Self-Assembled Monolayers

Side-by-Side Patterning of Multiple Alkanethiolate Monolayers on Gold by Edge-Spreading Lithography**

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The ability to generate multicomponent patterns of high chemical and structural complexity is central to many scientific areas, including the fabrication of DNA arrays for monitoring gene expression,[1] the development of novel displays,[2] and the study of surface-related phenomena such as wetting, nucleation, and adhesion.[3] The methodology of patterning can vary depending on the type of materials involved and the resolution that needs to be achieved. Techniques such as photolithography,[1b] inkjet printing,[4] and microcontact printing,[5] as well as scanning probes,[6] can be used to introduce multiple functionalities at a surface with spatial control. Several of these techniques have reached high levels of maturity and sophistication, but the procedures often involve a number of lithographic steps, which necessitates alignment between them. This drawback has spurred the search for extended or alternative patterning methodologies. In a recent approach, Ryan et al. used a photomask that transmitted different wavelengths in different areas in combination with a monolayer of a photosensitive alkanethiol on gold.[7] Another approach suggested by Tien et al. involved the use of a multilevel polydimethylsiloxane (PDMS) stamp to fabricate aligned patterns of proteins on substrates.[8] For the same purpose, Delamarche and co-workers introduced a method called affinity contact printing, which employs the specific recognition between target proteins and their complementary binding partners on a PDMS stamp.[9] As recently demonstrated by Whitesides and co-workers,[10] the parallel patterning of multiple polymers, proteins, or cells with microfluidic systems might be straightforward, even though these methods are generally limited to the fabrication of simple and continuous patterns that result from constraints imposed by the channel geometries.

Herein, we describe an approach for patterning multiple self-assembled monolayers (SAMs) of alkanethiolates on

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gold in a simple and convenient way without the need for alignment steps. We rely on the recently introduced technique of edge-spreading lithography (ESL).[11] The concept behind ESL is fairly simple: alkanethiol molecules are delivered from a PDMS stamp onto a coinage-metal substrate by the surface of a relief structure. Our previous studies only established the patterning of just one type of monolayer, but we now extend this technique to the side-by-side patterning of multiple SAMs by successive printing steps. We used monodispersed silica beads as the guides because: a) they are commercially available in a wide range of sizes; b) they can readily assemble into ordered two-dimensional (2D) arrays over relatively large areas; c) they are inert to most organic solvents and are mechanically more robust than most polymer beads of equivalent size; d) their hydrophilic surfaces support the spreading of thiols; and e) they can be easily removed from the substrate by sonication without leaving any notable residues on the surface. Figure 1 shows a schematic illustration of our approach in its simplest form, that is, the side-by-side patterning of two monolayers. A planar PDMS stamp was inked with an alkanethiol such as sulfanylhexadecanoic acid (SHA, $HS(CH_2)_{15}COOH$), and printed onto silica beads (1.6 µm diameter) deposited on a thin film of gold. Upon reaching the surface of the gold, the molecules formed a SAM around the circular footprint of each bead. As long as the supply of molecules was maintained through contact between the stamp and the array, the area of the SAM expanded radially by reactive spreading.[11,12] In a second step of ESL another thiol, such as eicosanethiol (ECT, $HS(CH_2)_{19}CH_3$), was printed in the same way to form a SAM that nucleated at the edges of the SHA monolayer rings. Once the stamp was removed and the beads were lifted off, a monolayer pattern of concentric rings was observed by lateral force microscopy (LFM).[13]

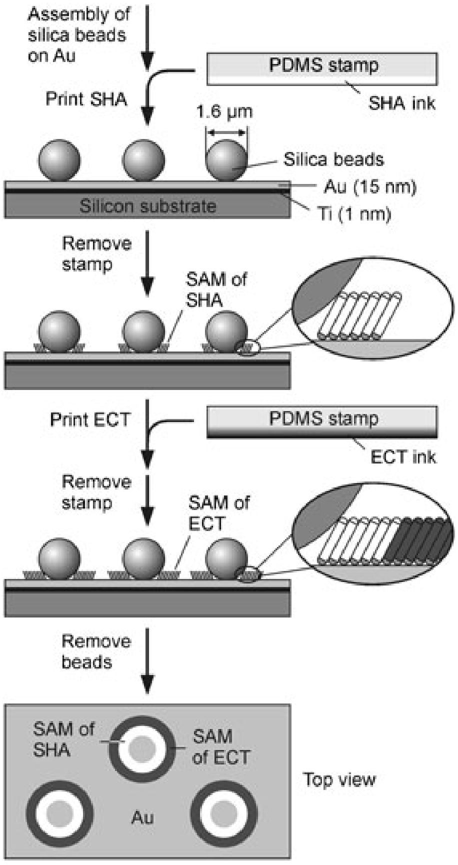

Figure 1. Schematic illustration of the ESL procedure used for side-by-side patterning of SHA and ECT monolayer rings on a gold substrate. The process involves two successive prints that are performed on a 2D array of silica beads supported on a thin film of gold. In the first step, SHA molecules (white) are guided from a planar stamp to the gold surface where they assemble into a monolayer, as directed by the circular footprint of each bead and lateral spreading. In the second step, ECT molecules (black) are applied in a similar fashion, thus forming a SAM that emerges from the edges of the SHA monolayer. Removal of the beads yields an array of concentric rings of SHA and ECT SAMs on the surface.

The functional groups involved in our experiments yield strong differences in contrast when imaged by LFM, as demonstrated by the control experiments shown in Figures 2a and b. The carboxy-terminated SAM appears bright as a result of the relatively strong adhesion forces between the COOH groups and the polar surface of the silicon nitride tip employed for our measurements.[14] Conversely, the methyl-terminated regions interact more weakly with the tip, which results in a darker appearance under LFM.[14] Figure 2c shows the result of a successive ESL experiment as described above. The resultant pattern was an array of concentric rings with an hexagonal arrangement in which the SHA and ECT portions were resolved clearly, both having a width on the order of

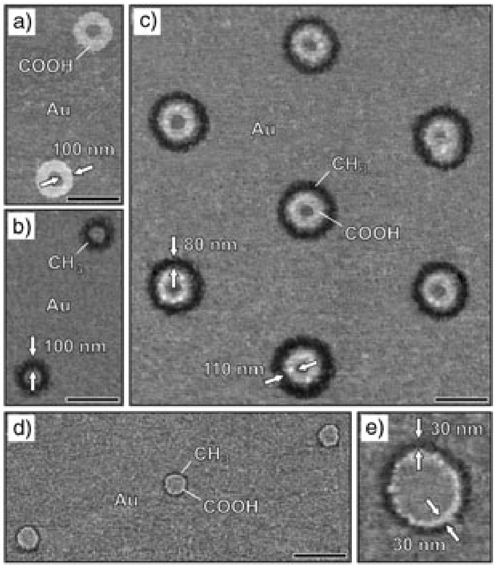

Figure 2. LFM images of carboxy- and methyl-terminated thiolate monolayer rings that were patterned on gold by ESL using SHA and ECT with 1.6-µm-diameter silica beads as guides. The COOH group appears bright, whereas the CH_3 group appears dark, as confirmed by reference measurements (a, b). These rings have a width of ≈100 nm, which was achieved with 1.0-mM ink solutions and a printing time of 1 min. c) Hexagonal array of concentric rings with well-resolved monolayer rings of 80- and 110-nm width. In this case, the printing times were 1 and 2.5 min for SHA and ECT, respectively. A decrease in the concentration of thiol in the ink to 0.1 mM along with contact times of 50 s and 2 min were key to confining the line width to 30 nm and below (d, e). All scale bars correspond to 500 nm.

100 nm. We used this approach to investigate the lower limits of resolution by decreasing the concentration of thiol molecules in the ink and the printing time. Figures 2 d and e reveal striking results: the line widths were reduced to 30 nm and less without compromising the contrast or accuracy of the rings. It was difficult to elucidate the integrity of the SAMs on the molecular level, but if a close packing arrangement and a lattice constant of 0.501 nm[15] were assumed, the width of these rings corresponds to about 60 molecules. In principle, further reduction of the line width should be possible, although there may be several obstacles for both fabrication and analysis.

To demonstrate the versatility of our approach we added another alkanethiol, 12-hydroxydodecanethiol (HDDT, $HS(CH_2)_{12}OH$), and increased the number of successive prints from two to three (Figure 3). The use of HDDT proved advantageous since the resulting SAM appears gray in the LFM image, thus providing a sufficient contrast to both SHA and ECT monolayers. Insertion of the HDDT printing step inbetween those for SHA and ECT resulted in a concentric triple-ring system with high structural definition (Figure 3 a). The width of each monolayer ring could be varied independently by tuning both the concentration of the ink and the printing time (Figure 3 b). Furthermore, the SAMs could be arranged in any order (Figures 3 c and d); switching of the printing order did not have any adverse effect on the appearance of the SAMs under LFM for the majority of samples. The monolayers shown in Figure 3 involve only three types of thiols and just a few of their possible combinations, but increasing the number of successive prints or adding more thiols to the process should be straightforward provided that suitable compounds are selected.[16]

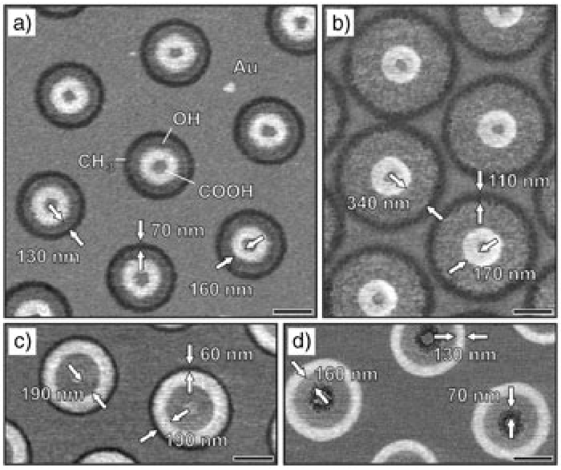

Figure 3. LFM images of concentric rings of carboxy- (bright), hydroxy- (gray), and methyl-terminated (dark) thiolate monolayers on gold. a) The rings were fabricated under the following conditions: 1 min for SHA, 1.5 min for HDDT, and 3 min for ECT. b) An increase in the printing times for HDDT and ECT to 3.5 and 4 min, respectively, resulted in wider rings for these two monolayers. c, d) The position of each monolayer in the concentric structure could be varied by changing the printing order. The pattern in (c) was generated by printing HDDT for 1.5 min, followed by printing of SHA and ECT for 3 min each. The sample shown in (d) was prepared by printing both ECT and HDDT for 1 min, and SHA for 2 min. All scale bars correspond to 500 nm.

To increase the versatility of our approach further, we explored the inclusion of non-thiol-based inks in the ESL experiments. Figure 4 illustrates one demonstration, in which 1-octadecylamine (ODA, $H_2N(CH_2)_{17}CH_3$) was selected as the non-thiol compound in conjunction with SHA and ECT. Amines can form monolayers on gold surfaces, but the stability of these layers is much lower than that of their thiol counterparts.[17] We deposited 2.3-μm silica beads on 30 nm of gold and made three successive prints (Figure 4 a). After lift-off, the gold was etched in an aqueous solution containing both Fe^{3+} ions and thiourea.[18] Inspection of the etched sample by scanning electron microscopy (SEM) showed the presence of concentric gold rings on the substrate which were separated by a distinct, well-defined gap (Figure 4 b). This

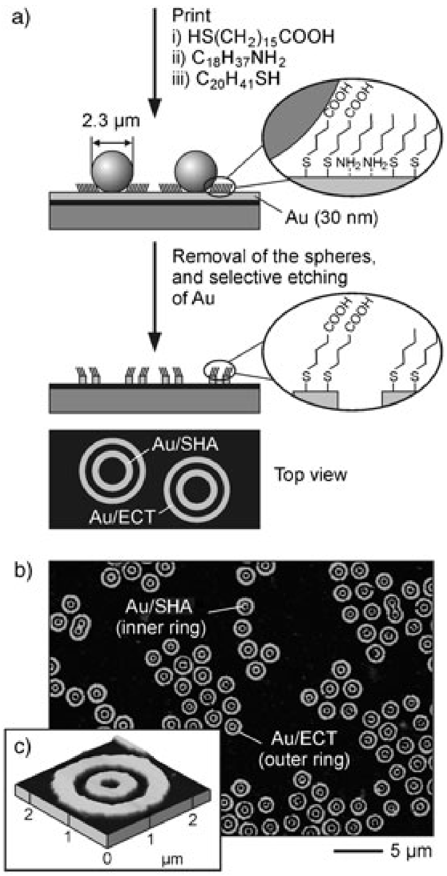

Figure 4. Fabrication of concentric gold rings by ESL and selective etching. The procedure depicted in (a) involves a 2D array of silica beads and an alkyl amine monolayer sandwiched between two concentric rings of thiolate SAMs. The amine monolayer has dual functions: it largely resists the adsorption of thiols while providing sufficient transparency during wet etching of the gold. b) SEM image showing an array of concentric gold rings that were fabricated with 2.3-μm-diameter silica beads and contact times of 1.5 min for SHA, 4 min for ODA, and 7 min for ECT. c) AFM image of the 3D topography of a pair of concentric gold rings. The gap between the two rings is 250 nm wide. The widths of the inner and outer rings are 260 and 340 nm, respectively.

finding reveals two characteristics of the ODA film: it was dense enough to resist the displacement by ECT molecules during ESL, but unlike the thiol monolayers, it was not sufficiently robust to protect the underlying gold from etching. Both the order and density of the array were low in this example, although the contrast and accuracy that could be achieved for individual rings were excellent as depicted by the atomic force microscopy (AFM) image in Figure 4c. Similar results were not obtained when ODA was replaced with either 1-octadecanol ($HO(CH_2)_{17}CH_3$) or *n*-octadecane ($CH_3(CH_2)_{16}CH_3$). It is probable that in both these cases the interaction between the molecules and the gold surface was too weak, such that adequate monolayers were not formed. These findings highlight some of the possible limitations of this technique.

In summary, we have extended ESL from a novel microfabrication technique to a versatile tool capable of patterning multiple alkanethiolate SAMs on gold at the sub-100-nm scale without any need for alignment. Well-defined concentric rings of monolayers were achieved by using 2D arrays of silica beads as guides in successive printing steps with a planar PDMS stamp. While the width of the rings could be varied between 30 and 340 nm, the most attractive feature of this technique is its flexibility in the print order of the different alkanethiols—a finding that was quite surprising. When a non-thiol ink was incorporated, we demonstrated fabrication of concentric gold rings by a combination of successive prints and selective wet etching. The 2D arrays of silica beads served as a convenient model system for these initial demonstrations; however, the technique should be extendable to guides comprising other materials (for example, polymers, oxides, or metals) and with different geometries.[11a] Modification of the SAMs shown here, backfilling, or the use of other functional inks may also be helpful in further increasing the chemical complexity of the patterns.

Experimental Section

Gold substrates were prepared by e-beam evaporation (SEC 6000, CHA Industries) of 15 nm of gold (99.999 %, Kurt J. Lesker Company) onto a silicon wafer (Montco Silicon Technologies) that had been primed with 1 nm of titanium (99.995 %, Kurt J. Lesker Company) to promote adhesion between the gold film and the silicon substrate. The gold-coated wafer was then cut into smaller pieces ($\approx$1 cm^2), which were subjected to an air plasma treatment (Harrick Scientific Corp.) for 1 min to remove possible organic contaminants. Monodispersed silica beads were purchased from Duke Scientific (1.6 ± 0.06 μm) and from Bangs Laboratories (2.3 ± 0.1 μm). The commercial samples were diluted with deionized (DI) water to give suspensions containing $\approx$0.15 wt % of beads. A drop of the bead suspension was placed onto a freshly prepared gold substrate, and a 2D array was formed by capillary interaction while the water slowly evaporated.

Planar PDMS slabs were prepared from Sylgard 184 (Dow Corning) by curing the mixed prepolymers of PDMS on a flat polystyrene surface (Falcon 1001 petri dish, Becton Dickinson Labware) in an oven at 60°C for $\approx$20 h. The slabs were cut into pieces ($\approx$1 cm^2) which were used as stamps for inking and printing. Sulfanylhexadecanoic acid (Aldrich) was purified by recrystallization from toluene (Fisher Scientific). Eicosanethiol (Robinson Brothers Ltd.) was used as received. Hydroxydodecanethiol was kindly provided by Prof. G. M. Whitesides at Harvard University. Octadecylamine was from Aldrich; octadecanol and octadecane were both from Fluka, and used without further purification. In all examples, except for the high-resolution experiments, ethanolic solutions (1.0 mM) of these compounds provided the inks. Stamps were inked by covering one side entirely with the ink solution for 1 min, then dried with a stream of air, and placed by hand onto a colloidal array for various times. After each print, samples were allowed to rest for several minutes before further processing. Lift-off was accomplished by sonication in DI water for $\approx$1 min. Gold was etched in a solution of $Fe(NO_3)_3$ (20 mM, Fisher Scientific) and thiourea (30 mM, Acros Organics) in DI water at room temperature with gentle stirring. After removal from the etch bath, the samples were rinsed with DI water and dried in a stream of air.

AFM measurements were performed with a multimode Nanoscope III atomic force microscope (Veeco Instruments), operated under ambient conditions and in the contact mode to record both friction and height simultaneously. All measurements were conducted by using silicon nitride cantilevers (Veeco) with spring constants ranging from 0.06 to 0.58 N m^{-1}. SEM images were obtained with a Siron XL field-emission microscope (FEI Company) operated at an acceleration voltage of 5.0 kV. The width of the ring patterns was determined with an image analysis program (Image Tool 3.0, UTHSCSA).

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