Supporting Information

Multilength-Scale Chemical Patterning of Self-Assembled Monolayers by Spatially Controlled Plasma Exposure: Nanometer to Centimeter Range

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In our work, it is the combination of micro- or nanochannel-flowed plasma and predeposited OTS-SAM with the self-limiting nature while interacting with the air plasma which allows us to demonstrate the most desired features in soft lithography (nanoscale resolution and hierarchical processing). We have demonstrated that the plasma-induced oxidation and etching is limited to the carbon chain of OTS-SAM. Therefore, the interaction with the air plasma is confined to the OTS-SAM. In conventional plasma- or vapor-based surface patterning techniques using microfluidic networks (μFN), low-viscosity plasma or vapor can reduce the processing time and allow for large-area patterning, in comparison with those using viscous fluids. However, the main issue of these methods is the strong interaction of plasma with exposed surfaces and boundary effects in micro- or nanochannels, which can limit the achievable resolution (as shown in Figs. S1−S4). Therefore, the SAM-based technique for self-limiting plasma modification is necessary for achieving the goals of nanoscale and hierarchical processing. One additional problem with direct plasma exposure to surfaces without coverage by a SAM is related to the residue deposits of PDMS stamps (Fig. S5). This also can prevent hierarchical processing on the PDMS-contacted regions.

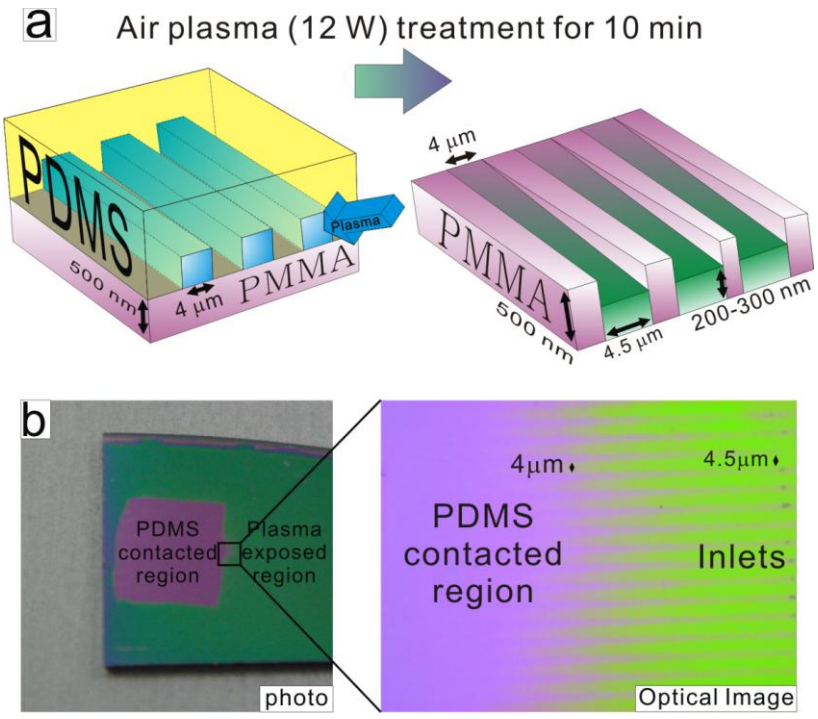

Figure S1. Channel-mediated plasma modification of a 500-nm-thick PMMA film without the use of a self-limiting SAM while interacting with the air plasma (optical images). (a) Schematic illustration of the poly(dimethylsiloxane) (PDMS) stamp (channel width: 4 μm; channel height: 1 μm) and the modified poly(methyl methacrylate) (PMMA) film topography. The air plasma conditions (12W, 0.6 Torr) are identical to that used for modifying OTS self-assembled monolayer, which is significantly less reactive than that used by Langowski et al. (50 W oxygen plasma, 0.66 Torr).[40] However, the PMMA surface topography is still significantly roughened by the plasma treatment, as reported in ref. 40. (b) The surface topographic modification can be seen in the optical image due to the interference effect in transparent PMMA film on Si substrate. When light is reflected from both sides of the PMMA film, the violet region corresponds to a film thickness of ~500 nm, while the green region corresponds to a film thickness of ~200−300 nm. Besides the reduction in PMMA film thickness, we have also confirmed the existence of lateral expansion [~4.5 μm vs. 4 μm (channel width)] of the modified region near the plasma inlets. This shows that this technique is limited to channel width >10 μm and is very difficult to be applied for nanoscale surface chemical patterning.

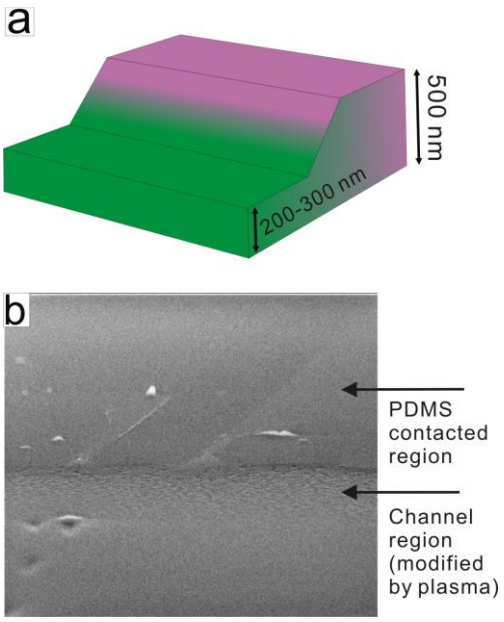

Figure S2. Channel-mediated plasma modification of a 500-nm-thick PMMA film without the use of a self-limiting SAM while interacting with the air plasma (FE-SEM image). **(**a) Schematic illustration of the modified PMMA surface topography. (b) FE-SEM image of the the plasma-modified PMMA surface topography, which was indued by the plasma treatment (under the same conditions as shown in Fig. S1).

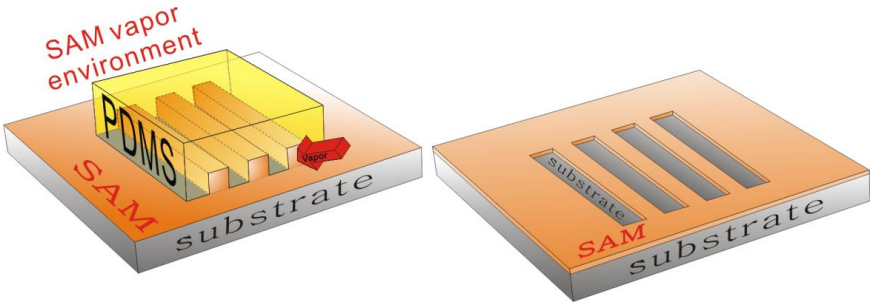

Figure S3. Schematic illustration of channel-mediated vapor deposition of a patterned SAM. The procedured used by us is similar to that reported in ref. 41. The substrate to be patterned was covered by the PDMS stamp (channel width: 1.3 μm) and placed in a teflon container filled with an octadecyltrimethoxysilane (ODS) vapor at 150˚C for 3 hr.

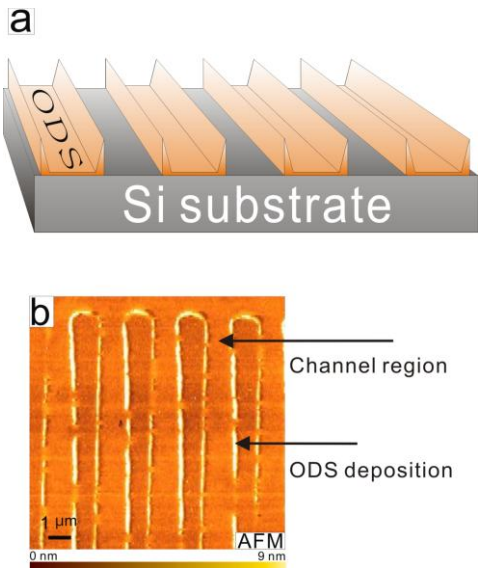

Figure S4. Boundary effects of microchannels in channel-mediated vapor deposition of a patterned SAM. (a) Schematic illustration of the deposited ODS structure. (b) AFM topographic image of the deposied ODS structure.

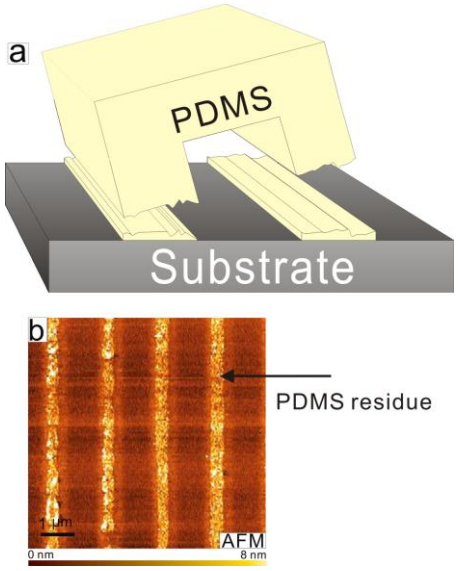

Figure S5. Residual PDMS pattern created by physical contact of the PDMS stamp with a surface which is not covered by a SAM layer. (a) Schematic illustration of the deposited PDMS structure. (b) AFM topographic image of the deposited PDMS structure. This result demonstrates the importance of surface SAM coverage for hierarchical processing.

In Fig. S6, we present images as evidence for the uniformity and smoothness of channel-mediated plasma modification of OTS-SAMs. This is in sharp contrast to other techniques based on channel-mediated vapor deposition or plasma modification without surface coverage by a self-limiting SAM. The issue of strong stamp-plasma-surface interactions can be avoided by using a self-limiting SAM (OTS-SAM in our process).

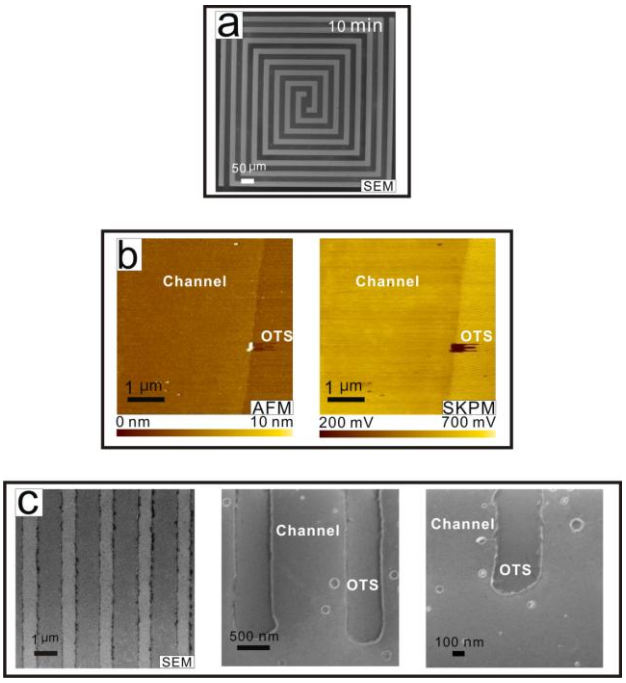

Figure S6. Uniform and smooth chemical modification of OTS-covered surafce via channel-mediated plasma modification. In contrast to the case of plasma-modified polymer surfaces (Figs. S1 and S2), plasma-induced modification of OTS-covered Si surfaces is very uniform and smooth, as evidenced by (a) FE-SEM as well as (b) AFM and SKPM images of the OTS-covered surface afte μCFP process. In Fig. S6(c), we show that, for the case of narrow channels [shown in Fig. 1(a)], the regions of darker contrast near the channel boundaries are FE-SEM imaging artifacts since at higher magnifications we did not observe such features. Comparing with the result show in Fig. S5, we also confirm the absence of residual PDMS created by physical contact of the PDMS stamp with a OTS-covered surface.