"Submerged Micro-Contact Printing" (SµCP): an Unconventional Printing Technique of Thiols using High Aspect Ratio, Elastomeric Stamps

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A technique for micro-contact printing of thiols in liquid media is presented. Elastomeric poly(dimethyl siloxane) stamps are used to pattern gold surfaces with thiol-based self assembled monolayers. The liquid (water in this case) has been used as an incompressible support, and, advantageously, also acts as a medium in which alkylthiol ink molecules are poorly miscible. Consequently, we have been able to produce patterned thiol monolayers using stamps with aspect ratios unsuitable for conventional micro-

contact printing (i.e. 15:1), and present evidence to suggest that it is possible to use stamps with aspect ratios up to 100:1.

Introduction

Micro-contact printing (μCP) using self-assembled monolayer (SAM) "inks" has been developed for rapid patterning of molecules over large areas. μCP is used to pattern gold surfaces using thiols, glass using silanes, etc.[1] Unfortunately, conventional μCP suffers from problems that limit pattern resolution.[2] These include limits on the structural aspect ratio and the printing conditions dictated by the elastomeric stamp.

Stamps containing high aspect ratio structures (defined as the ratio of structure width versus structure height) are unable to support the printing pressure and tend to deform.[3] With sufficient deformation, areas of the stamp not intended for patterning come into contact with the substrate. Similar problems occur due to the stamp's weight and due to interfacial adhesion.[4] In high aspect ratio structures (i.e. structures with ratios much greater than 1:1) the "roof" between structures has a tendency to collapse, when the distance between structures is larger than the structure height, or lean on their neighbors causing "pairing", when structure height is larger than structure width, which is obviously detrimental to the production of the required SAM pattern. Attractive forces, such as electrostatic charges, between the neighboring structures or between the structure and the bulk of the elastomer,[5] can exacerbate this. These problems limit the available stamp aspect ratios to a maximum of 10:1.[6] Here we concentrate on the problem of "roof" collapse.

The volatility of the "ink" molecules can also cause problems during stamping, especially when long contact periods are required. Ink molecules evaporating from areas of the stamp not in contact with the substrate can cross the intervening gap and attach to the substrate surface.[7] This causes ink contamination of areas not intended to be inked, and hence adversely affects the choice of the inking molecule and contact time. Similarly, loss of resolution and contact time constraints can occur due to molecular diffusion of the ink molecules at interfacial contact points between the stamp and the substrate.[8] The longer the contact time, the higher the possibility that ink molecules will diffuse along the surface of the substrate, causing further intra-pattern contamination. Limiting the contact time can

alleviate volatility and diffusion problems, however this can adversely affect the organization of the transferred layer: longer contact times allow the ink molecules to organize into a SAM over increasingly large areas.[9]

The problem of structural collapse could be alleviated if the μCP is carried out in a liquid medium that supports the stamp during printing, and coincidentally confines the inking molecules to the area of mutual contact. Xia and Whitesides have published results to show that the spreading of thiols microcontact printed under water can be used to reduce the feature dimensions of subsequently etched gold substrates.[10, 11] In this case, the authors use the fact that the spreading of their thiol molecules reduces inter-patterned areas to sub-micron dimensions, defining the etch dimensions of the underlying gold substrate. Hovis and Boxer have also applied this method for the production of lipid bilayer membranes.[12] However, although these authors use this technique for production of the patterned bilayers, no systematic study is made of the effects of the water acting as a supporting medium for the stamping process itself. Roca-Cusachs *et. al.* have examined the effect of submerging high aspect ratio, elastomeric posts in water and ethanol to examine the effect of the liquid on post collapse.[5] Here we describe the development of a submerged micro-contact printing (SμCP) technique, for patterning thiol SAMs on a gold surface under water, using elastomeric stamps with aspect ratios much higher than those used in conventional μCP, and concentrate on finding the maximum possible distance between structures prior to structural "roof" collapse. The considerations required for the use of water and other supporting liquid media for SμCP are also described.

Materials and Methods

Elastomeric stamp fabrication for μCP has been described previously.[1] Here we use positive stamps, fabricated from poly(dimethyl siloxane) (PDMS; Sylgard 184, Dow Corning), where the structures protrude from the bulk PDMS surface. The PDMS stamps were replicated from silicon-based molds that have been structured using either deep reactive ion etching (DRIE) or focused ion beam (FIB)

techniques.[13] The microstructures were designed to have various aspect ratios, including some unsuitable for conventional μCP. The stamps were then inked using 10 mM alkylthiol (octadecylmercaptan, Aldrich Chemical Co.) solution in ethanol, and used to pattern gold surfaces.

Fig. 1 depicts the conventional (in air) and unconventional (submerged) μCP techniques. For SμCP, the gold substrate is completely submerged in doubly distilled water, leaving ~10 mm of water above the surface. Any air bubbles on the surface are manually removed. The inked stamp is then fully introduced into the water at an angle, to reduce bubble formation, and placed onto the surface of the gold (initially at an angle for the same reason). Pattern transfer proceeds for some time (~1 min) by manually applying pressure to the stamp, before the stamp is removed and dried using a stream of dry nitrogen gas. For comparison, conventional printing was attempted using similar conditions, although in most cases with a reduced contact time (~15 s) due to the collapse of the stamp.

Indirect optical characterization of the patterns was realized using a stream of water-saturated air, directed across the patterned substrate surface. Advancing contact angle measurements using water show that the thiol surface is more hydrophobic (110°) than the bare gold (80°). Therefore, the water droplets prefer to condense on the hydrophilic gold surface, but not the patterned, hydrophobic SAM surface. This can be viewed under a microscope to give an idea of the pattern fidelity at scales greater than 1 μm^2. Direct pattern characterization, at the microscale, was performed via contact mode atomic force microscopy (AFM/LFM).

Results

Images of a SAM pattern, produced using 2.5 μm diameter structures from a DRIE mold, are given in Fig. 2. Optical images of water condensed on the substrate reveal that the patterning has been successful over large areas (up to 1 cm^2). The droplets on the substrate surface (Fig. 2*a*) are large with a square shape. The corners of the square correspond with the gaps in the pattern between the SAM covered areas. In places the water droplets produce interconnects with each other around the hydrophobic SAM

patterns. The presence of thiol in these areas would cause the adjacent droplets to have a higher contact angle and hence not allow such a liquid interconnect to form. This suggests that there has been little thiol contamination between the patterned areas.

The pattern is hard to discern in topographic AFM images due to the roughness of the gold substrate (Fig. 2b). In friction mode (Fig. 2c), the circular areas of the hydrophobic thiol SAM, contained by non-patterned, hydrophilic gold substrate, are clearly seen. Sectional profiles of the friction mode image give a diameter of 2.52 μm and a pattern periodicity of 4.87 μm. Sectional profiles of the topographical image give a tentative step height of ~1 nm, consistent with the thickness of a monolayer coating of the thiol.

A stamp containing structures with a 15:1 aspect ratio (12.5 x 12.5 μm^2, 850 nm tall and 25 μm period), produced from a FIB mold, was used to compare conventional and submerged printing techniques. Optical images of the stamp when placed onto a microscope slide reveal that, in air, the stamp collapses over a short period of time (Fig. 3a), whereas in the submerged case the water supports the stamp and prohibits structural collapse (Fig. 3b). SμCP faithfully reproduced the thiol pattern (Fig. 3d), but no pattern could be discerned using the conventional technique.

FIB modification has also been used to produce stamps with aspect ratios of 46:1 (37.5 x 37.5 μm^2, 75 μm period, 800 nm tall), 83:1 (20 x 20 μm^2, 40 μm period, 240 nm tall) and 167:1 (40 x 40 μm^2, 80 μm period, 240 nm tall), which were used to examine the limits of the support of the SμCP technique using water. Fig. 4 presents optical images of the stamps placed on a microscope slide. In each case, the stamp subjected to conventional μCP is seen to collapse. Under water however, the stamp resists collapse at ratios of 46:1 and 83:1. Indeed, even with the application of extra pressure to the rear of the stamp, using a pair of tweezers, the stamps do not collapse, although the 83:1 ratio stamp displays some structural deformation. This suggests that it may be possible to produce stamps for SμCP with ratios in the order of 100:1. At ratios of 167:1 the stamp collapses even when it is submerged.

Discussion

These results show that it is possible to use μCP techniques under submerged conditions for the production of thiol-based SAMs on gold. The pattern fidelity of the SAM has been found to be controllable at dimensions down to 1 μm (although we believe that the minimum dimension can be reduced to sub-micron dimensions), and thiol patterns have been produced using stamps with aspect ratios unsuitable for conventional printing (i.e. 15:1).

The possibility of using aspect ratios much larger than those available conventionally has advantages when it comes to producing the original mold. For example, to produce a 10 $μm^2$ mold structure at a 10:1 ratio, 100 $μm^3$ of substrate material must be removed; at a 15:1 ratio, 67 $μm^3$ of material needs to be removed; and at a 100:1 ratio, only 10 $μm^3$. When using a "direct write" method such as FIB for mold fabrication, such a reduction shortens the required production time for the mold, especially when numerous or large area structures are to be fabricated. The ability to produce large area structures on the stamps consequently allows large SAM patterns to be produced for, for example, large area gate dielectrics.[14]

The advantages of performing SμCP in liquid media are defined by the incompressibility of water, and the immiscibility of the ink molecules within. The coefficient of compressibility (K_T) of water is low ($K_{300K\ (water)} \sim 4.5 \times 10^{-5}\ bar^{-1}$).[15] This is due to water's high density, which itself is due to the cohesive nature of inter-molecular hydrogen bonding. In comparison, the coefficient of compression of a (perfect) gas, $K_{T\ (gas)} = 2 \times 10^5$. $K_{T\ (water)}$, and indeed the coefficient of air is higher ($K_{300K\ (air)} = 0.999\ bar^{-1}$).[16] Hence the water is more able to withstand the applied force and supports the PDMS stamp during printing.

Resolution loss due to contamination by ink molecules, either by diffusion or evaporation, can be avoided by choosing a liquid in which the ink molecules are immiscible. Hence longer printing times can be allowed for. Application of this technique in conjunction with methods for selectively inking the stamp surface, such as via contact inking,[17] should further reduce contamination of the non-patterned

substrate surface. SμCP can have the added advantage of aligning the ink molecules prior to printing. For example, the presence of water will cause thiol molecules to align with their sulfur group in the water and the hydrophobic hydrocarbon tail on the stamp surface. This places the sulfur groups in the optimum position for contact with the substrate.

The liquid to be used in a particular SμCP application can therefore be chosen by considering the required properties. Of prime importance is the miscibility of the ink molecules in the liquid media (itself depending on the liquid polarity and hydrophobicity), and the liquid surface tension. Lowering the ambient temperature, and/or changing the viscosity of the medium (liquid or gel), can cause a decrease in the diffusion speed of the ink molecules in the liquid medium.

The choice of supporting liquid, or the careful addition of, for example, a salt, will alter the forces acting on the structures in the stamp and can reduce structural collapse or pairing.[5] Increasing the viscosity of the liquid will allow more external force to be applied before the stamp collapses. Further, if no external force is applied to the stamp, changing the buoyancy of the stamp in the liquid medium can cause the contact force with the substrate to be minimized. This is particularly important when attempting to stamp nanostructures, as the contact force in this case must be low to avoid collapse. Of course, in both cases, the supporting medium/solute should not interfere with the formation of the SAM on the substrate surface.

Conclusion

A method of μCP involving a liquid medium for stamp support has been investigated. We have been able to utilize stamps with aspect ratios unsuitable for conventional μCP, and believe that stamps with aspect ratios in the order of 100:1 could be used. Faithful replication of the intended pattern is possible over large areas, which bodes well for applications where this is necessary, such as micro-array formation. Further examination of the effects of the experimental conditions on the printing results will further confirm that SμCP improves on traditional μCP techniques with respect pattern resolution and

fidelity, and will prove to be an invaluable technique in the field of large area surface functionalization. Such experiments should concentrate on the effect of pressure on pattern structure size and surface wettability, the effect of interfacial phenomena, temperature and viscosity, and the speed of diffusion processes.

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Figure captions:

Fig. 1 Schematic diagram of (*a*) conventional and (*b*) submerged micro-contact printing methods. The PDMS stamp is produced with the required surface structures (1). It is then "inked" with the thiol (2) and placed in contact with the gold substrate (3). A small amount of pressure is applied manually (4) before the stamp is removed, leaving the patterned SAM on the substrate. In air, the applied pressure causes the stamp to deform; when submerged, the water supports the stamp.

Fig. 2 Images of the gold substrate patterned with thiol via submerged μCP. An optical image of droplets of water on the patterned surface (*a*) shows that the droplets are confined in the hydrophilic (non-SAM patterned) area of the gold surface [bar = 5 μm]. A raised thiol pattern can faintly be seen over the rough gold substrate in a topographical AFM image (*b*). This pattern can be seen more clearly in the corresponding friction mode image (*c*) [bar = 1 μm].

Fig. 3 (*a*) Optical images (1-4) showing the collapse of a PDMS stamp with an aspect ratio of 15:1 when using conventional μCP. The stamp collapses against a glass microscope slide from the outer edges to the center in under 15 s. (*b*) Optical images of the same PDMS stamp using SμCP with pressure applied to the backside. The water initially encroaches into the stamp from the bottom left hand corner of images 1-3. The stamp's structures can be seen in the submerged image (4), and remains so for up to 1 minute, proving that the presence of the water prohibits stamp collapse. Squares are drawn around the structures in the upper corner of 4 as an aid to the eye. [bar in each case = 50 μm]. (*c*) Topographical and (*c*) friction mode AFM images of a gold surface patterned by SμCP using a stamp with an aspect ratio of 15:1 [bar = 10 μm]. Inset is a sectional profile of the elastomeric stamp. Using conventional μCP techniques with this stamp we are unable to produce a patterned SAM.

Fig. 4 Optical images of stamps with ratios of (a) 46:1 [bar = 75 μm], (b) 83:1 [bar = 40 μm] and (c) 167:1 [bar = 80 μm] used to examine the limits of the SμCP technique before stamp collapse occurs. In

each case, 1 shows the collapse of the stamp using conventional μCP, 2 shows the stamp under SμCP conditions, and 3 shows the stamp under SmCP conditions with extra pressure applied to the rear of the stamp. The stamp resists collapse at an aspect ratio of 83:1, although some structural deformation is seen when the extra pressure is applied. Note: the images have been contrast enhanced to show detail.
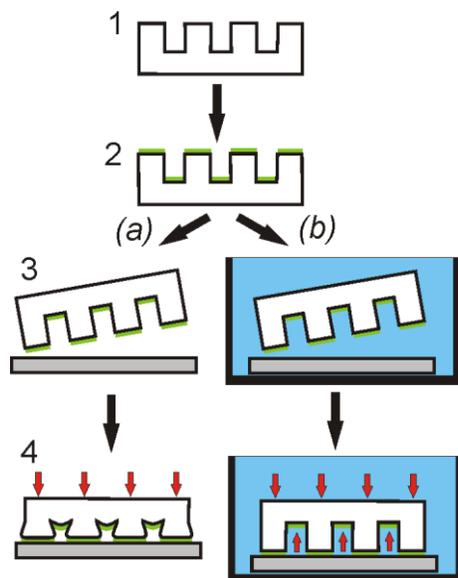
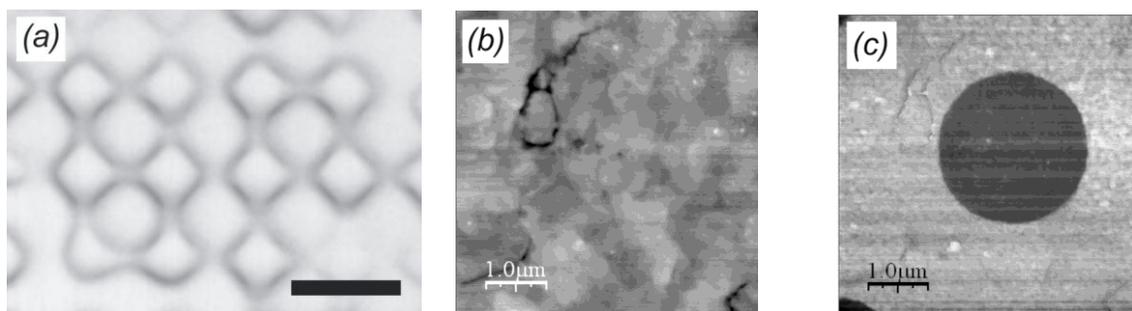Figure 1 *(Bessueille et. al.)*

Figure 2 *(Bessueille et. al.)*

Figure 3 *(Bessueille et. al.)*
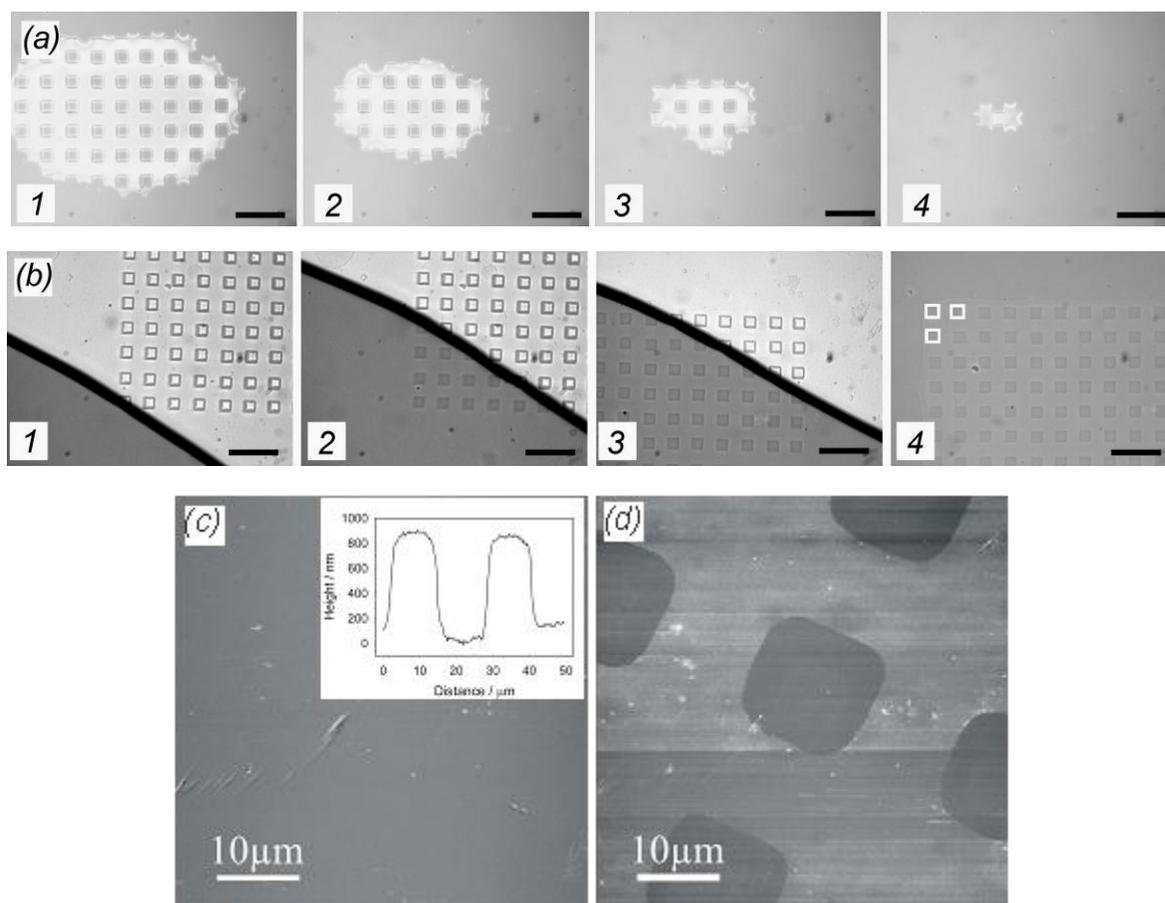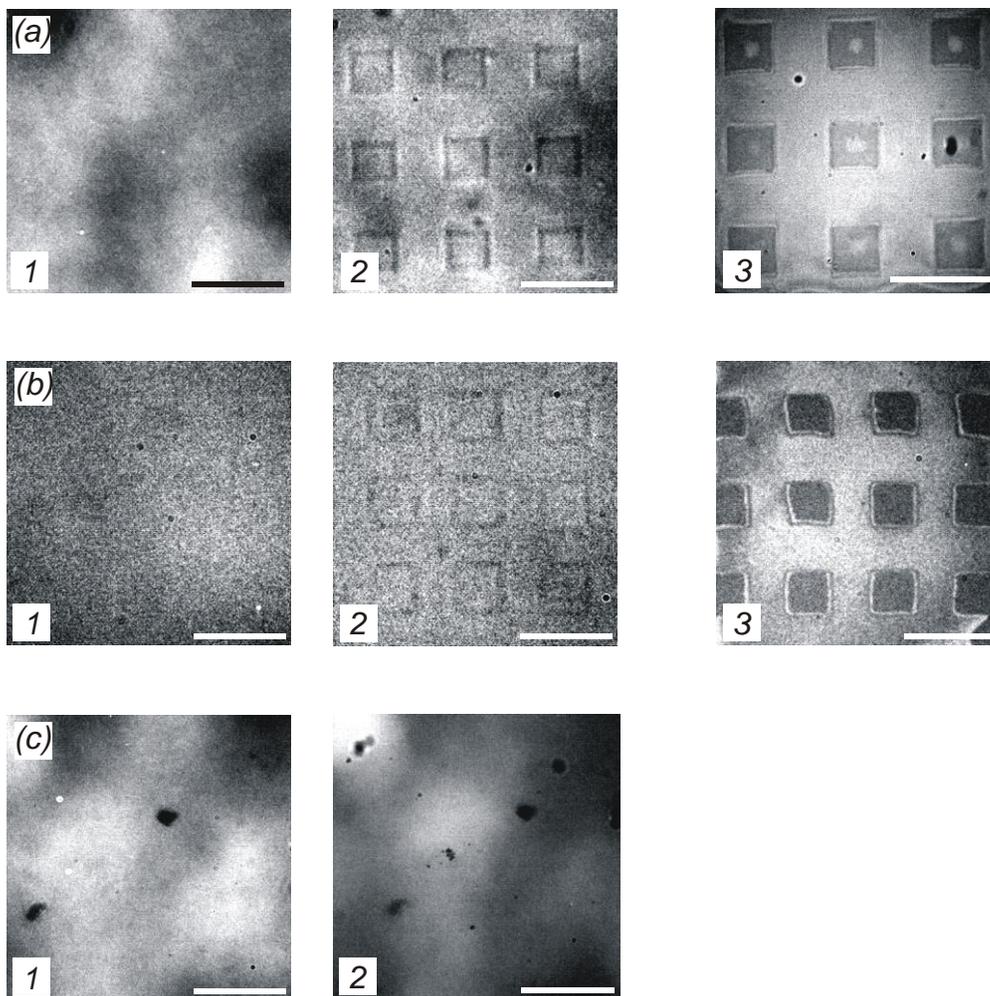
Figure 4 *(Bessueille et. al.)*

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