

Recent progress in soft lithography

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The future of nanoscience and nanotechnology depends critically on techniques for micro- and nanofabrication. An emerging set of methods, known collectively as soft lithography, uses elastomeric stamps, molds, and conformable photomasks for patterning two- and three-dimensional structures with minimum feature sizes deep into the nanometer regime. The powerful patterning capabilities of these techniques together with their experimental simplicity make them useful for a wide range of applications. This article reviews recent progress in the field of soft lithography, with a focus on trends in research and steps toward commercialization.

The spectacularly successful fabrication techniques that have emerged from development efforts in microelectronics – photolithography, electron-beam lithography, etc. – are extremely well suited to the tasks for which they were principally designed: forming structures of radiation-sensitive materials (e.g. photoresists or electron-beam resists) on ultraflat glass or semiconductor surfaces. Significant challenges exist, however, in adapting these lithographic methods for emerging applications and areas of research that require unusual systems and materials (e.g. those in biotechnology, plastic electronics, etc.); structures with nanometer dimensions (i.e. below 50-100 nm); large patterned areas (i.e. larger than a few square centimeters); or nonplanar (i.e. rough or curved) surfaces. These established techniques also involve high capital and operational costs. As a result, some of the oldest and conceptually simplest forms of lithography – embossing, molding, stamping, writing, etc. – are now being re-examined for their potential to serve as the basis for nanofabrication techniques that avoid these limitations¹. Considerable progress has been made in the last few years, mainly by combining these approaches or variants of them with new materials, chemistries, and processing techniques.

Some of the most exciting work in this field falls into an area known as 'soft lithography', named for its use of soft,

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elastomeric elements in pattern formation^{2,3}. The earliest soft-lithographic method represents a form of contact printing that uses a high-resolution elastomeric stamp with a chemical ink capable of forming a self-assembled monolayer (SAM) on a target substrate⁴. This monolayer can guide material deposition on or removal from the substrate to yield patterns of other materials. Interest in this technique is derived from its ability to form structures with dimensions deep into the submicron regime using ordinary chemical laboratory apparatus without expensive facilities. The invention of the microcontact printing (μ CP) method launched a body of related work, led initially by the inventors of μ CP (the Whitesides group at Harvard University), that explores the use of these elastomeric elements not only as stamps for printing, but also as soft molds for imprinting^{5,6} and conformable phase masks for a type of near-field photolithography^{7,8}. These techniques have achieved widespread use in academic and industrial laboratories around the world for applications in fields ranging from photonics and biotechnology to microfluidics and electronics. The sophistication and performance of soft-lithographic patterning methods is advancing very rapidly. This paper highlights recent research trends in soft lithography, with some emphasis on our own work. It also provides a brief account of efforts to innovate and move certain of these techniques out of the laboratory and into commercial manufacturing settings.

Fabricating stamps, molds, and conformable photomasks

The soft lithography process can be separated into two parts: fabrication of the elastomeric elements and use of these elements to pattern features in geometries defined by the element's relief structure. These two processes are typically quite different, although it is possible in some cases to use patterns generated by a stamp to produce a replica of that stamp. The structure from which the stamp is derived is known as the 'master'. It can be fabricated by any technique that is capable of producing well-defined structures of relief on a surface. Many elastomeric elements can be generated from a single master, and each such element can be used many times in patterning. Often, an established lithographic technique, such as one of those developed for the microelectronics industry, defines the master. Fig. 1a schematically illustrates the steps. Here, photolithography

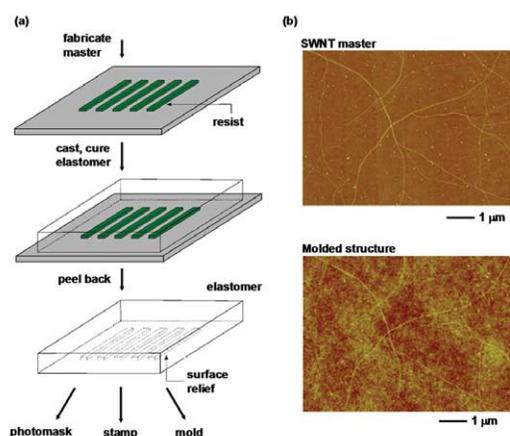


Fig. 1 (a) Schematic illustration of the procedure for building PDMS elements for soft lithography. (b) AFMs of a 'master' that consists of a submonolayer of SWNTs with 0.5–5 nm diameters on a SiO₂/Si substrate (top frame) and a molded structure in poly(urethane) formed by soft imprint lithography using a PDMS element generated from the SWNT master (bottom frame). The results demonstrate the successful operation of soft lithography at the single nanometer scale.

patterns a thin layer of photoresist on a Si wafer. Elastomeric elements are generated by casting a light- or heat-curable prepolymer against this master. The elastomer poly(dimethylsiloxane) or PDMS (Sylgard 184, Dow Corning) is commonly used for this purpose. With optimized materials and chemistries, this fabrication sequence has remarkably high fidelity. In fact, recent work shows that relief with nanometer depths⁹, and both nanometer depths and widths¹⁰, can be reproduced accurately. Fig. 1b shows atomic force micrographs (AFMs) of part of a master that consists of single-walled carbon nanotubes (SWNTs) on an SiO₂/Si wafer, and of a relief structure formed by soft imprint lithography using a PDMS mold generated with this master. At these length scales (tube diameters of 0.5–5 nm), the molecular structure of the polymers, their conformation, and the degree of crosslinking can play significant roles. This question of ultimate resolution in soft lithography (and in conventional imprint lithography), as well as its dependence on polymer chemistry and physics at these extreme nanoscale dimensions, are topics of basic interest.

Solid object printing

Although μ CP is extremely useful for a wide range of applications, its resolution encounters practical limits at around 100–200 nm, mainly because of the combined effects of: (i) surface diffusion of molecular inks; (ii) disorder at the edges of the printed SAMs; and (iii) the isotropic nature of many of the etching and deposition methods used to convert

the patterned SAMs into patterns of functional materials. Recent research in soft lithography has sought to avoid these effects and expand the range of materials that can be patterned by substituting for the molecular inks those that exist as solid, rigid structures at room temperature. One such technique uses specially tailored surface chemistries as interfacial 'glues' and 'release' layers to control the transfer of solid inks from relief features on a stamp to a substrate^{11,12}. The method involves four components: (i) a stamp with relief features in the geometry of the desired pattern; (ii) a method for depositing a thin layer of solid material onto this stamp; (iii) a means for bringing the stamp into intimate physical contact with a substrate; and (iv) surface chemistries that prevent substantial adhesion of the deposited material to the stamp and promote its strong adhesion to the substrate. There are many recently reported embodiments of this new form of soft lithography. In one exemplary case, a pattern of thin Au is printed from the surface of a stamp onto a substrate that supports a SAM with exposed thiol groups^{11,13}. Covalent bonds between the SAM and Au form upon contact of stamp to substrate; removing the stamp causes failure at the Au/stamp interface (Au does not adhere strongly to PDMS) and transfer to the substrate, to which the Au bonds well. Stated another way, this transfer printing process defines patterns of thin Au on uniform SAMs. μ CP, by comparison, defines patterns of SAMs on uniform Au films. The approach, which we refer to as nanotransfer printing (nTP), is purely additive (i.e. material is only deposited in locations where it is needed) and it can generate complex patterns of single or multiple layers of materials with nanometer resolution over large areas in a single process step. Decal transfer lithography (DTL) is a related technique that uses PDMS itself as the ink material^{14,15}. Methods related to DTL and nTP have been developed independently by groups at IBM¹⁶, Princeton¹⁷, Massachusetts Institute of Technology¹⁸, and other places.

Fig. 2 shows a set of representative structures formed by nTP and DTL. Figs. 2a and b show optical micrographs of patterns of Cu and Au thin films printed onto substrates coated with thiol-terminated SAMs^{11,19}. Figs. 2c and d show a low-resolution optical image and a high-resolution scanning electron micrograph (SEM) of arrays of Au dots, where the transfer is guided simply by differential noncovalent surface forces associated with the low and high energy surfaces of the PDMS stamps and glass substrates, respectively²⁰. Figs. 2e

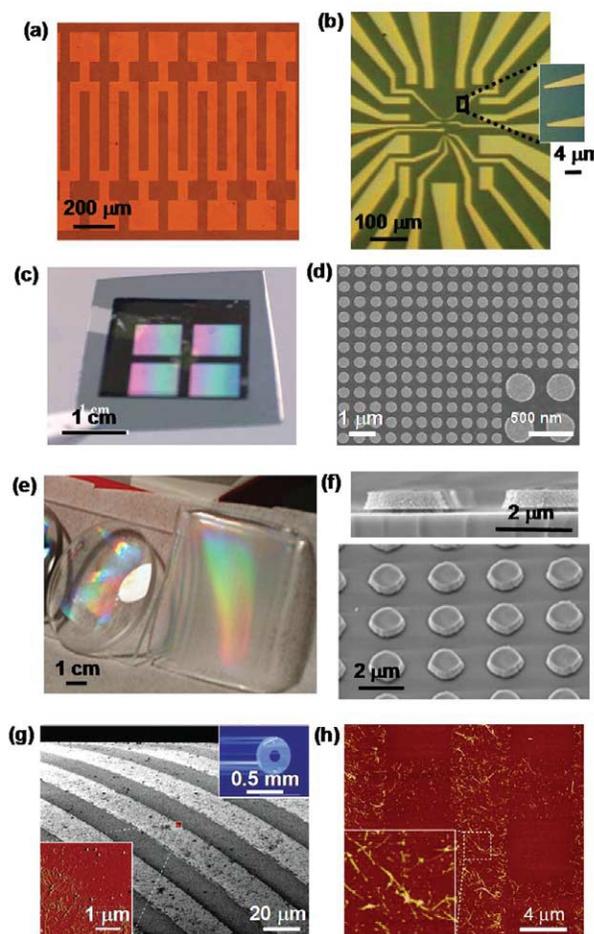


Fig. 2 Optical images, SEMs, and AFMs of patterns of metals (a-d), dielectrics (e,f), and SWNTs (g,h) formed by soft-lithographic transfer printing with solid inks of these materials. (Part (a) reprinted with permission from¹⁹. © 2004 American Institute of Physics. Part (b) reprinted with permission from¹¹. © 2002 American Chemical Society. Parts (g,h) reprinted with permission from²¹. © 2004 American Chemical Society.)

and f show optical images and SEMs of PDMS structures transferred to glass substrates coated with amorphous Si thin films, and the structure of pixel elements obtained subsequently by etching¹⁵. The chemistry of the solid ink transfer in this case involves surface bonding resulting from the reaction of hydroxyl groups on the PDMS and the glass/Si surfaces. Figs. 2g and h show a slightly different capability²¹. Here, the inks are submonolayer collections of individual SWNTs deposited onto the surface of a stamp using a controlled flocculation process²¹. As in the case of Figs. 2c and d, the transfer occurs as a result of differences in the surface energies of the stamps and substrates. Fig. 2g shows the ability to print patterns of SWNTs onto a curved microcapillary tube. Fig. 2h presents AFMs of patterns formed by printing twice using a stamp with lines and spaces.

The structures in Fig. 2 are primarily two-dimensional in nature. They result from the transfer of solid inks from the raised regions of relief on the stamps to the substrates. Inks in the recessed regions do not transfer because they do not contact the substrate during printing and are not connected to the inks on the raised regions. If sufficient metal is deposited onto the stamps, particularly when the flux of metal is not collimated or oriented perpendicular to the stamp surface, then it is possible to form solid ink coatings that have substantial three-dimensional structure^{16,22-24}. Figs. 3a and b show arrays of Au nanocapsules formed by a continuous coating on a stamp that has arrays of circular wells²⁴. In this case, Au-Au cold welds²⁵ form by contact of the Au coating on the stamp with a similar coating on the substrate and drive the transfer. Figs. 3c and d show Au 'L-shaped' nanostructures formed by printing with a stamp that has arrays of raised lines and is coated with an angled deposition of Au²⁴. In this case, a thiol-terminated monolayer on a GaAs substrate guides the transfer¹³. The mechanical integrity of these structures and the ability to pattern them without substantial formation of nanocracks depends

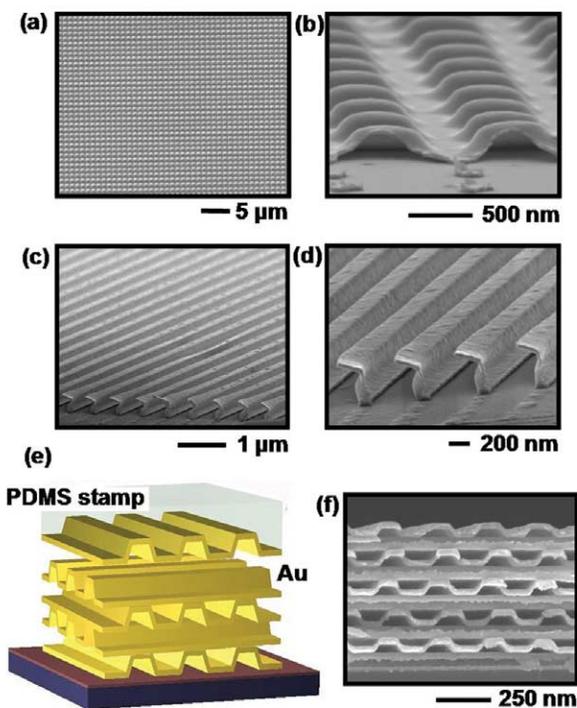


Fig. 3 SEMs of three-dimensional Au nanostructures formed by nTP of single layers (a-d) and multilayer stacks (e,f). (Parts (a-d) reprinted with permission from²⁴, © 2004 American Chemical Society. Parts (e,f) reprinted with permission from²², © 2003 American Chemical Society.)

critically on carefully controlled deposition and processing conditions²⁴. Multiple printing steps using such coatings can generate complex three-dimensional nanostructures, such as the one illustrated schematically and in an SEM in Figs. 3e and f. Here, an SAM chemistry bonds the first array of Au nanochannels to the substrate (GaAs in this case); subsequent layers bond to one another by Au-Au cold welding²².

In addition to the examples in Figs. 2 and 3, in which metal, dielectric, and polymer coatings as well as SWNTs are applied directly to the stamp by vapor or liquid phase deposition, a stamp can be inked by contacting it with a substrate that supports the solid ink material. With this approach, it is possible, for example, to print patterns of semiconductor micro/nanowires generated by applying 'top down' lithography (i.e. patterning of resists and etching) to bulk single-crystal wafers^{26,27}. Fig. 4a schematically illustrates the process²⁶⁻²⁹. In this case, anisotropic wet etching of a substrate generates arrays of wires on the surface of the wafer. We refer to a collection of semiconductor micro/nanostructures generated in this manner as a microstructured semiconductor (μ s-Sc), which can be printed onto unusual device substrates such as plastic or paper to build high-performance transistors and other electronic and photonic components. Before the wires completely detach from the substrate, the substrate can be removed from the etching bath and placed into contact with a stamp. Suitable surface chemistries bind the wires to the stamp such that they detach from the substrate when the stamp is peeled away²⁷. Contacting the wire-coated stamp against a target substrate can lead to their transfer from the stamp, provided that the adhesion to the substrate is sufficiently strong. Fig. 4b shows an SEM of rods of single-crystal InP (μ s-InP) on the surface of a stamp after they are lifted off from a bulk wafer^{27,29}. Here, the stamp binding chemistry uses reactions between -OH groups on the PDMS stamp and those on a thin layer of SiO₂ on the surface of the μ s-InP. Placing this stamp into contact with a photocurable poly(urethane) (NOA 72) cast as a thin liquid film on a poly(ethylene terephthalate) substrate and then curing the polymer binds the wires to the plastic substrate. Removing the stamp leaves the wires embedded in plastic, with their top surfaces exposed and aligned with the surface of the substrate. The right frame of Fig. 4b shows an SEM of these printed μ s-InP rods^{27,29}. These transfer-printing procedures work with other semiconductor micro/nanowires. It is also

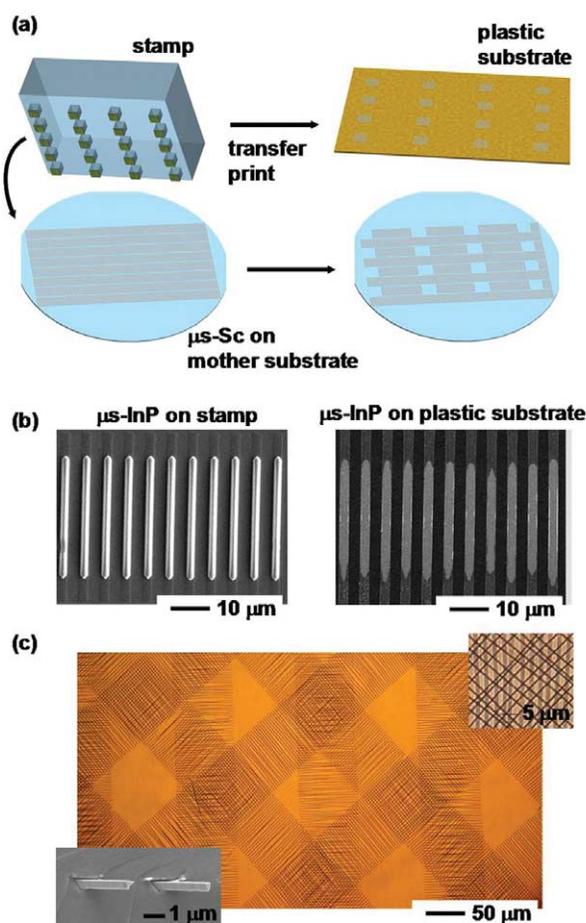


Fig. 4(a) Schematic illustration of the process for using a PDMS stamp to pick up semiconductor micro/nanowire arrays ($\mu\text{s-Sc}$) from a bulk wafer and transfer these wires to a plastic substrate. (b) SEMs of InP rods ($\mu\text{s-InP}$) on a PDMS stamp (left) and transfer printed onto a plastic substrate (right). (c) Top-view optical micrograph of a trilayer stack of transfer-printed arrays of GaAs nanowires on a plastic substrate. Upper and lower insets show an optical micrograph and an SEM, respectively, of this structure. (Parts (b,c) reprinted with permission from²⁷. © 2004 American Chemical Society.)

possible to perform the printing multiple times in order to build up multilayer structures of $\mu\text{s-Sc}$. Fig. 4c shows, as an example, a three-layer stack of transfer-printed arrays of $\mu\text{s-GaAs}$ nanowires with different orientations in each level²⁷. The optical micrograph at the top right and the SEM at the bottom left provide different views of this structure. The same photocurable poly(urethane) that is used for the transfer electrically isolates the different levels of wires.

Three-dimensional nanofabrication using a conformable photomask

Printing onto curved substrates (Figs. 2g and 2h), printing structured solid films (Figs. 3a-d), and multilayer printing (Figs. 3e, 3f, and 4c), represent routes to three-dimensional nanostructures that could be useful for applications in diverse

areas of technology including optics, chemical separations and sensing, and thermal management. There remains, all the same, a need for general three-dimensional nanofabrication approaches that are more far reaching and adaptable. The difficulty of performing three-dimensional nanofabrication with conventional techniques and the many possible uses of such nanostructures in photonics, data storage, catalysis, microfluidics, and other areas, are creating interest in patterning techniques that offer three-dimensional capabilities. One recently developed soft-lithographic method uses PDMS elements, not as stamps or molds, but as optical components for patterning structures in photosensitive materials^{23,30}. Fig. 5a schematically illustrates the process. The PDMS optical element, which functions as a phase mask, forms a perfect, conformal contact with a photopolymer film. General surface forces (i.e. van der Waals type interactions) drive this contact; externally applied pressure is not required. These same forces drive contact in the printing procedures described in the previous sections. Here, this passive process yields optical alignment of the mask to the polymer with nanometer precision in the normal direction. Ultraviolet (UV) light passing through this element, which has features of relief comparable in dimension to the wavelength, generates a three-dimensional intensity distribution that exposes a photopolymer film throughout its thickness. Developing away the parts of the polymer that are not crosslinked by the UV light yields a three-dimensional nanostructure in the geometry of the intensity distribution with feature sizes as

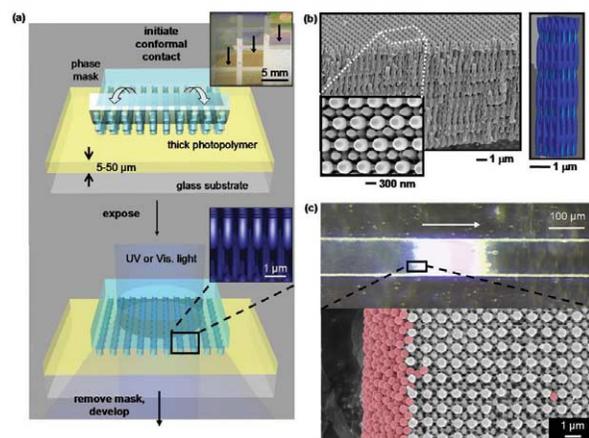


Fig. 5 (a) Schematic illustration of the use of a PDMS phase mask for three-dimensional nanofabrication of structures in a photosensitive polymer. (b) A typical structure and optical modeling of the intensity distribution that defined it. (c) Use of this type of structure as a filtering element in a microfluidic channel. (Part (b) reprinted with permission from²³. © 2004 Wiley-VCH. Part (c) reprinted with permission from³⁰. © 2004 National Academy of Sciences, USA.)

small as 50 nm. Because exposure of the polymer occurs in the proximity field region of the mask, we refer to the technique as proximity field nanopatterning (PnP)^{23,30}. The proximity geometry places requirements on the spatial and temporal coherence of the light source that can be easily met even with low-cost setups (e.g. a handheld lamp with an interference filter is sufficient). Only the spot size of the light source and the size of the phase mask limit the size of the patterned areas. Nanostructures with thicknesses up to 100 μm can be achieved; only the structural integrity and optical absorption of the photopolymer limit this thickness. This method appears to hold exceptional promise as a general platform technology for large-area, three-dimensional nanopatterning – a capacity that conventional photolithography currently lacks.

Fig. 5b shows an SEM of a typical three-dimensional structure formed with this PnP technique. Rigorous coupled-wave analysis can model accurately the optics associated with this method³⁰. Simulations that quantitatively describe some of the fabricated structures appear in Figs. 5a and b. A wide range of periodic and aperiodic structures can be generated by adjusting the geometry of the mask, which can be defined according to the procedures of Fig. 1. There are many potential applications for this technique. Fig. 5c shows a simple example in microfluidics. Here, PnP forms a three-dimensional polymer nanostructure integrated directly into a microfluidic channel for filtration, separation, and mixing purposes. The colorized SEM shows the separation of a suspension of 500 nm poly(styrene) beads (red) from a flow that moves from left to right.

Commercialization efforts

The preceding discussion focuses on research in new soft-lithographic techniques. These and other methods have already demonstrated value for laboratory and research purposes. Nevertheless, although μCP was first described ten years ago, the path to commercialization of soft lithography for high-volume manufacturing remains challenging. One of the most significant difficulties during the first five to seven years was to define sets of applications that can be profitably addressed by soft-lithographic capabilities. Three areas appear to be promising: systems for microfluidics, large-area electronics, and drug discovery. (While photonics appears to constitute another promising field of use, recent and dramatic changes in this area of business have slowed

progress in developing commercially relevant applications.) Several large and small companies are actively developing soft-lithographic manufacturing systems for these applications. Fluidigm is a well-known example in microfluidics. Here, PDMS elements are not used as patterning tools, but rather as integral components of the final devices. In the area of drug discovery, Surface Logix is notable. This company uses PDMS membrane masks to pattern and control the responses of cell-based assays, providing a method for high-throughput predictive screening of new drug candidates. Collectively, most activity exists in the area of large-area electronics, where IBM, Philips, and Lucent (most recently through collaborations with DuPont) have achieved impressive milestones in the development of μCP for defining circuit metallization. The attractive features of μCP for this application are: (i) high resolution; (ii) compatibility with useful materials for these systems (which include organic electronics); (iii) potential for low cost; and (iv) the ability to pattern large areas in a single processing step. The main challenge in commercializing μCP for large-area electronics involves reliably achieving registration of printed patterns to existing features on a substrate. The solution to this problem combines optimized methods for manipulating the stamp during printing, and stamp designs that maximize in-plane rigidity (to minimize distortions) while maintaining mechanical bendability to facilitate printing. The latter goal can be achieved with composite stamps that incorporate thin layers of PDMS against backing layers of some high-modulus material (glass, plastic, etc.)^{24,31,32}. The Philips group has an ingenious method for using a stamp of this type with an array of sequentially activated air actuators to control contact with a substrate. This system, which they refer to as a wave printer, enables total registration errors of less than 2 μm across an entire 6" wafer. Fig. 6a shows a schematic illustration and picture of this printer³³. The IBM group uses a thin composite stamp that is gradually unbent as it is brought into contact with a substrate, as shown in Fig. 6b. They have implemented this approach with optimized SAM inks and etchants for patterning large-area thin film transistor backplane circuits (Fig. 6c) for liquid crystal displays³⁴. The Lucent group has demonstrated similar composite stamps for patterning 6" x 6" organic electronic backplane circuits for flexible electronic paper displays^{35,36}. They (now the University of Illinois at Urbana-Champaign) currently work with DuPont to

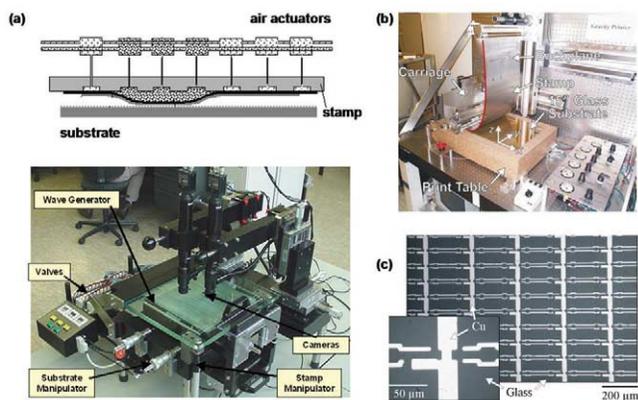


Fig. 6(a) The Philips wave printer μ CP system (top: schematic illustration; bottom: image of the printer). (b) The IBM printing system designed for fabricating 15" active matrix backplane circuits for displays. (c) A typical pattern formed with the IBM printer.

integrate similar stamps into flexographic printers for volume manufacturing of these devices³⁷.

Conclusions and outlook

The field of soft lithography has expanded rapidly over the last ten years, beginning with the pioneering work of a single laboratory and growing into an enterprise that involves the efforts of dozens of independent groups in academia and industry. The practical utility of these methods and the rich range of phenomena in materials science, chemistry, and

physics that governs their operation are likely to continue to fuel interest in this area for years to come. This article briefly describes some recent topics of research in soft lithography, including fundamental limits in resolution, transfer printing of solid inks and objects, and three-dimensional nanofabrication with conformable phase masks. Many other interesting results continue, of course, to emerge from different laboratories around the world. Collectively, these efforts have considerable value for a wide variety of research applications. Recent work indicates promise for the successful transfer of some of the most well-developed methods out of the laboratory and into manufacturing settings for important applications that cannot be addressed effectively with other lithographic methods. Taken together, these developments, the growing importance of these techniques for research in nanoscience and technology, and the interesting science that continues to emerge from research in soft lithography suggest an exciting future for this field. **MT**

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