatively, hydrosilylation with alkenes results in substitution of only 50% of the exposed Si–H sites, leaving remaining atoms susceptible to oxidation.15,16 Similarly, alkynes can achieve at most a 75% substitution of Si–H bonds via the hydrosilylation reaction.17,18 Nonetheless, long-chain alkenes and alkynes can effectively protect passivated silicon via hydrophobic chain–chain interaction similar to thiolated SAMs on gold.19–21 Simple alkyl SAMs, however, are inert and not amenable to traditional functionalization protocols.

Although carbanion-based covalent monolayer integration provides a durable, robust surface, it is not amenable to traditional soft lithographic techniques, and robust methods for patterning traditional inorganic semiconductors are largely lacking. Microcontact printing (μCP) is a mature, powerful, and versatile tool for patterning self-assembled monolayers (SAMs) on a wide variety of surfaces.22–30 However, the approach has not been well developed for pattern transfer to technologically important substrates such as oxide-free silicon, and its application remains limited largely to noble metal surfaces. Furthermore, the resolution of traditional μCP is near 1 μm, limited primarily by ink diffusion.31–37

Recent reports of soft-lithographic approaches toward Si–H patterning and functionalization have appeared. Buriak and co-workers utilized polymer-embedded Pd nanodots to replicate patterns of organic SAMs on Si–H.38 The technique relies on a Pd-catalyzed hydrosylilation between surface Si–H sites and alkyne molecules physisorbed on the Pd surface. Although the approach replicates nanodot patterns at the 100 nm scale, it does not protect unreacted Si–H areas from oxidation, and it cannot replicate features of arbitrary geometry. In another study, Zuilhof and co-workers patterned functionalized silicon via reactive μCP with amine nucleophiles.39 The method functionalizes Si with various organic species and replicates features in the ∼5 μm domain. Because the approach relies on diffusive pattern transfer, edge resolution of printed features is limited to ∼300 nm. Moreover, the technique utilizes reactive functionalized SAMs grafted directly to the inorganic substrate that normally do not protect the substrate–SAM interface from degradation.40–45 Such monolayers cannot be stabilized via...
hydrophobic chain—chain interactions because of the presence of a large terminal functional group, permitting access by destructive agents to the underlying surface.4,5,10,11,21

In contrast to traditional reactive printing, inkless μCP transfers pattern using the specific reaction between a surface-immobilized substrate and a stamp-bound catalyst, without relying on diffusive SAM formation. The technique significantly expands the diversity of patternable surfaces and obviates the feature size limitations imposed by molecular diffusion, facilitating replication of very small (<200 nm) features.44–48 Until now, however, inkless μCP has been used only for the patterning of relatively disordered molecular systems, which do not protect underlying surfaces from degradation.

Here, we report a simple, reliable high-throughput method for patterning passivated silicon with reactive organic monolayers and demonstrate selective functionalization of the patterned substrates with both small molecules and proteins. The technique utilizes a preformed, uniform bilayered NHS-modified silicon substrate, which is hydrolyzed in a pattern-specific manner with a sulfonic acid-modified acrylate stamp to produce chemically distinct patterns of NHS-activated and free carboxylic acids. The approach completely protects silicon from chemical oxidation, provides precise control over the shape and size of the patterned features in the 100 nm domain, and gives rapid, ready access to chemically discriminated patterns that can be further functionalized with both organic and biological molecules. The approach is general and should be applicable to other technologically relevant surfaces.

**SAM COMPONENTS**

Our protocol, shown schematically in Figure 1, is a form of inkless μCP.44–48 In this approach, a stamp-immobilized catalyst is brought into contact with a surface bearing functional groups with reactivity cognate to that of the immobilized catalyst; pattern is transferred through catalysis in areas of conformal contact. Because pattern transfer does not rely on ink transfer from stamp to surface, the diffusive resolution limitation of traditional and reactive μCP is obviated, permitting routine transfer of objects in the 100 nm domain. To protect underlying silicon from oxidation damage and/or electronic degradation, we required a highly ordered molecular system that provides complete functionalization of all surface-exposed silicon atoms with stable carbon—silicon bonds. Concurrently, to facilitate μCP, we required a system that supports immobilization of sterically bulky reactive groups. To simultaneously satisfy both requirements, a bilayered system was used, composed of an ordered protective primary SAM upon which was built a secondary reactive overlayer. Because the primary SAM provides complete protection of all surface-exposed silicon atoms with stable carbon—silicon bonds, the reactive overlayer to yield surface

![Figure 1. Catalytic μCP on passivated semiconductors.](Image)

(a) Passivated oxide-free semiconductor. (b) The primary SAM forms stable covalent bonds with the substrate, resulting in complete termination of all surface-exposed atoms and yielding a chemically inert, closely packed system that does not degrade in harsh environments. (c) The reactive overlayer forms stable C—C bonds with the primary SAM. (d) The elastomeric stamp makes conformal contact with the substrate and catalyst modifies the reactive overlayer in areas of conformal contact. (e) An acrylate stamp contains covalently bound catalyst. The mechanical rigidity of the stamp supports sub-100-nm high- and low-aspect ratio features.

terminated overlayer, simultaneously protects silicon from oxidation and SAM degradation while providing latent functionality that both facilitates μCP using acid catalysts and permits covalent attachment of both organic and biological molecules following stamping. The protocol achieves complete termination of all surface-exposed Si atoms with Si—C bonds, providing oxygen and water migration to the Si—SAM interface.9

AFM analysis showed both the primary monolayer 4 and reactive overlayer 5 were uniform and with very low roughness (4: \(R_q = 0.366\, \text{nm}, R_a = 0.287\, \text{nm}\), \(Z\) range = 3.34 nm; 5: \(R_q = 0.320\, \text{nm}, R_a = 0.256\, \text{nm}\), \(Z\) range = 2.42 nm; see Supporting Information for AFM images). Surface 4 showed minimal contact angle hysteresis (2°) consistent with the formation of a highly ordered densely packed molecular surface.41 Formation of the reactive overlayer to yield surface 5 resulted in a significant increase in contact angle hysteresis (22°), consistent with the formation of a loosely packed overlayer and/or NHS-ester hydrolysis during goniometry. XPS analysis revealed the presence of fluorine on surface 5, confirming carbene insertion to the primary protective SAM. The XPS Si 2p spectrum of the NHS-modified substrate showed no observable oxide, demonstrating the stability of the bilayer system even under oxidative environments (UV light, air; Figure 2a).

**CHEMICAL FUNCTIONALIZATION OF THE NHS-MODIFIED SAMS**

To demonstrate the reactivity of NHS-modified surfaces toward organic molecules, we exposed a freshly prepared NHS-SAM subs
trate to mono Boc-protected ethylenediamine (Figure 2). The XPS C 1s signal of the resulting Boc-protected ethylenediamine-modified surface showed an additional sharp peak at 286.5 eV, corresponding to the presence of C—C, C—O, and C—N bonds in the surface-grafted SAM (Figure 2b). Concomitantly, the intensity of this secondary peak in the initial NHS-modified substrate, which has fewer sp³-hybridized carbons, was significantly diminished. Deprotection of the Boc-modified substrate with 25% TFA in dichloromethane resulted in reduction of the sp³ C 1s peak intensity, consistent with selective hydrolysis of the Boc moiety. These secondary modifications of the NHS-modified SAMs were accomplished with no detectable silicon oxidation, demonstrating complete passivation of the underlying Si—SAM interface by the primary protective SAM toward high temperatures, UV light, basic solutions, and strong acids (see Supporting Information for Si 2p XPS spectra). These findings were also supported by literature where propenyl-functionalized substrates were able to withstand prolonged exposure to air (65 days) without silicon oxidation. These results emphasize the remarkable stability of the primary SAMs toward degradation and desorption.

**CATALYTIC POLYURETHANE/ACRYLATE STAMPS**

The formation of stable reactive patterns on oxide-free silicon relies on a hydrolytic reaction between NHS-functionalized SAM (5) and a sulfonic acid-modified catalytic stamp. We have
previously utilized oligo(ethylene glycol)-modified polyurethane/acrylate (PUA) stamps for this process. These materials offer both the opportunity for ready functionalization with a range of catalytic moieties and the ability to carefully control the modulus of elasticity. The latter property facilitates the creation of high aspect ratio features necessary for nanoscale pattern transfer.

Patterned and flat sulfonic acid-modified catalytic PUA stamps were prepared by reacting the components of a prepolymeric mixture with 2-mercaptoethanesulfonic acid at 50 °C for 5 min, followed by degassing under vacuum at room temperature (Figure 3). The resulting mixture was cast against a Si/SiO2 master, covered with a transparent glass slide, and polymerized under UV light at room temperature for 2 h. Following polymerization, the stamp was peeled off from the master, washed extensively with ethanol and water, dried under a stream of filtered nitrogen, and kept at ambient temperature. Figure 5 shows SEM images of the patterned stamp and corresponding master, demonstrating the fidelity of the molding technique.

Featureless stamps were prepared in a similar manner by polymerizing prepolymeric mixture between two flat glass slides. Catalytically inactive stamps were prepared by polymerizing initial PUA mixtures without 2-mercaptoethanesulfonic acid.

**HYDROLYZING EFFICIENCY OF THE CATALYTIC PUA STAMPS**

To determine the efficiency of NHS hydrolysis, we reacted featureless catalytic and inactive control stamps with NHS-terminated monolayers at room temperature for various times. Sulfonic acid stamp-treated surfaces show a carbon XPS signal diminished to the same extent as that produced by 1 M HCl (Figure 4), indicative of complete and selective NHS hydrolysis. Inactive stamps produced no changes in SAM composition visible by XPS. The fluorine signal remained constant under all conditions, suggesting that transformations induced by both sulfonic acid stamps and HCl solution were specific to the NHS groups and did not affect other components of the bilayered molecular system.

The hydrolysis efficiency of the sulfonic acid PUA stamp was also evaluated via secondary reactions of the NHS-modified SAMs with perfluorinated alkyl amines (Figure 5). Stamp and HCl-hydrolyzed samples and unmodified NHS-SAM were reacted with a dichloromethane solution of pentadecafluorooctan-1-amine for 2 h at room temperature, and carbon and fluorine concentrations of the resulting surfaces were analyzed by XPS. Figures 4 and 5 show that stamp- and HCl-modified SAMs showed essentially identical carbon and fluorine concentrations before and after reaction with perfluorinated amine, whereas the NHS-SAM surfaces showed a significant increase in both fluorine and carbon signal intensities after the reaction with the fluorinated amine (Figure 5). These results confirm not only that the sulfonic acid PUA stamp induces equivalent changes in the NHS-SAMs as does HCl solution but also that neither stamp- nor HCl-hydrolyzed free acid SAMs react with primary amines without coupling reagents. The observed difference in chemical reactivities of free acid- and NHS-terminated SAMs can be exploited to selectively functionalize patterned NHS substrates with heterobifunctional linkers and biomolecules, providing a simple and efficient method for patterning and functionalizing passivated oxide-free silicon with a variety of organic and biological molecules.

**NANOFEATURES ON PASSIVATED SILICON**

Our goal was to develop an effective approach to pattern passivated silicon through soft lithographic techniques. Because our method does not rely on diffusive pattern transfer, it can achieve resolutions near those of such instrument-intensive
techniques as photolithography and routine e-beam lithography. To demonstrate the utility of our approach for the creation of chemoselective patterns on oxide-free silicon, surface 5 was reacted for 4 min at room temperature with a patterned polyurethane-acrylate stamp bearing covalently bound sulfonic acid moieties. The catalytic stamp hydrolyzed NHS moieties in areas of conformal contact, yielding a patterned bifunctional substrate bearing regions of NHS activated and free carboxylic acids. Figure 6 demonstrates the efficiency of the technique across the entire substrate surface, yielding 125 nm features. To the best of our knowledge, this pattern contains one of the smallest SAM features replicated through soft lithography. The catalytic stamp can be used repeatedly without losing efficiency. Control acid-free stamps failed to produce any discernible change in the NHS-modified SAM.

### SECONDARY FUNCTIONALIZATION OF THE PATTERNED SUBSTRATES

With an effective approach for patterning passivated silicon at 100 nm length scales in hand, we turned to functionalization of silicon surfaces with (bio)organic materials. By exploiting the...
differential reactivities of activated and free carboxylic acids, we affixed nitrilotriacetic acid-terminated (NTA) heterobifunctional linkers to the NHS-functionalized regions of surface 9. A 20 mM solution of lysine-N,N-diactetic acid and 100 mM solution of trie

Figure 6. SEM images of NHS-patterned SAMs on oxide-free silicon: 125 nm lines (left) and 160 nm lines (right).

Figure 7. Soft-lithographic patterning and functionalization of passivated silicon with organic and biological molecules. (a) SEM image of the patterned NHS-modified substrate 9. (b) Fluorescent micrograph of GFP-modified substrate 12.
thylamine in a 1:1 DMF—water mixture was reacted for 1 h at room temperature with NHS-patterened substrate 9. Following the reaction, the substrate was thoroughly rinsed with water, DMF, and ethanol and dried under a stream of filtered nitrogen. The resulting NTA-patterened surface was used as a template for the selective attachment of hexa-histidine-tagged GFP (Figure 5). Fluorescence microscopy clearly shows differential fluorescence intensity between GFP-modified and hydrolyzed free carboxylic acid regions (Figure 7b). The size and shape of the replicated pattern integrity is completely conserved even after multiple surface modifications further demonstrate the remarkable stability of carbon passivated surfaces and the selectivity of the patterning semiconductor surfaces. We continue to explore catalytic lithography as a generally applicable approach for the patterning of semiconductor surfaces with a broad range of inorganic, organic, biological, and polymeric materials. Precise control over terminal functional groups is achieved by varying both heterobifunctional linkers and carbene donors in the reactive interface. The ability to create patterned organic—semiconductor interfaces without expensive, complex instrumentation offers myriad opportunities in fields such as electronics, nanotechnology, biochemistry, and biophysics, and will facilitate an understanding of fundamental properties of (bio)organic and inorganic interfaces. We continue to explore catalytic lithography as a generally applicable approach for the patterning of semiconductor surfaces and will report our results in due course.

**CONCLUSIONS**

The approach reported here offers a universal method for patterning semiconductor surfaces with a broad range of inorganic, organic, biological, and polymeric materials. Precise control over terminal functional groups is achieved by varying both heterobifunctional linkers and carbene donors in the reactive overlayer, while the underlying inorganic surface is robustly passivated with a highly ordered inert carbonaceous monolayer. The ability to create patterned—semiconductor interfaces without expensive, complex instrumentation offers myriad opportunities in fields such as electronics, nanotechnology, biochemistry, and biophysics, and will facilitate an understanding of fundamental properties of (bio)organic and inorganic interfaces. We continue to explore catalytic lithography as a generally applicable approach for the patterning of semiconductor surfaces and will report our results in due course.

**ASSOCIATED CONTENT**

Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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