

Catalytic Stamp Lithography for Sub-100 nm Patterning of Organic Monolayers

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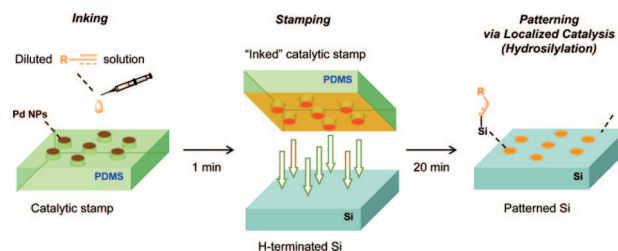
Patterning of organic nanostructures^{1–6} to control surface chemistries on technologically relevant substrates is of wide interest for the realization of molecular-scale engineering, ranging from electronics² to bioactive interfaces.³ In addition to the traditional photolithographic approach,⁴ imprint lithography-based techniques can provide a high throughput, large-area, and cost-effective route for this purpose.^{5a} Microcontact printing (μ CP), for example, has become a widely used, viable patterning tool to produce organic micron-scale motifs,^{5b} but challenging problems such as ink diffusion and stamp deformation make sub-100 nm patterning less routine.^{5a,c,d} Catalytic molecular transformations, as demonstrated by scanning probe techniques,⁶ are promising to this end, and its μ CP offshoot has just emerged recently.⁷ Herein, we describe our approach toward sub-100 nm patterning of organic monolayers through the integration of catalysis and stamping: catalytic stamp lithography.

Our strategy was initiated through the design of a novel type of patterning medium, a PDMS-based stamp patterned with an array of transition metal nanoparticle (NP) catalysts.⁸ Briefly, pseudo-hexagonal close packed NP arrays, presynthesized on oxide-capped silicon substrates via the use of self-assembled block copolymer (polystyrene-*block*-poly-2-vinylpyridine; PS-*b*-P2VP) templates,⁹ were transferred onto a surface of PDMS through a simple peel-off procedure (Supporting Information, SI). Due to the truncated cone shape of the NPs, the PDMS–NP interface is flat, leading to good contact with the printed surface (SI). Via modulation of the molecular weight of the PS and/or P2VP blocks, nanopatterns of various metals can be synthesized with center-to-center spacings of, for instance, 50–180 nm and nanoparticle diameters of 10–70 nm (Au, Ag, Pd, Pt; SI).⁹ A similar transfer approach was reported by Spatz et al. to fabricate patterned Au NPs on hydrogels for cell adhesion studies.¹⁰ The use of the self-assembly based process to produce catalytic stamps is inexpensive and efficient, since e-beam, nanoimprint lithography, and other techniques to produce the parent masters are avoided.

The demonstrative reaction employed here was Pd NP-catalyzed hydrosilylation¹¹ of terminal alkenes/alkynes on H-terminated Si surfaces. Because the reaction is catalyzed by solid NPs, pattern formation is not affected by ink diffusion or stamp deformation (localized catalysis). Direct chemical modification of Si substrates¹² is an ideal starting point for a broad range of applications. Scheme 1 illustrates the typical conditions of catalytic stamp lithography: a Pd catalytic stamp was inked with a dilute solution of terminal alkenes/alkynes for 1 min and then applied to freshly prepared flat H-terminated Si [either (100) or (111)]. Stamping was normally carried out for 20 min under light continuous pressure. The subsequent release of the catalytic stamp resulted in a duplication of the original pattern of Pd NPs on the silicon surface with arrays

of alkyl/alkenyl groups covalently attached to Si surface; the released stamp was reusable for subsequent inking/stamping (*vide infra*).

Scheme 1^a



^a Typical reaction conditions for catalytic stamp lithography (1 min inking and 20 min stamping) and the concept of localized catalysis. Catalytic hydrosilylation takes place only underneath Pd NPs.

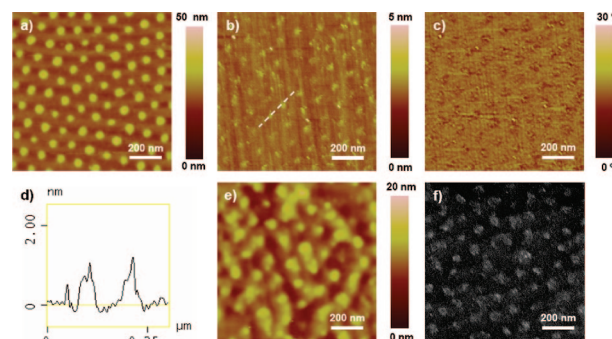


Figure 1. (a) AFM height image of a parent Pd catalytic stamp with NP diameters of 40 nm and a center-to-center spacing of 110 nm. (b) 1-Octadecyne-stamped Si(111)–H surface and corresponding phase image (c). (d) Section analysis along the dashed line in (b). (e) AFM height image of a 1-octadecyne-stamped Si(111)–H surface, followed by wet chemical etching with 40% NH_4F (aq). (f) SEM image of the sample from (e).

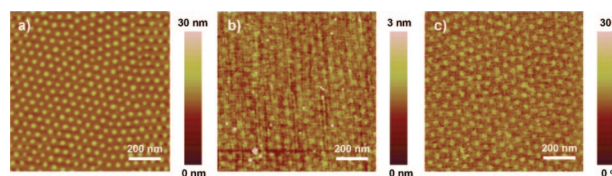


Figure 2. (a) AFM height image of a Pd catalytic stamp with NP diameters of 20 nm and center-to-center spacing of 60 nm. AFM height (b) and phase (c) images of the 5-hexyn-1-ol stamped Si(111)–H surface.

Figure 1 summarizes the results of catalytic stamp lithography (a–d) and its subsequent use as an etch stop (e,f), using a 5 mM 1,4-dioxane solution of 1-octadecyne as an ink. Tapping mode AFM height images of a Pd catalytic stamp and a stamped Si(111)–H

surface show pseudohexagonal arrays of Pd NPs (a) and hydrosilylated 1-octadecyne molecules (b), with center-to-center spacings of 110 nm in both the stamp and resulting surface pattern. The AFM phase image (c), simultaneously recorded with the height image (b), substantiate the existence of hydrophobic 1-octadecenyl groups surrounded by H-terminated Si.¹³ The section analysis (d) along the dashed line in (b) showed that each domain is approximately 1.3 nm tall, suggesting the molecules are loosely packed and significantly tilted from the surface normal (the theoretical length of 1-octadecenyl group with all *trans* conformations is ~2.2 nm). These domains were, however, still visible after aggressive etching with 40% NH₄F (aq) for 5 min (e). The greater topographic contrast after etching was enough to be observed by SEM as well (f). Similar stability results could be achieved using HF (aq) or KOH (aq), indicating that the 1-octadecyne molecules were bounded via covalent Si–C bonds (SI).

Additional evidence was collected to prove the pattern formation by catalytic stamping. First, a series of control stamping experiments resulted in no visible patterns, as shown by AFM: (i) the use of neat 1,4-dioxane (no alkenes/alkynes included), (ii) stamping with the standard alkene/alkyne ink solution on oxide-capped Si(111) surface (no Si–H bonds), (iii) use of catalytically inactive Au NP stamps with the standard alkene/alkyne ink solution. Second, each stamp could be reused multiple times (at least 12 times, SI) with no apparent degradation of the quality of the surface patterns, suggesting the catalytic nature of Pd NPs on PDMS. Furthermore, XPS analysis of the stamped sample revealed neither the formation of silicon oxides, which is known to be facilitated in the presence of transition metals,¹⁴ nor the contamination by PDMS¹⁵ and/or Pd (SI). All of these observations strongly supported the premise of localized catalytic hydrosilylation-induced pattern formation.

The resulting silicon surface patterns are tunable with respect to sizes/spacings and properties, using different catalytic stamps and inks, respectively. AFM height images in Figure 2 show the Pd catalytic stamps with NP diameters of 20 nm and a center-to-center spacing of 60 nm (a) and the stamped Si(111)–H surface (b) using 5-hexyn-1-ol (5 mM in dioxane) as the ink. Again, a clear pattern transfer was observed, and in this case, hydrophilicity of OH termination in the ink molecule was also confirmed by the phase image (c). Thus, wide varieties of functional molecules with terminal C=C/C≡C groups were compatible with this method.

Finally, to further demonstrate the scope of the approach, subsequent modification of the patterned surfaces was performed

(Figure 3). After the patterned stamping of 1,7-octadiene on Si(100)–H_x, the remaining blank hydride-terminated regions on the ω -alkene-terminated surface were etched with 4 M KOH (aq) for 30 s and then soaked in O₂-saturated H₂O overnight to remove any residual Si–H groups that could react in the next step.¹⁶ Next, a UV-mediated thiol-ene reaction¹⁷ with 1,9-nonanedithiol was carried out to produce thiol-terminated patterns. Immersion into a toluene solution of tetraoctyl-ammonium bromide-capped Au NPs (diameter: ~5 nm) resulted in selective assembly of Au NPs on surface thiol groups (Figure 3b,c).¹⁸

In summary, we have demonstrated a stamp-based nanoscale patterning technique of organic monolayers, termed catalytic stamp lithography, based upon nanoparticle-catalyzed hydrosilylation on Si–H_x-terminated substrates, as a model reaction. Using catalytically patterned stamps produced via self-assembled block copolymer templates, features as small as 20 nm could be obtained over a large area (~1 cm²), in a relatively short time (<30 min) fashion. The scope and limitations of catalytic stamp lithography are currently under investigation.

Acknowledgment. We gratefully appreciate the support from NSERC, the National Institute for Nanotechnology, the NRC, University of Alberta, and CFI.

Supporting Information Available: Detailed experimental procedures, additional AFM images, and XPS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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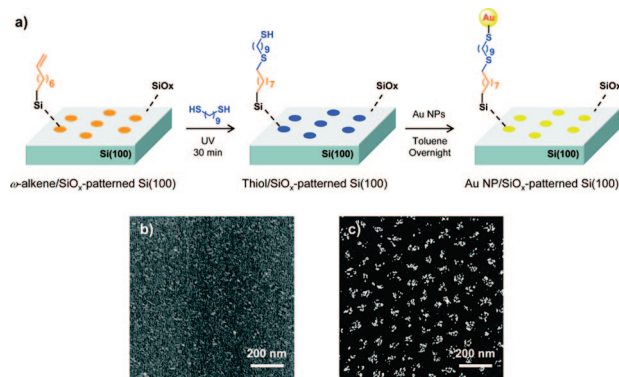


Figure 3. (a) Outline of procedure for modification of ω -alkene/SiO_x-patterned Si(100). (b) SEM images of Si(100)–H_x patterned with hexagonal arrangements of regions of thiol-terminated groups. (c) Assembly of 5 nm Au NPs on the surface shown in (b).