

Alkylsiloxane self-assembled monolayer formation guided by nanoimprinted Si and SiO₂ templates

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Alkylsiloxane self-assembled monolayers (SAMs) were formed on surface relief created by nanoimprinting and etching recesses into Si and SiO₂. Rather than exhibiting the isolated domains seen on unpatterned surfaces after limited formation time, the SAM on nanoimprinted surfaces became continuous and uniform after only a short (~5–10 min) reaction time. The hydrocarbon chains are densely packed and nearly vertically oriented. X-ray photoemission spectroscopy indicates complete hydrolysis and elimination of Cl from the octadecyltrichlorosilane precursor. The results suggest that the pattern edges enhance the nucleation rate, leading to the rapid coverage, and provide in-plane order within the SAM. © 2006 American Institute of Physics.
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Self-assembled organic monolayers (SAMs) have numerous applications, such as seeding layers for crystal nucleation and growth, antistiction coatings, wetting layers for improved biocompatibility, and in molecular electronics. Within small regions, the molecules forming the SAM are vertically aligned and close packed. However, the SAM forms nonuniformly on a surface, the size of the ordered “domains” is limited, and extended reaction times are needed to obtain a SAM that covers the surface with a dense, uniform monolayer. Even after complete coverage, adjacent domains can have different in-plane orientations, with disordered domain boundaries separating adjacent domains. The boundaries create irregularities that can dominate the properties of the SAM and limit its use. The domain boundaries become especially important when the size of the structure or “device” incorporating the SAM is comparable to the domain size.

Previous studies have shown that patterned surfaces can influence the formation of SAMs and organic thin films. Monolayers of vapor deposited polythiophenes were selectively formed on exposed Si regions surrounded by oxide patterns created by local oxidation nanolithography.¹ Thin films were formed by vapor deposition on SiO₂ surfaces with shallow periodic grooves, and the structure was improved by the pattern.² Nanoimprint lithography (NIL) has been applied to thin films of poly(vinylidene fluoride) to increase the local crystalline order in confined nanoscaled regions.³ However, liquid-phase growth of a self-assembled monolayer on a nanopatterned surface has received limited attention.⁴ This letter demonstrates the use of surface relief formed by nanoimprint lithography to accelerate and guide the formation over a large area of octadecylsiloxane (ODS) polymerized monolayers formed from a liquid-phase precursor. The

influence of the patterned surface is discussed in terms of enhanced nucleation and ordering promoted by the surface relief.

Nanoimprint lithography,⁵ along with reactive ion etching, was used to create shallow recessed lines 5–14 nm deep across the entire sample. Both chemically oxidized Si surfaces and ~200 nm thick thermally grown SiO₂ surfaces were investigated. The pitch of the pattern was 190 nm, and the recessed regions were either ~100 or ~150 nm wide. SAMs were also prepared on corresponding unpatterned chemically oxidized Si and unpatterned 80 nm thick thermally grown SiO₂.

To obtain repeatable, OH-terminated, hydrophilic surfaces (~5° water contact angle), the samples were treated in H₂SO₄:H₂O₂ for 30 min. The SAM was then formed by immersing the samples into 10 mM solutions of the SAM precursor octadecyltrichlorosilane (OTS) in bicyclohexyl solvent for times varying from 5 min to 24 h at ≤25 °C under an Ar ambient. Surfaces covered with a fully formed SAM were hydrophobic when pulled from solution and were free of large poly-ODS aggregates. The chemicals used to form the SAM were stored in a glove box, the reaction took place in a dry Ar environment, and care was taken to minimize trace moisture, which can cause the reaction to occur in



FIG. 1. Atomic-force micrographs of SAM formed on unpatterned SiO₂ for 5 min. Scales: (a) $x=y=2.5\ \mu\text{m}$, $z=5\ \text{nm}$ full scale; (b) $x=y=750\ \text{nm}$, $z=5\ \text{nm}$ full scale.

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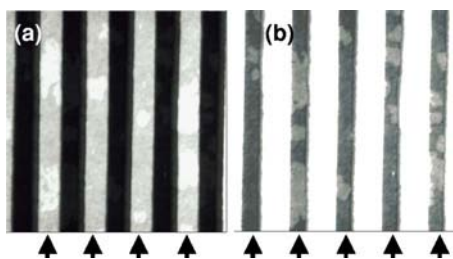


FIG. 2. Atomic-force micrograph showing domains formed in 2 min on SiO_2 surface patterned by nanoimprint lithography. Two views of the same AFM image showing surfaces (denoted by arrows) of (a) raised regions and (b) recessed regions. Scales: $x=y=1 \mu\text{m}$, $z=15 \text{ nm}$ full scale.

the bulk of the liquid, rather than preferentially on the surface.

SAM formation on the thermal-oxide-covered surfaces was studied in more detail. On an unpatterned surface for a short SAM formation time of 5 min, isolated, approximately equi-axed islands with 50–100 nm diameters and larger, irregular islands with 300–500 nm diameters were found, along with some branched dendritic domains (Fig. 1). The density of the larger islands was approximately $2 \mu\text{m}^{-2}$; these sparse islands were measured to be 1.9 nm high by atomic-force microscopy (AFM). Their diameter increased as the reaction proceeded. After adjacent domains grew together, further exposure filled in voids within each domain and reduced the defect density. A fully saturated SAM was formed within 24 h, with no further improvement seen for longer times. The fully formed SAM was found to be $2.5 \pm 0.2 \text{ nm}$ thick by ellipsometry (using an index of refraction of 1.45), corresponding to a nearly vertical alignment of the molecules and within the range expected for alkylsiloxane SAMs.^{6,7}

By contrast, the SAM formed much more rapidly on patterned oxide surfaces ($\sim 12 \text{ nm}$ deep etched recesses). After only 2 min, approximately 30 islands (μm^{-2}) were observed. They appeared on both the raised and recessed regions, as indicated by the two views of the same atomic-force micrograph shown in Fig. 2; apparent correlation between the islands on adjacent raised and recessed regions suggests that the SAM is also formed on the vertical walls of the etched structures. Within 5–10 min the entire surface of the patterned sample was covered with a continuous and uniform SAM; no island-like domains were seen by AFM (Fig. 3). The nanoimprinted pattern was clearly replicated, and the step height was the same before and after SAM formation. Fourier transform infrared spectroscopy (FTIR) measurements confirmed the formation of the SAM, and x-ray photoelectron spectroscopy (XPS) semiquantitatively indicated an amount of carbon equivalent to approximately 1 ML

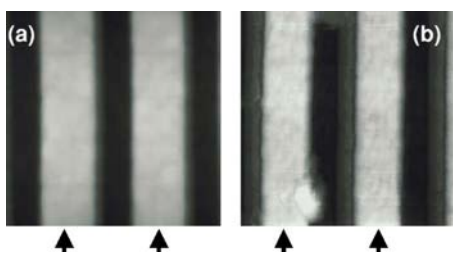


FIG. 3. Atomic-force micrographs of patterned SiO_2 . (a) Without SAM and (b) after SAM formation for 5 min. Scales: $x=y=500 \text{ nm}$, $z=20 \text{ nm}$ full scale. (Arrows indicate raised regions.)

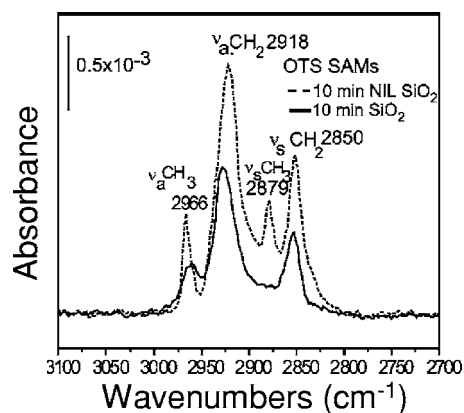


FIG. 4. p -polarized FTIR spectra of SAMs on unpatterned and NIL-patterned SiO_2 (reacted with OTS for 10 min). The data for the NIL-patterned sample show that the hydrocarbon chains are densely packed and that most chains are nearly vertically oriented.

of alkylsiloxane molecules. The SAM formed on the nanoimprinted surface within 5–10 min is very similar to that formed on the unpatterned surface after 24 h and quite unlike the sparse deposit on unpatterned substrates after this limited deposition time. A detailed, polarized FTIR analysis (Fig. 4) of the positions of the absorption bands in the 2800–3000 cm^{-1} range showed that most alkylsiloxane hydrocarbon chains are densely packed, and the presence of pronounced νCH_3 bands suggests that most alkylsiloxane chains are nearly vertically oriented. The weak νCH_3 bands for the SAM formed for the same length of time on unpatterned SiO_2 indicates a poorly packed SAM.

The lack of discernible XPS peaks from Cl in the lower energy region indicates that the Si–Cl bonds have fully hydrolyzed in the SAMs on patterned and unpatterned substrates after short times. Water contact angle ($\geq 112^\circ$) and thermal stability measurements suggest that the condensation reaction following hydrolysis formed the Si–O–Si linked bonds on the surface characteristic of a fully polymerized SAM.

Additional insight was obtained by observing SAM formation on chemically oxidized Si surfaces. On unpatterned Si surfaces chemically oxidized by $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, isolated SAM domains were observed after 5 min exposure to the SAM precursor, as on the thermally oxidized surfaces. Within the domains, cells with a lateral spacing of $\sim 30 \text{ nm}$ and subnanometer vertical surface topography are visible [e.g., see superposed circles in Fig. 5(a)], but the lateral ordering of the cells decreases rapidly with increasing distance. On surfaces with a shallow ($\sim 5 \text{ nm}$ deep) etched pattern, no isolated islands are observed after a 5 min exposure, indicating complete coverage by the SAM. On the raised regions of the patterned surfaces, cells are observed within the SAM [Fig. 5(b)], as on unpatterned surfaces. However, on the patterned surfaces the cells appear to be aligned with the pattern edges, creating a quasiperiodic structure with longer-range order of the cells. When the width of the patterned feature is comparable to the cell size, a single row of cells is seen, with the cell size possibly constrained by the feature. The line-edge roughness visible before SAM formation decreases as the SAM forms; this behavior appears consistent with the structure within the SAM allowing the SAM on the raised regions of the pattern to continue growing unsupported a short distance along the edge to reduce the apparent line-

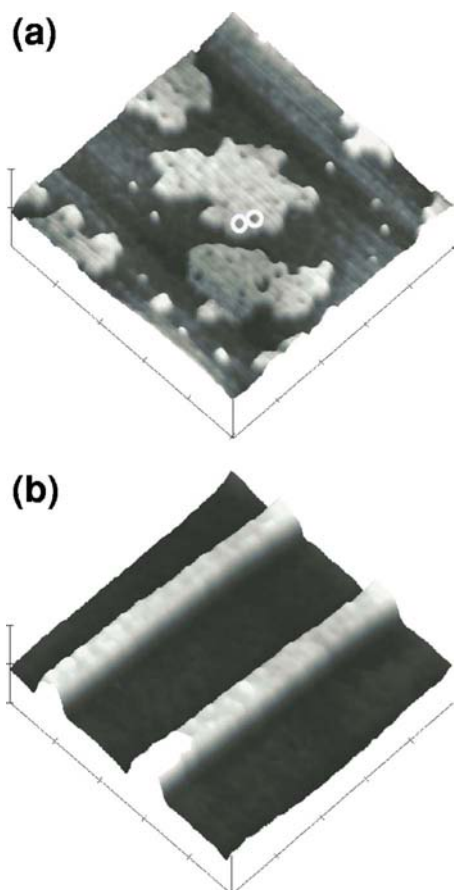


FIG. 5. Atomic-force micrographs of (a) isolated domains on unpatterned chemically oxidized surface, showing cells within domains. Within a domain the lower (dark) regions correspond to the centers of cells; two cells have been marked by white circles. (b) Continuous domains on patterned chemically oxidized surface, showing aligned cells on raised features of pattern. Scales: $x=y=100$ nm/division, $z=10$ nm/division.

edge roughness. Atomic-force micrographs suggest that a similar structure of cells is present in the recesses, but less readily imaged.

The rapid formation of a SAM across the entire nanoimprinted surface suggests that nucleation occurs primarily at the pattern edges and that the SAM expands across the narrow width of each region. After 5 min, the density of domains on the surface of the unpatterned oxide is about $2 \mu\text{m}^{-2}$. The same density of nuclei on the patterned surface would form one nucleus every $5 \mu\text{m}$ along a stripe. To cover the entire stripe within 5 min, the SAM would have to grow at a rate of $1 \mu\text{m}/\text{min}$, which is one or two orders of magnitude greater than the expansion rate of domains on unpatterned surfaces. Rapid nucleation at the edges of the stripe is more probable. Because of the enhanced nucleation, only a

small expansion of the domain across a stripe is needed to cover the entire surface, explaining the SAM's rapid coverage of the entire patterned surface, while only a sparse density of isolated domains is formed on the unpatterned surface.

Some applications of SAMs rely on in-plane ordering of adjacent domains so that the domains grow together without forming highly disordered domain boundaries. Obtaining large areas with in-plane orientation requires that the pattern edges influence the in-plane orientation within each domain so that adjacent domains have similar in-plane orientations, as found for "graphoepitaxy" of inorganic layers formed from vapor-phase or liquid-phase precursors.⁸⁻¹⁰ The cell alignment on raised regions, the smoothing at edges, and previous reports on other organic systems¹⁻⁴ suggest that such ordering is possible.

In summary, self-assembled ODS monolayers were formed on surface relief created by nanoimprinting and etching recesses into both Si and SiO₂. The SAMs on nanoimprinted surfaces were uniform and continuous without island-like domains after only a short (~ 5 – 10 min) reaction time. XPS indicates full hydrolysis and elimination of Cl from the OTS precursor; FTIR shows that the majority of the hydrocarbon chains are densely packed and nearly vertically oriented. The pattern edges appear to enhance the nucleation rate, leading to the rapid coverage, and also increase the in-plane order within the SAM.

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