Nanostencil Printing

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Large-Area Nanocontact Printing with Metallic Nanostencil Masks**

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The development of molecular-printing techniques that can be used to create dense arrays of sub-100 nm patterns has been driven by scientific interest in new physical and chemical properties at the nanometer scale. For example, nanoscale arrays of molecules are important for the creation of high-throughput protein assays with improved sensitivity[1] and for the design of arrays of transistors based on organic crystals.[2] Moreover, hierarchical patterns of micro- and nanoscale structure exhibit unique properties, such as surface-plasmon focusing,[3] ultranarrow surface-plasmon resonances,[4] and superhydrophobicity.[5] Significant effort has been devoted toward the improvement of high-resolution self-assembled-monolayer (SAM) patterning methods, such as microcontact printing (μCP)[6] and dip-pen nanolithography (DPN).[7] The printing of large-area molecular arrays in which both the feature size and pitch are on the nanometer scale is still a challenge, however, because of lateral diffusion of the molecular inks. Although sub-50 nm resolution is possible with DPN, high-density nanoarrays are difficult to obtain because the spacing of the pen arrays is tens of microns.[8] μCP enables printing over areas larger than 1 cm^2, although the deformation of the elastomeric stamps (typically poly(dimethylsiloxane), PDMS) restricts the features to micrometer resolution.

Several strategies have been explored to address the drawbacks of conventional μCP so that parallel printing methods can be extended into the nanoscale. Sub-100 nm molecular patterning has been pursued by 1) decreasing the physical contact area between the stamp and substrate to reduce the diffusion of the molecules;[9] 2) changing the stamp materials from PDMS to a polymer with a higher Young modulus to prevent mechanical collapse of the stamps;[10,11] and 3) using chemically patterned flat PDMS slabs that circumvent both the mechanical and diffusion issues encountered in μCP.[12,13] Although these approaches have improved the resolution of the printing of individual features significantly (down to approximately 100 nm), most of the patterns are still limited to micrometer spacing.

Herein, we report a nanocontact printing method that can be used to create large-area arrays of molecular patterns with both high density (400 nm spacing or less, depending on the master) and high resolution (features as small as 50 nm). Nanostencil masks consisting of Au films of nanohole arrays attached to a flat PDMS slab were used to improve the resolution of printed molecular patterns. The solid portion of the Au hole-array film acted as a vapor-transport barrier, and the nanohole areas determined the size and shape of the patterned molecules. By using nanohole films of different thicknesses, we tested whether the nanostencil masks printed edge patterns or 1:1 patterns. Furthermore, we demonstrated the generation of hierarchical patterns from a single nanostencil mask by either replacing the flat PDMS slab with a patterned PDMS slab or by combining nanostencil printing and μCP in a two-step printing process.

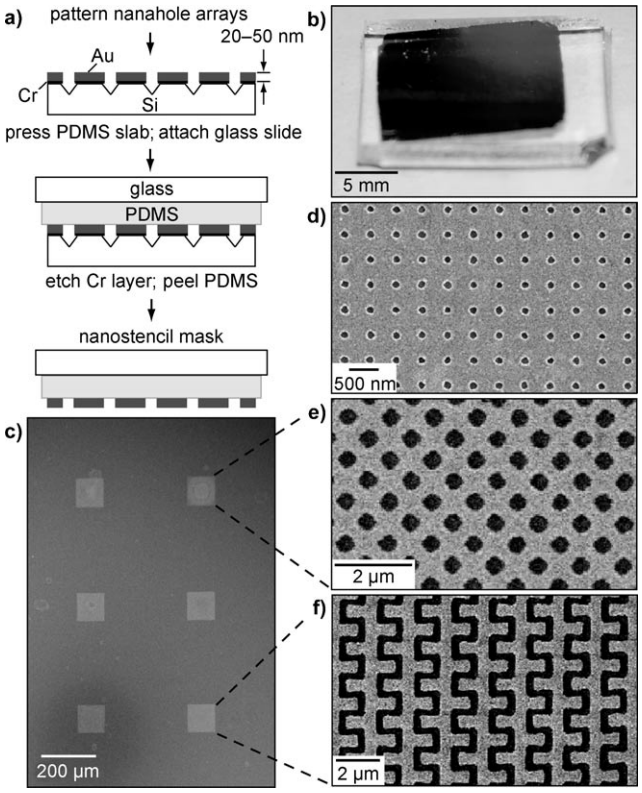

Figure 1. a) Fabrication of nanostencil masks. b) Optical micrograph of a nanostencil mask. c) SEM image of a nanostencil mask perforated with different types of patterns. d) Circular holes in the nanostencil mask shown in (b). e) Square holes and f) meandering lines in the mask in (c).

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Figure 1a depicts the fabrication scheme to produce nanostencil masks. These masks are composed of two parts: 1) a thin Au film perforated with openings that define the areas through which molecules diffuse, and 2) a flat PDMS slab that supports the Au nanohole arrays and acts as a reservoir for the molecular inks. Au films perforated with hole arrays were fabricated on Si by a large-area nanofabrication technique known as PEEL (a combination of phase-shifting photolithography, etching, electron-beam deposition, and lift-off of the film).[4] To attach this film to a support layer, we soaked a flat slab of PDMS (1 mm thick) in 3-mercaptopropyltrimethoxysilane for 5 min and then brought it into contact with the Au nanohole film. This step increased adhesion between Au and PDMS and prevented buckling of the Au film or separation of the Au film from the PDMS upon inking. A glass backing was placed on the PDMS as a support for multiple printing events. Without the glass support, cracks in the Au film were more likely to occur from flexing of the nanostencil stamp as it was released from the substrate. Subsequent etching of the Cr layer (5 nm) between the Si substrate and the Au film enabled removal of the Au nanohole film/PDMS slab/glass slide from the Si substrate to yield nanostencil masks in which a smooth Au film covers a large area ($0.8 \times 1.2\ cm^2$; Figure 1b). To demonstrate the versatility of nanostencil printing, we prepared Au films perforated with different arrays of nanohole shapes (Figure 1c–f). These representative patterns were selected to show 1) high-throughput printing with nanometer-scale pitch and feature sizes, 2) continuous and isolated structures, and 3) multiple nanopatterns from a single mask.

After inking a nanostencil mask with an ethanolic solution (0.5 mM) of octadecanethiol (ODT), we dried the mask under a stream of N_2 for 1 min. The mask was then placed in conformal contact with a thin (15 nm) Au film on a Si wafer. Relatively short contact times (2 s) and a small applied pressure ($1.5\ g\,cm^{-2}$) were used to minimize lateral spreading of the molecules after transport from the PDMS slab through the nanoholes to the Au substrate. To evaluate the performance of our nanostencil printing method, we compared the sizes of the patterned ODT and the nanoholes (Figure 2). After the ODT patterns had been printed by using a nanostencil mask with circular holes (Figure 1d), the sample was backfilled with a solution of mercaptohexadecanoic acid (MHA) to increase the chemical contrast between the hydrophobic ODT and hydrophilic MHA regions. The average diameter of the ODT spots in the lateral force microscopy (LFM) image was approximately 190 nm. Although the pitch of the array was the same as the spacing of the holes (400 nm), the printed ODT islands were larger than the holes in the nanostencil mask (ca. 120 nm) because of some spreading of the ODT molecules on the Au substrate (Figure 2a). The lateral diffusion observed with our nanostencil printing method was less than the lateral spreading that occurs in conventional μCP.[14] Because the PDMS is not in contact with the substrate as it is in μCP, the vapor transport of ODT from PDMS to the Au substrate is slower. Also, lateral diffusion on the substrate was minimized because of the self-assembly of the ODT molecules on the nanohole films during the inking process. The contact-printing time and the molecular weight of the inks can be used to tune the sizes of the molecular patterns (see the Supporting Information).

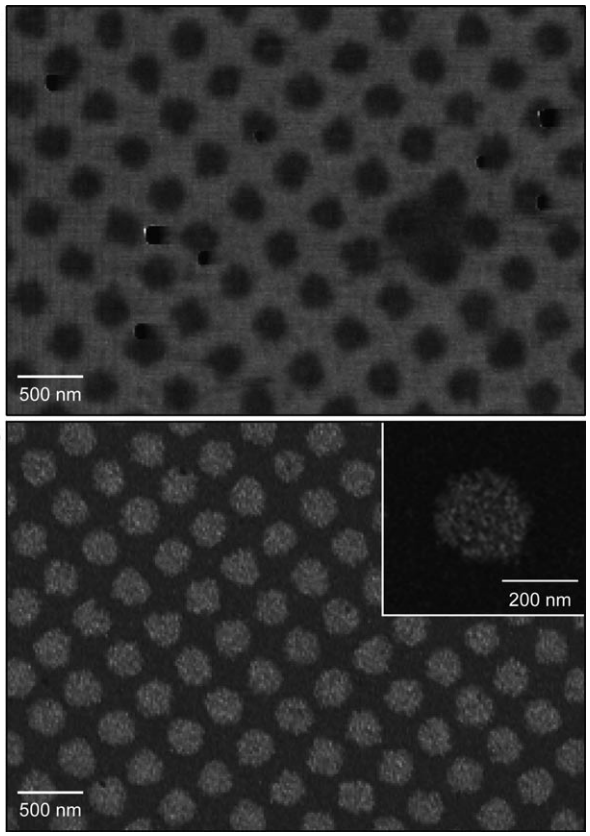

Figure 2. a) LFM image of ODT-dot patterns formed by nanocontact printing on an Au substrate by using a nanostencil mask with circular holes. b) SEM image of the same patterned area following Au etching.

We tested the quality of the molecular patterns by using them as etch resists. After nanostencil printing with ODT on an Au substrate, we selectively etched the Au in an aqueous solution of KOH (1M), $Na_2S_2O_3$ (0.1M), $K_3[Fe(CN)_6]$ (0.01M), and $K_4[Fe(CN)_6]$ (0.001M) at 70°C with gentle stirring.[15] Figure 2b shows an SEM image of Au disks that were protected by ODT during wet chemical etching. The Au pattern that remained on the substrate was similar to the printed ODT patterns in the LFM image, and the pattern was uniform over the entire 0.5 cm^2 patterned area.

Nanostencil printing is unique because the overall shape of the printed molecular patterns can be tuned simply by changing the thickness of the Au hole-array films. When we used an Au film with isolated square openings (Figure 1e) and meandering lines (Figure 1f), we obtained solid patterns of dots and lines from 20 nm thick nanostencil masks (Figure 3a–c). When the thickness of the Au film in the nanostencil masks was increased to 50 nm, the molecules were directed exclusively along the sidewalls of the patterned openings and were transferred to the Au substrate as edge patterns (Figure 3d–f). Significantly, these 1D and 2D patterns were obtained from a single nanostencil mask. These edge-printing results have interesting characteristics when compared to those of μCP or other patterning techniques. First, the resolution of patterns produced by nanostencil

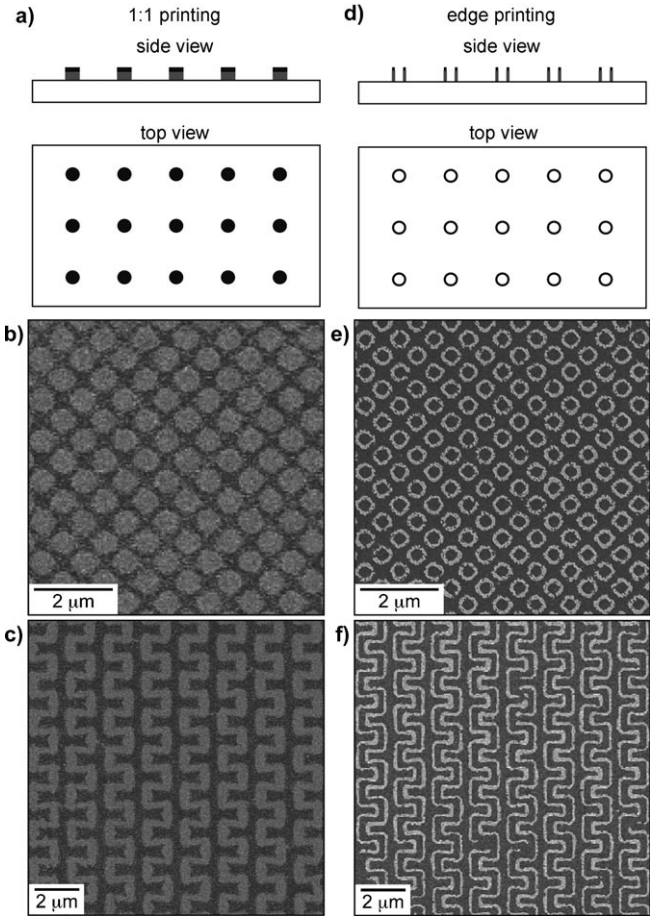

Figure 3. SEM images of Au patterns prepared by printing and etching with b,c) a 20 nm thick Au nanostencil mask and e,f) a 50 nm thick nanostencil mask: depending on the thickness of the Au film, the molecular patterns formed with the nanostencil masks were either solid (a–c) or outlines of the structures (d–f).

printing was much higher than that observed with other contact-printing methods. The widths of structures created with nanostencil masks with thick films were approximately 50 nm, whereas the smallest line widths obtained by μCP are approximately 150 nm.[16] Second, ringlike patterns can be printed multiple times, as sacrificial patterns defined by photoresist or polymer spheres are not required.[17–19] Third, nanostencil printing can produce different geometric arrays of ringlike structures. Colloidal lithography only enables the formation of circular rings, and the ring patterns are limited to random or hexagonal arrays.[20]

Nanostencil printing can also create hierarchical molecular patterns in one or two printing steps to produce microscale superlattices composed of nanoscale molecular arrays. An advantage of PEEL is that the free-standing Au films can be attached to substrates with arbitrary topographies. By attaching the Au nanohole arrays to patterned PDMS slabs, we could control the nano- and microscale patterns independently (Figure 4a). For example, Au circular-nanohole arrays determined the nanoscale patterns (120 nm diameter, 400 nm spacing), and the relief pattern on the PDMS defined the microscale patterns (5 μm diameter, 20 μm

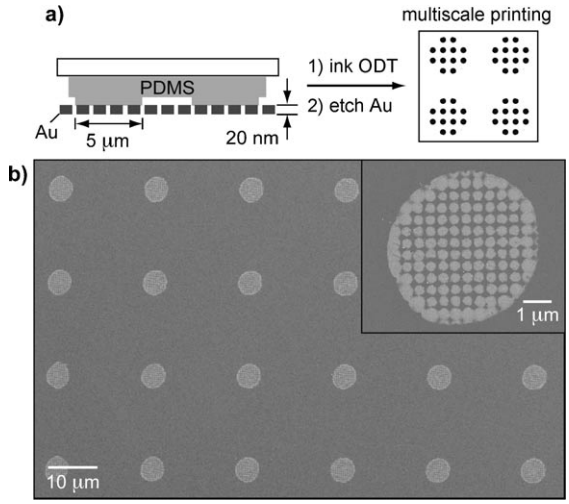

Figure 4. a) Hierarchical patterning with a nanostencil mask on bas-relief-patterned PDMS. b) SEM images of a hierarchical Au pattern created by printing with an Au film perforated with nanoholes (120 nm diameter and 400 nm pitch) and attached to a post array (5 μm post diameter) on a PDMS slab.

pitch; Figure 4b). Isolated patches of molecular arrays were obtained because the ODT ink was only transferred from the stamp to the substrate in areas where the mask was in direct contact with the PDMS.

Other types of hierarchical arrays could also be patterned by printing with a nanostencil mask followed by μCP. Patterns with dense arrays of nanometer and micrometer length scales have rarely been reported because conventional methods can only generate arrays of features of one length scale at a time: on the nanometer (e.g. DPN) or micrometer scale (e.g. μCP). By using a nanostencil mask of nanohole arrays with subsequent μCP of microscale lines, we printed hierarchical patterns of ODT (Figure 5a). We tailored the quality of the SAM in the micrometer-scale lines by controlling the amount of ink in the PDMS stamp. When there was enough ink to form a densely packed SAM on Au, we observed solid micrometer lines and nanopatterns after Au etching (Fig-

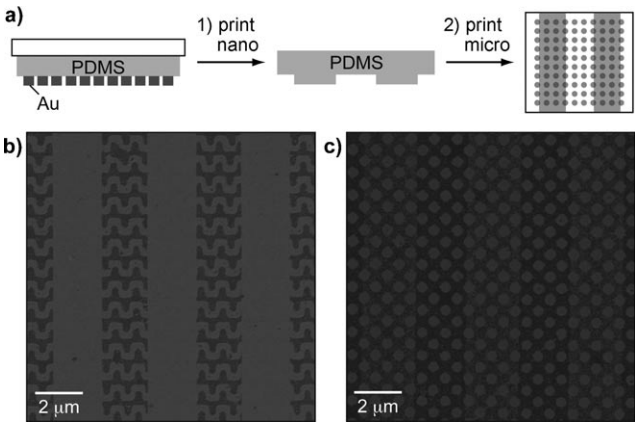

Figure 5. a) Hierarchical patterning by sequential printing with a nanostencil mask and a bas-relief-patterned PDMS stamp (1.8 μm lines with 2.2 μm spacing). b,c) SEM images of nanoscale meandering lines (b) and square dots (c) overlaid with micrometer lines.

ure 5b). In contrast, when the concentration of ODT was low, the Au nanodots showed through the micrometer lines because of incomplete SAM formation (Figure 5c).

In summary, we have developed a new type of nanopatterning element: a nanostencil mask. These masks are mechanically stable and reusable. We controlled the transport of molecules from the stamp to the substrate by changing the thickness of the nanohole films so that either solid features or outlines of patterns resulted. We have also developed one- and two-step hierarchical patterning methods by combining nanoholes with patterned μCP masks and by sequential printing with a combination of nanostencil masks and PDMS stamps. This nanocontact printing method can increase throughput in the fabrication of biological assays and electronic circuits and can generate model substrates for studies of cell-adhesion and cell-proliferation mechanisms.

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