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Plasma induced patterning of polydimethylsiloxane surfaces

Shuchen Hsieh*, Yue-An Cheng, Chiung-Wen Hsieh, YiLen Liu

Department of Chemistry and Center for Nanoscience and Nanotechnology, National Sun Yat-sen University, Kaohsiung, Taiwan

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ABSTRACT

We report on a plasma-based method to fabricate chemical and physical patterns on polydimethylsiloxane (PDMS) surfaces. A copper TEM grid was placed on cured, planar (2D) and periodic (3D) PDMS surfaces, and the samples exposed to a low-pressure "air" plasma. The pattern of the grid was precisely replicated, forming hydrophilic channels only where the grid wires contacted the PDMS surface. Exposed regions of the surface between the mesh wires were not chemically modified and retained their hydrophobic character. This plasma-based procedure provides a simple, fast, and inexpensive method for creating patterned chemical functionalities on 2D and 3D PDMS surfaces for directed assembly and for the development of micro-scale sensors and bio-chip devices.

1. Introduction

Materials and substrates with engineered surface patterns are used extensively for applications in electronic [1], optical [2], magnetic [3,4], chemical [5], and biological [6,7] devices and materials. In particular, surfaces with patterned chemical functionalities can serve as templates for directed self-assembly of nanoparticles [8,9], biomolecules, and antibodies [10,11], and are employed in the development of micro-scale biochip and sensor devices.

Polydimethylsiloxane (PDMS) is a silicon-based organic polymer with unique viscoelastic, properties. Surface patterns on PDMS are largely used in the fabrication of micro-fluidic systems [12]. Further, PDMS stamps are used in soft lithography to create replica patterns on other surfaces [13]. A variety of methods have been used to pattern PDMS surfaces including: (1) utilizing pre-existing silicon molds which are replicated in the PDMS surface and can be subsequently transferred to other surfaces [12]; (2) direct laser beam micro-machining [14,15] of PDMS from a combination of photochemical decomposition and photo-dissociative bond breaking in the electronically excited states (the size and shape depends on focusing optics); (3) using a scanning probe instrument to mechanically scratch patterns into the PDMS surface [16,17]; (4) UV/ozone treatment of the PDMS [18,19] to render a more hydrophilic surface (a glassy surface layer is expected to form due to the conversion of $-CH_3$ groups to –OH terminal group functionalities); and (5), chemical modification of PDMS surfaces by exposure to a plasma.

Plasma treatment can be used to remove organic contaminants from samples, for surface activation, and for deposition of materials on a substrate [20–22]. RF plasmas are composed of ionized gases, at reduced pressure, and are often used to activate a silicon or polymer surface, converting a native hydrophobic surface to a hydrophilic one [23,24]. UV photons produced by the plasma have also been shown to contribute to modification of the polymer through bond breaking and reforming with reactive gas species from the plasma [14,25–28]. Although electron energies in the plasma are quite high, the temperature of the plasma gas is actually quite low, near room temperature. Polymer surface modification by plasma is commonly achieved using oxygen as the active gas species [29,30]. Decomposition of organic materials is initiated by reaction with atomic oxygen from the plasma followed by desorption of volatile by-products. Conversion of organo-silicon materials to silicon oxides by exposure to an oxygen plasma environment, is a phenomenon that is well documented [31].

Here, we report a plasma-based process for creating both chemical and physical patterns on PDMS surfaces using a copper TEM grid as a mask. Precise replica patterns of the grid were created on planar (2D) and textured (3D) PDMS samples, exhibiting hydrophilic channels only where the grid wires contacted the surface. A mechanism for this process is proposed.

2. Experimental

2.1. Sample preparation

PDMS (Sylgard 184, Dow Corning, Midland, MI, USA) was prepared using a 10:1 pre-polymer to curing agent mixture that was

* Corresponding author. Tel.: +886 7 525 2000x3931; fax: +886 7 525 3908.
E-mail address: shsieh@facmail.nsysu.edu.tw (S. Hsieh).

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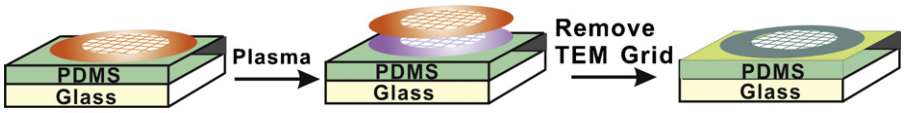

Fig. 1. Schematic illustration of the plasma patterning process. A copper mesh grid was placed on the PDMS surface and the sample exposed to a plasma. A replica pattern of the grid consisting of shallow, hydrophilic channels was created only where the grid was in contact with the PDMS, Exposed regions of the PDMS surface between the grid wires remained hydrophobic.

stirred for 5 min and then poured into a steel washer that was placed on a clean glass microscope slide. The resulting PDMS samples (1–2 mm thick) were then cured in an oven for 1 h at 110 °C. The annealing process produced hard, smooth films, with an RMS roughness of about 0.5 nm as measured with an atomic force microscope (AFM).

Textured, 3D PDMS samples were prepared by soft lithography using a commercial recordable compact disk (CD-R) [32]. The Al and polycarbonate layers of the CD-R were separated by peeling them apart with tweezers, exposing the underlying periodic structure of the two adjacent surfaces (1.5 μm pitch, ~100 nm depth). For our experiments, we used the Al surface as the master. A steel washer was placed on the aluminum and the PDMS mixture poured into the center. The sample was cured on a hot plate for 2 h at 70 °C, and then the PDMS mold was peeled off, replicating the periodic surface structure of the CD-R aluminum layer. The PDMS mold samples were then adhered to a glass microscope slide with the textured surface exposed for further processing.

Our approach for creating patterns on a PDMS surface is illustrated schematically in Fig. 1. A copper TEM grid (1000 mesh EMITECH – square type – 3.2 mm diameter) was placed on a cured PDMS sample surface and then exposed to a low-pressure "air" plasma (53.3 Pa, 2 min, 10.5 W – Harrick Scientific Products, Inc. Model PDC-001). These conditions resulted in the formation of highly reproducible chemical and physical patterns on the PDMS surfaces. Lower power settings (6.8 W), and shorter times at the 10.5 W setting (30 s) did not result in significant reaction and subsequent chemical pattern formation. Longer exposures at 10.5 W created deeper channels, but were less reproducible. In a series of experiments, we found that wetting the PDMS surface prior to placement of the grid and then drying under a stream of nitrogen gas, greatly improved the precise replication and reproducibility of the plasma-induced patterns. A similar observation was reported by Hoeppener et al. [33,34] in their study of bias-induced oxidation of a self-assembled monolayer surface using an electrode, and they proposed that the water produced better conformal contact. In our study, a copper TEM grid was placed on both pre-wetted and non-wetted PDMS samples and exposed to the plasma, but the pre-wetted samples produced more uniform channels. Both types of samples exhibited the same chemical conversion, only on regions of the surface where the wire mesh masked the PDMS. Pre-wetted samples were used in all experiments reported here.

2.2. Characterization

Water contact angle measurements were performed on various regions of the PDMS sample before and after plasma treatment using a PGX model instrument (Belgium, Deerlijk) at room temperature.

Following plasma treatment, the patterned samples were imaged with an AFM (Asylum Research, MFP-3D) operating in contact mode under ambient conditions. The scan angle was set to 90° so that the fast scan direction was perpendicular to the long axis of the cantilever. This allowed us to simultaneously measure topography and lateral force (friction). A silicon cantilever (Olympus, AC240) with a nominal spring constant of 1 N/m was used for all images with a scan rate of 1.0 Hz and image pixel density of 512 × 512.

3. Results and discussion

Water contact angle measurements were used to characterize the chemical nature of the PDMS surface at each stage of the patterning process. Before plasma treatment (but after curing), the water contact angle for the PDMS surface was 104°, indicating a hydrophobic surface. After plasma treatment, the water contact angle was reduced to 46° on the area outside where the TEM grid had been (and also on an unpatterned PDMS surface), indicating a hydrophilic surface. On the patterned region that was covered by the TEM grid during plasma treatment, the water contact angle was 92°. This was less than the value we measured before exposure to the plasma, indicating a change in the chemistry of the surface despite being covered by the grid. Since the water contact angle is a measure of the average surface energy of the area the droplet covers, any effects due to micron or nanometer scale physical and chemical structures, cannot be unambiguously determined. The details of these local changes to the surface were investigated using AFM.

Fig. 2a, shows an AFM topography image (60 μm × 60 μm) of a PDMS sample following the plasma patterning process. The gray

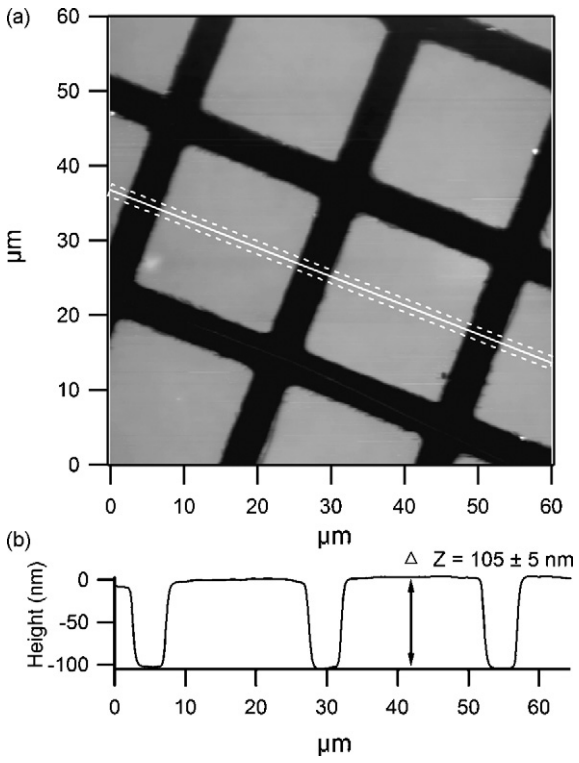

Fig. 2. (a) Height linage (60 μm × 60 μm) of a patterned PDMS surface. The dark channels are 105 ± 5 nm deep as shown in the line scan in (b). The width of the channels is 5.5 ± 0.55 μm and the spacing between grid lines is 19 μm, These values correspond well to the TEM grid dimensions (pitch = 25 μm).