Soft Lithography

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Self-Assembly Meets Nanofabrication: Recent Developments in Microcontact Printing and Dip-Pen Nanolithography

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Since their first detailed description in the late 1980s,[1–3] self-assembled monolayers (SAMs) of long-chain alkanethiols on gold have been the method of choice for anyone interested in modifying surfaces with well-defined molecular thin films that can carry almost any imaginable chemical functionality. Molecularly close-packed SAMs with crystalline order are obtained by simply immersing a clean gold substrate into dilute (mM) solutions of alkanethiols for several hours. The thiol groups form a covalent thiolate–Au bond (with ionic character) with the surface, and with increasing surface coverage the alkyl tails stretch into an all-*trans* configuration. The surface chemistry is then entirely defined by the nature of the functional group at the ω end of the long-chain alkanethiols used. The facile formation of these self-assembled monolayers has opened a general route to molecular-level control over surface order and chemistry. Accordingly, SAMs have been used as model surfaces to study protein adsorption,[4] to influence the charge mobility in semiconducting materials in field-effect transistors,[5] and to act as ultrathin dielectrics.[6]

The next breakthrough in the field came with the discovery of microcontact printing (μCP, Figure 1) by Whitesides and Kumar[7] which brought microfabrication within the reach of every chemistry, physics, and biology laboratory, without the need for any significant investment in equipment or cleanroom-type infrastructure.

Contact printing relies on the rapid formation of SAMs in those areas that are in contact with a rubber stamp inked with alkanethiols. These stamps are made of micropatterned elastomers cast against photolithographically prepared masters, and they form a conformal contact with the substrate. Once in contact, a monolayer of alkanethiol molecules is diffusively transported onto the surface. Contact times are typically in the order of seconds, but despite these short contact times high-quality SAMs are formed that differ very little from the crystalline SAMs formed from solution as demonstrated by scanning tunneling microscopy (STM) images, which reveal their crystalline order.[8] The patterned SAMs can then be used, for example, as etch-resists to protect those areas of gold covered by SAMs against wet etchants. Alternatively, the remaining bare gold can be covered with a SAM that contains a different terminal group, leading to chemically patterned surfaces.

Despite the obvious attractiveness of using patterned SAMs to replace photoresists in the fabrication of microelectronics, it has been very difficult to integrate microcontact printing into the fabrication of electronic devices in a

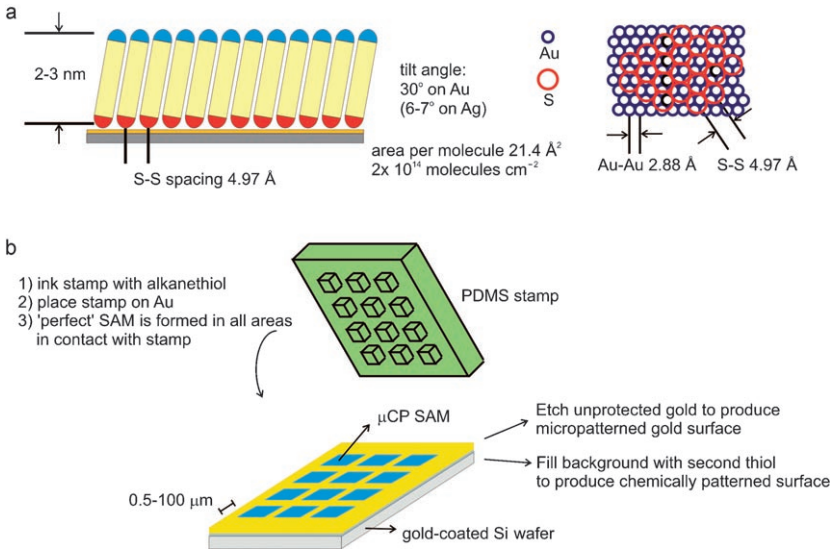

Figure 1. a) Structure of self-assembled monolayers (SAMs) of alkanethiolates on gold, and b) formation of patterned SAMs using microcontact printing (μCP). PDMS = poly(dimethyl siloxane).

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manufacturing environment because of the distortion in the replicated patterns as a result of the uncontrolled transfer and spreading of the ink molecules. As soon as the stamps are in contact with the surface, the alkanethiols start to diffuse rapidly across the gold surface, thereby broadening SAM-protected features. Furthermore, ink can also transfer through the vapor phase from those areas of the stamps not in contact with the surface. Several approaches have focused on low-vapor-pressure and slow-diffusing inks as well as complicated inking strategies to improve the quality of the SAMs and the edge resolution.

A breakthrough in the understanding of ink transport and the timescales involved in stamp contact and monolayer formation was reported in a recent paper on high-speed microcontact printing by Schmid and co-workers.[9] In a careful analysis of the mechanics of the printing procedure and a numerical diffusion simulation of the ink transfer, they concluded that μCP can be performed up to three orders of magnitude faster than previously reported. The key to their success is the careful control over the inking of the stamp: with high ink concentrations and short printing times, there is no depletion of ink beyond the stamp protrusions which leads to an overall homogeneous deposition of SAMs, independent of feature size. In effect, this means that a printing time of 3 ms (but not 1 ms) using a concentration of 16.6 mM of hexadecanethiol ink is sufficient to create "perfect" pattern replication in printed and etched gold patterns (Figure 2). These recent results demonstrate that there is a well-defined processing window, where the concentration of ink and the length of the printing time combine to give perfect SAMs (as judged from etch-resistance, but certainly indicating the formation of monolayers with crystalline order), but where surface diffusion, diffusion through the vapor phase, ink depletion, and stamp distortion are all avoided (Figure 2b). With this major improvement in control over pattern replication and the concomitant increase in overall printing speed, microcontact printing could now indeed become a commercially attractive microfabrication technology. The scaling down of feature sizes will certainly need to be the next goal to determine if nanopatterning would be feasible; however, this will be far from trivial owing to unresolved problems regarding suitable stamp materials and ink diffusion on the (sub-)100 nm scale as discussed below.

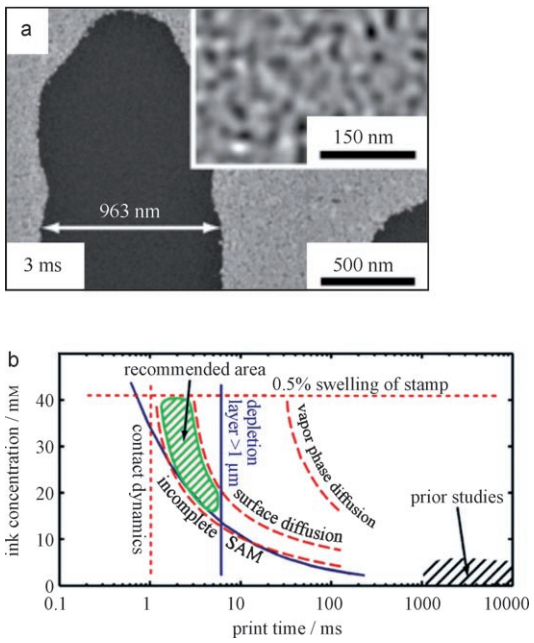

Figure 2. a) SEM image of features produced using "high-speed" printing followed by etching, demonstrating the excellent feature reproduction after a 3-ms printing step with a 16.6 mM concentration of hexadecanethiol ink. b) Semiquantitative graph illustrating the processing window for high-speed μCP, with crucial parameters such as ink-induced swelling (red dotted lines), the condition for complete SAM formation (blue solid line: simulation; red dashed line: experiment), surface diffusion, and vapor-phase diffusion.[9]

A fundamentally different approach based on bottom-up patterning of SAMs called dip-pen nanolithography (DPN) was introduced by Mirkin and co-workers (Figure 3).[10] Atomic force microscopy (AFM) tips dipped into alkanethiol inks are dragged across a gold surface, and the ink molecules are transported to the substrate by a capillary bridge of surface-bound water. Although the precise transfer process of the alkanethiol inks to the gold surface is complex and heavily influenced by the nature of the ink and the humidity of the environment, DPN is capable of "writing" SAM patterns as small as 15 nm—well below the smallest features feasible using microcontact printing.[11]

The major disadvantage of DPN is that the process is slow and only relatively small areas can be patterned. The design demands for scale-up by parallelization using multiple pens are truly

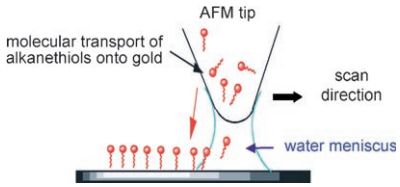

Figure 3. Patterning of surfaces using dip-pen nanolithography.

daunting, but Mirkin and co-workers have achieved that and made DPN 55000-times faster! In a recent report, they described a massively parallel method (called 2D DPN) to pattern large (1 cm^2) areas with 80–100-nm features arranged in complex patterns within 30 minutes.[12]

The technology adapted in this recent report was inspired by the "millipede" system, which features a two-dimensional array of fully controllable cantilevers.[13] Unlike the "millipede", the 2D DPN arrays do not feature independently actuated tips but instead form a 1-cm^2 bundle of 55000 tips, spaced 90 μm × 20 μm apart and with a tip radius of 60 nm (Figure 4a,b). To pattern an area of 1 cm^2 with 88 million dot features, every tip wrote 1600 fea-

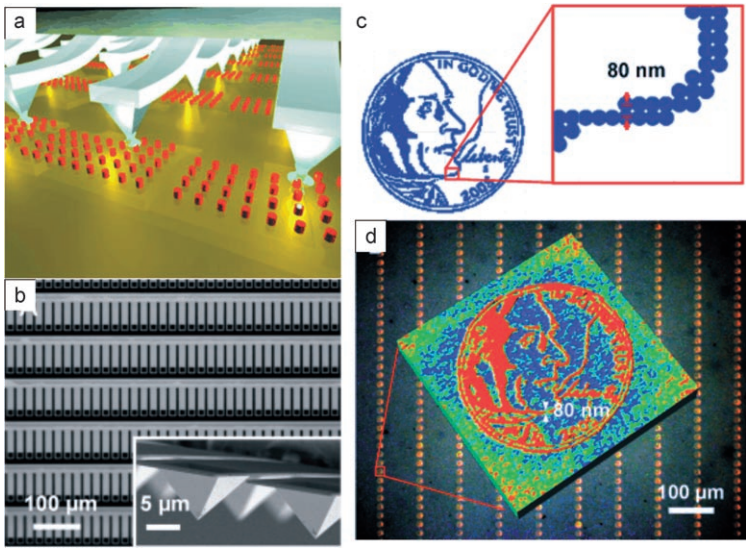

Figure 4. Massively parallel or 2D dip-pen nanolithography:[12] a) artist's impression of the arrays of cantilevers (shown in part b) writing nanoscale features; c, d) demonstration of the formation of complex features using 80-nm-diameter dots.

tures, each 100 nm in size. To allow transport of the alkanethiol ink onto the gold substrate, dwelling times of 80 ms at each dot were chosen which resulted in overall writing times for each dot in the order of 0.5 s. The pattern shown in Figure 4d consists of around 5×10^8 features and took approximately 30 minutes to complete. These speeds do not compare well with microcontact printing in which whole 4-inch (ca. 10 cm) wafers are patterned within a few milliseconds (including the times required to form conformal contact and remove the stamps after printing). However, DPN has a number of unique advantages. First, no stamp design or lithography is required. This means that complex patterns (e.g. the likeness of Thomas Jefferson from a 2005 US five-cent coin) can be written with one, generic array, thus saving time and significantly reducing the overall cost. A second advantage is that patterns can be composed, in principle, of SAMs containing many different terminal groups, if reliable procedures are developed for inking each tip with a different ink.[14] Both advantages mean that for the fabrication of prototype surfaces or devices, where scale and throughput are not of crucial importance but flexibility in design and materials choice are paramount, DPN is an extremely attractive technique.

The long-term impact of these recent breakthroughs is not easy to predict. Microcontact printing is already well-established as a micropatterning tool, but the recent work described above has the potential to dramatically improve the resolution and fidelity of the technique and make it a competitor to standard microfabrication technologies. This has major advantages for applications in device fabrication, but it should also provide a new stimulus for pushing μCP into the nanometer domain. With the printing conditions for microcontact printing optimized for the formation of (sub-)micron features, the patterning of sub-100 nm features still presents major obstacles. Spreading and vapor-phase diffusion of the ink will become much more pronounced when printing very small features. For nanopatterning, the elastomer commonly used (a cross-linked poly(dimethyl siloxane) with the brand name Sylgard 184) is no longer suitable, as a result of severe deformation of nanoscale features. Much harder materials are required to accurately replicate nanoscale features, yet the material needs to be sufficiently soft to make conformal contact possible. Initial attempts in this direction using bilayer stamps that combine hard and soft layers, as well as the use of high-molecular-weight inks to limit diffusion, have been explored, but the quest for suitable materials for "nanocontact printing" (nCP) is only just beginning.[15]

Dip-pen nanolithography, on the other hand, approaches nanopatterning in a "bottom-up" fashion and is an extremely powerful technique for patterning SAMs on the nanometer scale, but it is much less user-friendly and simply less well established. However, the hardware for DPN is developing very rapidly and Mirkin's recent results show that DPN can provide solutions for any applications requiring nanopatterns stretching over mm^2 to cm^2 areas. DPN can give new insights into the behavior of molecules at the nanometer scale,[16] arrays of biomolecules,[17] epitaxial growth of block copolymers,[18] or other areas of research where the effect of nanoscale modulations of surface chemistry could influence the behavior of materials deposited on top. An elegant demonstration was reported by Coffey and Ginger, who studied the phase separation of blends of semiconducting polymers on top of nanopatterned surfaces; their results could provide new insights for the development of more efficient optoelectronic devices.[19] Note, however, that many of these experiments will only really become accessible for routine use if reliable methods for inking 2D DPN arrays with multiple inks are developed.

One final issue that has not been addressed thus far and that seems to be taken for granted in the literature is the amazing speed at which high-quality SAMs can be formed using DPN and especially μCP: Millisecond contact times give high-quality SAMs that are indistinguishable from those that are formed when the substrates are left in alkanethiol solutions for hours. This rapid formation has been attributed to the high local concentration of ink near the surface, eliminating any diffusion limited steps. Whether this is sufficient to explain the formation of highly ordered SAMs is not clear, as there are no detailed studies of SAM formation in neat alkanethiols. Intriguingly though, chemical reactions leading to new covalent bonds between SAM end groups and molecules printed on top using μCP also seem to proceed much faster and without requiring activated functional groups or catalysts.[20,21] The formation of amide bonds between amine-terminated SAMs and carboxylic acid "inks" seems to proceed without the need for

activated esters or catalysts, and the effect is only observed when the "inks" are pressed onto the surface using PDMS stamps.[20] Preorganization of the reacting molecules on the PDMS stamp and in the SAM could influence the entropy of the reaction and perhaps enforces the effect that the high local concentration of reactants has on the overall reaction speed. These preliminary experiments represent some of the examples of using contact printing and DPN to not only pattern surfaces but also to control and confine chemical reactions on top of SAMs. In the future, we should expect SAMs and patterning techniques to be used routinely for fabricating nanopatterned surfaces with very complex molecules, to synthesize molecules where required on the surface, and perhaps as tools for driving chemical reactions that are not easily carried out in solution, where concentration, orientation, and external mechanical forces cannot be controlled with the same precision.

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