

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

We present a generic and efficient chemical patterning method based on local plasma-induced conversion of surface functional groups on self-assembled monolayers (SAMs). Here, spatially controlled plasma exposure is realized by elastomeric poly(dimethylsiloxane) (PDMS) contact masks or channel stamps with feature sizes ranging from nanometer, micrometer, to centimeter. This chemical conversion method has been comprehensively characterized by a set of techniques, including contact angle measurements, X-ray photoelectron spectroscopy (XPS), scanning photoelectron microscopy (SPEM), scanning electron microscopy (SEM), and scanning Kelvin probe microscopy (SKPM). In particular, XPS and SPEM can be used to distinguish regions of different surface functionalities and elucidate the mechanism of plasma-induced chemical conversion. In the case of an octadecyltrichlorosilane (OTS) monolayer, we show that exposure to low-power air plasma causes hydroxylation and oxidation of the methyl terminal group on an OTS-covered Si surface and generates polar functional groups such as hydroxyl, aldehyde, and carboxyl groups, which can allow subsequent grafting of dissimilar SAMs and adsorption of colloid nanoparticles onto the patterned areas with an achievable resolution down to the 50 nm range.

Beamlines

09A1 U5-SPEM

09A2 U5-Spectroscopy

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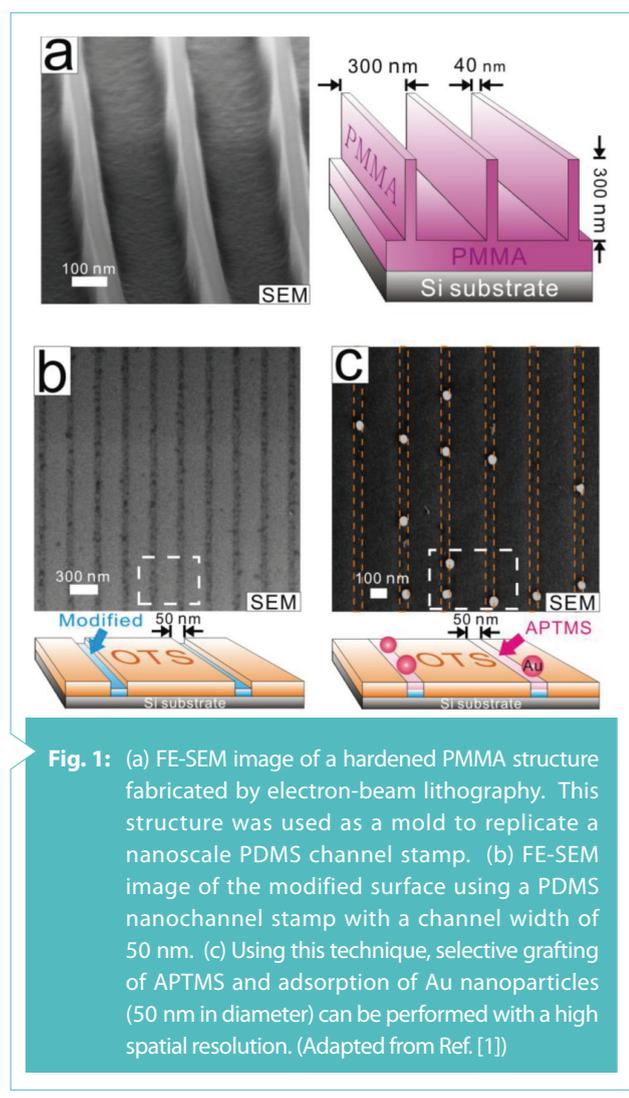
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One of the key challenges for implementing widespread applications based on nanotechnology is reliable large-scale integration of single nanoscale objects into functional devices and structures.¹ An attractive nanoassembly strategy should allow a large number of hierarchical and multilength-scale organization steps in order to interface nanoscopic devices and structures with the macroscopic world. Chemical patterning of self-assembled monolayers (SAMs) with designated surface features is a promising technique for achieving these goals.² In the past decade, several SAM patterning approaches have been demonstrated by means of photolithography, controlled exposure to energetic particle beams (electrons, ions, etc.), scanning probe microscopy, and stamp-based soft lithography.³ It has also been shown that patterned SAMs can be used as templates for selective adsorption or nucleation of various molecules, proteins, cells, colloidal particles,^{4,5} inorganic/organic crystals, and metals. Among these techniques, the soft lithographic method (parallel process) using an elastomeric stamp is one of the most versatile approaches, which can satisfy simultaneously the needs for scalability, high throughput, and low cost.² On the other hand, local chemical conversion of organosilane SAMs using the scanning probe technique (serial process) can offer the highest spatial resolution as well as possibilities of creating chemical templates for hierarchical self-assembly.⁴ The present work was inspired by these approaches. By combining their advantages, the method reported here could open up a new way for hierarchical and multilength-scale self-assembly of functional nanoscale devices and structures.

Here, to enhance the applicability of soft lithography, we report a soft lithographic method based on plasma-induced, self-limiting chemical modification of organosilane SAMs via poly(dimethylsiloxane) (PDMS) stamp-controlled plasma exposure. Using this approach, we can achieve SAM patterning from nanometer to centimeter dimension range. Additionally, we demonstrate that this patterning technique can be applied



to create versatile surface templates for site-selective grafting of dissimilar SAMs and adsorption of colloidal nanoparticles.

In order to achieve site-specific chemical modification and large-area patterning, we utilized PDMS elastomeric stamps fabricated by both photolithography and electron-beam lithography (EBL) as contact masks or channel stamps. By conformally contacting the PDMS stamps with surfaces terminated by organosilane SAMs, we can realize controlled exposure or flow of low-power air plasma on the patterned areas of pre-deposited organosilane SAMs. The patterning resolution can reach a spatial resolution of 50 nm when EBL-fabricated stamps are used (Fig. 1). In this study, we have also clarified the nature of plasma-induced chemical modification. The technique of synchrotron-based X-ray photoelectron spectroscopy (XPS) was applied to confirm the conversion of the surface methyl group ($-\text{CH}_3$) into polar functional groups such as carboxyl group ($-\text{COOH}$), aldehyde group

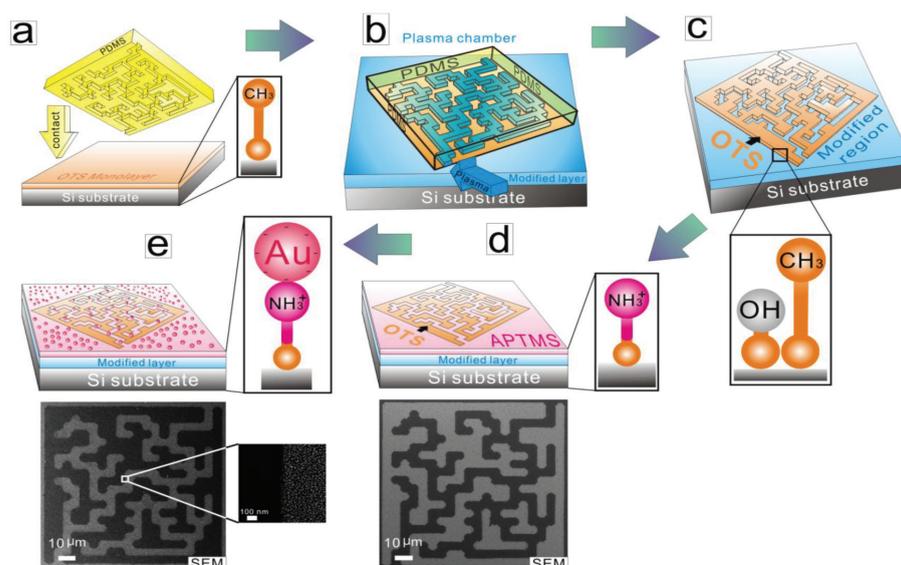
($-\text{CHO}$), and hydroxyl group ($\text{C}-\text{OH}$), which can allow subsequent grafting of dissimilar SAMs onto the patterned areas. Moreover, by using field-emission scanning electron microscopy (FE-SEM), scanning Kelvin probe microscopy (SKPM), and synchrotron-based scanning photoemission microscopy (SPEM), we have performed chemical mapping of different functional groups on the plasma-modified surface. Using the technique of SKPM, the surface potential changes are quantitatively measured at the surfaces of plasma-modified regions, dissimilar SAMs, and nanoparticles-adsorbed regions. By comparing all the microscopic results (SEM, SKPM, SPEM) in Fig. 2, we find that plasma-based pattern transfer using PDMS channel stamps is of high fidelity in terms of chemical conversion and lateral distribution of functional groups on the patterned surfaces.

Experimental

The schematic representation of process flow for selective surface chemical modification and controlled self-assembly based on microchannel-flowed plasma (μCFP) is shown in Scheme 1.

Conclusions

We have shown that μCFP -based chemical lithography can be efficiently applied to pattern SAM surfaces with designated surface functionalities. Using a complete set of characterization tools, we have confirmed the capability of multilength-scale chemical patterning with feature sizes ranging from nanometer to centimeter. In addition, the detailed conversion mechanism by air plasma has been elucidated. We provide convincing evidence that the plasma-induced oxidation and etching is limited to the carbon chain of OTS-SAM. The self-limiting nature of plasma modification process is very critical to achieve the exquisite spatial resolution by avoiding the strong interaction of plasma with the substrate. The patterned SAMs demonstrated here can be widely used as surface templates for hierarchical organization of single nanoscale objects such as molecules and nanoparticles. This method, due to its advantages of scalability, parallel processing, and general applicability, could open up a practical approach to interface nanoscopic devices and structures with the macroscopic world.



Scheme 1. Schematic illustration (not to scale) of selective surface chemical modification and controlled self-assembly based on microchannel-flowed plasma (μ CFP). (a) First, the PDMS channel stamp is in conformal contact with a Si substrate covered by an OTS monolayer with the terminal methyl group ($-\text{CH}_3$). (b) Local conversion of the terminal group occurs on the OTS monolayer region which is exposed to air plasma (the region within the channel). (c) The terminal group is now converted to polar surface groups such as $-\text{OH}$, $-\text{CHO}$, and $-\text{COOH}$ on the surface region exposed by μ CFP, while the terminal functional group remains as the methyl group on the surface region in contact with PDMS. (d) The modified region can be used to selectively graft the second layer (APTMS). (e) The region covered by APTMS can be utilized to adsorb the negatively charged Au nanoparticles.

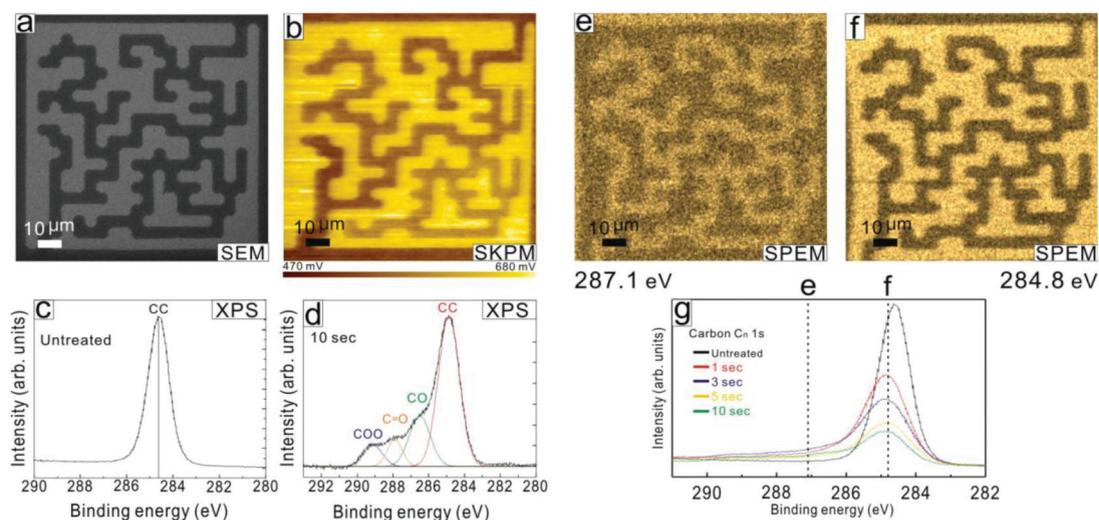


Fig. 2: (a) FE-SEM and SKPM image analysis of μ CFP surface treatment process. After μ CFP treatment for 3 min, a FE-SEM image composed of selectively modified OTS region (darker region) and unmodified OTS region (brighter region). (b) After μ CFP treatment (3 min), a surface potential (SKPM) image of selectively modified OTS region (darker region) and unmodified OTS (brighter region). (c) XPS C1s signal of an unmodified OTS monolayer. It originates from the C–C bond. (d) XPS C1s signal of a modified OTS monolayer after plasma exposure for 10 sec. There are three types of plasma-induced carbon bonds, involving with surface functional groups of hydroxyl ($-\text{OH}$), aldehyde ($-\text{CHO}$), and carboxyl ($-\text{COOH}$). SPEM image analysis of μ CFP surface treatment process. (e) and (f) SPEM images of a plasma-modified region after 3 min of μ CFP treatment. (e) In the binding energy window centered at 287.1 eV (window size: 0.75 eV), which corresponds to the C–O and C=O bonds. (f) In the binding energy window centered at 284.8 eV (window size: 0.75 eV), which mainly corresponds to the C–C bonding state. (g) XPS spectra after plasma treatment of 1 sec, 3 sec, 5 sec, and 10 sec. (Adapted from Ref. [1])

Experimental Station

Scanning Photoelectron Microscopy (SPEM) end station

Publications

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