The future of electronics manufacturing is revealed in the fine print

Ralph G. Nuzzo*

Department of Chemistry, University of Illinois, Urbana, IL 61801

Microelectronic devices are among the most complex structures produced by modern manufacturing technology. A state-of-the-art microprocessor in a personal computer, for example, contains as many as 30 million transistors interconnected by more than one billion discrete electrical junctions (1). To achieve this level of integration, the sizes that define the device components must be small, smaller by several orders of magnitude, for example, than the size of a typical cell found in the human body. The demand for greater performance and capacity in these systems, as famously characterized by Moore's Law (2), has seen the number of individual transistors on a chip increase by a factor of 2 approximately every 18 months. These development cycles ultimately predict that, in 10 years, the advances made in design and processing methodologies will yield architectures for the most sophisticated integrated circuits that contain more than one billion transistors operating at speeds that are at least a factor of 10 faster than the most capable chips available today (International Technology Roadmap for Semiconductors Update, http://public.itrs.net/reports.htm). These devices will possess functionalities that certainly would have been unimaginable in 1947 from the vantage point provided by the characteristics of the original point contact transistor of Brattain, Bardeen, and Shockley.

The manufacturing methods used to fabricate these devices are highly sophisticated and rely heavily on a key processing technique called photolithographic patterning (3). This methodology has come to dominate the technologies of microfabrication in much the same way as silicon has the materials used to construct semiconductor devices. Given the dominant positions of photolithography and silicon in this area of technology, it would be extremely difficult to bring forward advances in research that might serve to challenge their standing as defining paradigms. It would be altogether remarkable that both of these central dogmas might be challenged in this way. This issue of PNAS presents a report by Rogers *et al.* (4) that does precisely that. Those authors describe the application and validation of soft lithography (5) as a revolutionary new method for manufacturing complex, highly functional microelectronic structures, here a working prototype of a flexible display—an electronic sheet of paper—that incorporates pixel elements controlled by organic transistors (6).

Photolithography uses light to generate patterns in a photosensitive polymer, a so-called resist (7). These resist patterns are used in turn as templates for forming structures in a material, typically by such etching methods as reactive ion beam or wet chemical etching (8). Because the device structures in Si-based microelectronics are complex multilevel architectures, many applications of photolithographic patterning are needed to generate systems with any useful level of functionality. In this processing, the complex, hierarchical organizations found in an integrated circuit are generated on a layer-by-layer basis by using multiple deposition and etching steps mediated by photolithography-defined resist patterns (9). Because it is an optical technique, this type of patterning, although powerful, remains limited in some important ways. Ideally it is a planar patterning method and is poorly suited for making either three-dimensional structures or devices supported on a nonplanar substrate. It is a cumbersome process for making structures bearing specific chemical functionality. On large area substrates, many stepped exposures are needed to generate a complete pattern, which in turn generates a requirement for costly, high-precision processing tools. The short wavelengths needed to generate feature sizes in the 0.12-μM range also brings with it the need for process tools that are extremely expensive.

In seminal work recently recognized by the Nobel Prize in Chemistry, MacDiarmid, Heeger, and Shirakawa taught us that organic materials in fact could perform active functions.

Soft lithography (5) refers to a complementary set of patterning tools for fabricating small structures in thin-film materials that lift many of these constraints. Most of these methods share the property that they enable the construction of high-quality microstructures in a broad range of materials without the use of photochemical processes. Rogers and his coworkers (4) use a specific soft lithography patterning method called microcontact printing (μCP) (10) to construct the array of thin film transistors that serve as the switching elements of their display. In concept, the nature of the μCP process is a familiar one. Anyone who has used an inked stamp to print an address on an envelope or mark a date on their correspondence has performed a similar pattern transfer step. In μCP, however, the feature sizes on the elastomeric stamp used as the patterning tool are much smaller and the inks used vastly more specialized. The stamp used in μCP is prepared by casting and curing a soft elastomeric polymer (e.g., polydimetylsiloxane) against a master that carries in its relief structure the pattern one wants to transfer. This master can be made by a variety of techniques, including direct-write photolithographic patterning. The stamp can be reused many times as a pattern transfer tool, though, and in this way generates great potential for improving both the throughput and cost performance of the patterning process. To carry out the printing process, the stamp is inked with a compound that, when transferred to the substrate surface, will form a layer that can serve as an effective resist for subsequent patterning. In this report, the ink used consists of a molecule that binds very strongly to the substrate surface in the form of a self-assembled monolayer (SAM) (11). The latent image defined by the patterned SAM is sufficient to

---

See companion article on page 4835.

*E-mail: r-nuzzo@uiuc.edu.

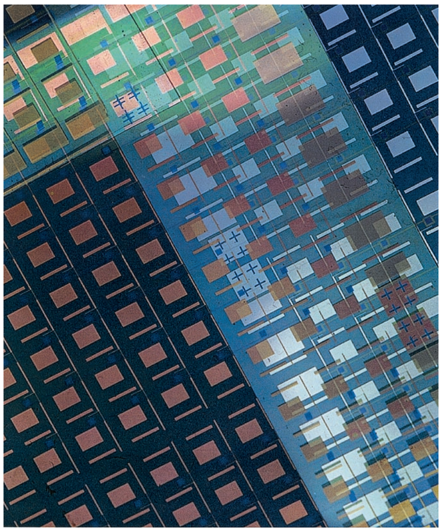

Fig. 1. Plastic display backplane circuits microfabricated using soft lithographic patterning methods (courtesy of F. Frankel, Massachusetts Institute of Technology, Cambridge).

direct the subsequent patterning of a thin film material by an etching step. Rogers *et al.* (4) use a SAM formed by an n-alkane thiol, $CH_3(CH_2)_nSH$, to direct the patterning of Au by wet etching (12); the metal microstructures obtained in this way form the electrodes and conduction paths needed to construct the organic thin film transistor arrays of the display. Fig. 1 shows an example of an integrated structure related to the subject of the PNAS report (4) that was fabricated in this way. The quality of the microstructures generated by the combined use of μCP and wet etching is exceptionally good. Of particular interest in the report of Rogers *et al.* (4) is the demonstration that soft lithographic patterning yields transistors with electrical properties that match those of similar devices fabricated with traditional processing methods.

A critical aspect of this work is the use made of a SAM as an etch resist. There are many molecular systems known that form SAMs on different substrate surfaces (13). These materials form via the spontaneous organization of molecules on a surface, a process that is thermodynamically driven and leads to thin organic films with extremely low densities of structural defects. Because they are only one molecule thick, SAMs are much thinner than the polymeric resists typically used in photolithographic patterning. The molecular ink used by Rogers *et al.* (4) produces a densely packed assembly of adsorbate molecules bonded to the Au surface in the form of a thiolate species (11). The surface chemistry involved in the formation of this SAM is shown in Fig. 2 along with an illustration of the surface properties that can be produced with them.

Alkanethiol SAMs on Au are among the most widely studied of these systems and provide one of the best-understood instances of spontaneous molecular organization known outside of the examples found in biology. These SAMs allow the physical properties of the surface to be varied by direct molecular design and are now widely used in studies of complex systems—microlithography, tribology (14), adhesion (15), biomaterials science (16), cell biology (17)—and as components of devices in molecular electronics (18), bioanalytical systems (19), and sensors (20). Fig. 2 shows a now classic application of a SAM, namely its use as a methodology for engineering the wetting properties of an interface at the molecular level (21): substitutions of the chain end functional groups (in this case by either carboxylic acid or methyl groups) allow the wetting properties of the gold surface to be patterned with hydrophilic and hydrophobic regions. As demonstrated by Whitesides and his coworkers (5), and reinforced by Rogers *et al.* (4), the dimensions of the patterning can be extended by soft lithography methods such as μCP to generate feature sizes that are both small and of extremely high quality. These latter capabilities are generating many new applications for microfabricated structures in broad areas of scientific research that traditionally have not enjoyed access to the high-cost capital equipment resources used for manufacturing microelectronic devices. Perhaps the most significant aspect of the report of Rogers *et al.* is that this patterning can be carried out with multiple levels of registration to construct the complex integrated architecture of a working flexible display. This is a central requirement for any patterning method to be useful in a commercially relevant way.

The second remarkable aspect of the report by Rogers *et al.* (4) is their use of an organic semiconductor (pentacene) as the active material in the construction of the display's thin-film transistor array. It was not so long ago that an organic material would be found only as a passive component in a device—for example, as the insulation on a wire. In seminal work recently recognized by the Nobel Prize in chemistry, MacDiarmid, Heeger, and Shirakawa taught us that organic materials in fact could perform active functions, notably serving as metallic conductors (22). Much of the recent interest in the area of molecular electronics, though, has been driven largely by an interest in organic semiconductors, materials that have demonstrated commercially useful performances in light-emitting diodes (23). The success of this application has engendered great interest in other device applications for these materials. Rogers *et al.* (4) report on the fabrication of devices (transistors) that find an inspiration in the venerable history of Bell Laboratories. The organic transistor (6) array that forms the heart of the display backplane establishes a major benchmark for the field. The display itself is a prototype but the metrics it demonstrates are instructive. The display incorporates 256 pixels, each with its own

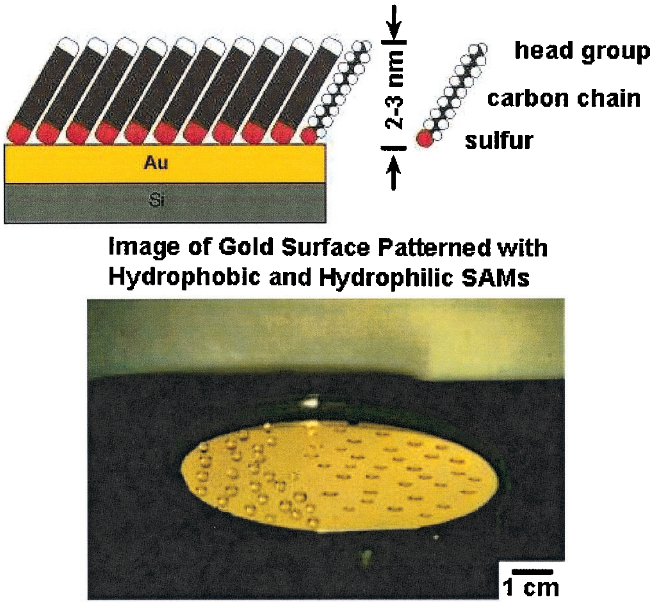

Fig. 2. A schematic depiction of the structure of a SAM formed by the adsorption of an n-alkane thiol on a gold surface (*Upper*). The physical properties of the surface can be controlled by substituting functional groups at the chain ends of the thiol adsorbate. In the example shown, the wafer presents carboxylic acid and methyl groups in the hydrophilic and hydrophobic regions, respectively (courtesy of G. Whitesides, Harvard University, Cambridge, MA).

switching transistor. The techniques developed in this work, though, provide a clear demonstration that the pixel sizes and numbers can be scaled easily to levels that would be suitable for a commercial product.

In closing, it seems appropriate to give consideration to what some might conclude are shortcomings of the designs described by Rogers *et al*. (4). The performances of the transistors in this demonstration certainly do not approach those of the most advanced silicon devices. The design rules and registration achieved by soft lithographic patterning in the construction of this prototype display, although impressive, still fall short of the benchmarks provided by the photolithographic processes used in state-of-the-art microelectronics manufacturing. These latter products and processes are those associated with the highest profit and highest performance segments of what is currently an almost $1 trillion industry. The prototype reported here, though, corresponds to an altogether new type of product—one that via its portability and low cost has the potential to fundamentally change how people interact with electronic systems. Further, it is fabricated by a new set of process technologies that have many important contrasts with and potential benefits (especially in the area of cost) over the manufacturing methods used in the high end of the microelectronics market. When viewed in this way, soft lithographic patterning has all of the earmarks of being a disruptive technology (24). The history of such technologies is worth considering carefully. It was not all that long ago, after all, that Noyce (25) and Kilby (26) brought forward their own visions of a disruptive technology, the integrated circuit, and in so doing forever changed the nature of the electronics industry.

1. Hinton, G., Sager, D., Upton, M., Boggs, D., Carmean, D., Kyker, A. & Roussel, P. (2001) *Intell. Technol. J.* **Q1,** 1–10.
2. Moore, G. E. (1996) *Daedalus* **125,** 55–80.
3. Jeong, H. J., Markle, D. A., Owen, G., Pease, F., Grenville, A. & von Bünau, R. (1994) *Solid State Technol.* **37,** 39–47.
4. Rogers, J. A., Bao, Z., Baldwin, K., Dodabalpur, A., Crone, B., Amundson, K. & Ewing, J. (2001) *Proc. Natl. Acad. Sci. USA* **98,** 4835–4840.
5. Xia, Y. & Whitesides, G. M. (1998) *Angew. Chem. Int. Ed.* **37,** 551–575.
6. Katz, H. E. & Bao, Z. (2000) *J. Phys. Chem. B* **104,** 671–678.
7. Wallraff, G. M. & Hinsberg, W. D. (1999) *Chem. Rev.* **99,** 1801–1821.
8. Lang, W. (1996) *Mat. Sci. Eng. R* **17,** 1–55.
9. Madou, M. J. (1997) *Fundamentals of Microfabrication* (CRC, Boca Ranton, FL).
10. Kumar, A. & Whitesides, G. M. (1993) *Appl. Phys. Lett.* **63,** 2002–2004.
11. Dubois, L. H. & Nuzzo, R. G. (1992) *Annu. Rev. Phys. Chem.* **43,** 437–463.
12. Kim, E., Kumar, A. & Whitesides, G. M. (1995) *J. Electrochem. Soc.* **142,** 628–633.
13. Ulman, A. (1991) *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly* (Academic, Boston).
14. Granick, S. (1999) *Phys. Today* **52,** 26–31.
15. Chaudhury, M. K. (1997) *Curr. Opin. Colloid Interface Sci.* **2,** 65–69.
16. Mrksich, M. & Whitesides, G. M. (1996) *Annu. Rev. Biophys. Biomol. Struct.* **25,** 55–78.
17. Mrksich, M., Dike, L. E., Tien, J., Ingber, D. E. & Whitesides, G. M. (1997) *Exp. Cell Res.* **235,** 305–313.
18. Reinerth, W. A., Jones, L., Burgin, T. P., Zhou, C. W., Muller, C. J., Deshpande, M. R., Reed, M. A. & Tour, J. M. (1998) *Nanotechnology* **9,** 246–250.
19. Wink, T., Vanzuilen, S. J., Bult, A. & Vanbennekom, W. P. (1997) *Analyst* **122,** R43–R50.
20. Flink, S., van Veggel, F. C. J. M. & Reinhoudt, D. N. (2000) *Adv. Mater.* **12,** 1315–1328.
21. Laibinis, P. E., Whitesides, G. M., Allara, D. L., Tao, Y.-T., Parikh, A. N. & Nuzzo, R. G. (1991) *J. Am. Chem. Soc.* **113,** 7152–7167.
22. Inzelt, G., Pineri, M., Schultze, J. W. & Vorotyntsev, M. A. (2000) *Electrochem. Acta* **45,** 2403–2421.
23. Bernius, M. T., Inbasekaran, M., O'Brien, J. & Wu, W. S. (2000) *Adv. Mater.* **12,** 1737–1750.
24. Christensen, C., Craig, T. & Hart, S. (2001) *Foreign Affairs* **80,** 80–95.
25. Noyce, R. N. (1961) U.S. Patent 2,981,877.
26. Kilby, J. S. (1964) U.S. Patent 3,138,743.