An Age-Old Printing Process Goes Nano

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ABSTRACT Patterning of surfaces has evolved from ancient applications in printed text and art to a host of complex technological applications found today. The desire and ability to shrink patterns to molecular dimensions has enabled new powerful devices, and the need for improved patterning methods continues to be a major research thrust. Commonly referred to as lithographic processes, many advanced printing processes have no true relation to the original concept of lithography. A new paper in this issue of *ACS Nano* discusses a new form of printing that utilizes block copolymer assemblies as ink reservoirs for pattern transfer. The results show that truly nanometer-sized features can be reproduced accurately over large areas. The parallels to the original form of lithography are quite fascinating, and this new process, called "molecular transfer printing", may hold great promise as a new tool for nanoscale pattern replication.

Lithography was invented in 1796 by Bavarian author Alois Senefelder as a low-cost method of reproducing artwork. The word itself, "lithography", comes from the Greek—*lithos* "stone" + *grapho* "to write"—and as the name implies, it is a method for printing using a polished stone (lithographic limestone). As originally defined, it had nothing to do with photons, imprint, electron beams, or X-rays. The more liberal uses of the term came much later.

The invention and development of printing is arguably the most important technological innovation made by mankind. The earliest documented examples of printing date back to 220 BC and exploited the ease of pattern replication through the use of woodblocks (Figure 1). Early printing was used for both artwork on fabric as well as for recording information on fabrics and paper. Printing has steadily evolved and has allowed the accumulation of accurate historical records, streamlined the process of communication, and contributed to the development of commerce, science, art, law, religion, and culture. Key developments in printing technology have emerged continually over time and have included the printing press, movable type, stone lithography, and offset printing. In many ways, photographic processes can be considered another form of printing and image storage and retrieval. Until the 20th century, nearly all printing techniques were developed and optimized for the storage of records meant to be accessed by the human eye; therefore, resolution beyond what the naked eye could observe (~50 μm) was not a strong driving force.

The development of semiconductor technology in the 1950s and the invention of the planar integrated circuit have led to an explosion of interest in printing and patterning for technological, not visual, purposes. An early integrated circuit (IC) chip device is shown in Figure 2. Upon its invention, it was quickly realized that the interconnects, gates, channels, and other features could be patterned inexpensively by printing methods. Over time, through miniaturization of this patterning, the number of devices per wafer was increased and hence the cost per device plummeted (and consequently, profits soared). Eventually, new photographic printing processes, coined "photolithography", dominated due to the ease of shrinking pattern size through optics. These developments led to the explosive growth of the semiconductor industry. Continued miniaturization has allowed the industry to follow Moore's Law, and

> The semiconductor industry remains profitable due mainly to advances in miniaturization of printing the many device structures.

Figure 1. Yuan dynasty (1206−1368) woodblock edition of a zaju play entitled Zhuye Zhou. Image courtesy of Wikimedia Commons (http://en.wikipedia.org/wiki/File:Yuan_dynasty_woodblock.jpg).

See the accompanying Article by Ji *et al.* on p 599.

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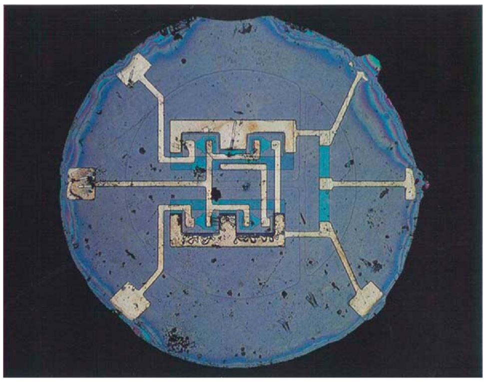

Figure 2. Early monolithic silicon integrated circuit chip. Invented by Robert Noyce, Fairchild Camera and Instrument Corp. Image courtesy of Fairchild Camera and Instrument Co.

to date, the industry remains profitable due mainly to advances in miniaturization of printing the many device structures.

Today, high-resolution patterning methods that enable the fabrication of functional devices have expanded from their initial applications in IC manufacture to a host of other technologically important areas such as displays, magnetic storage, photonic and optical devices, micromechanical systems (MEMS), sensor arrays, energy harvesting and storage, and a large number of biological applications. While most of these newer technological areas initially borrowed photolithographic patterning methods from the semiconductor industry, a number of powerful new patterning techniques have emerged over the years, some quite specific to niche applications. Additionally, conventional photolithographic processes are becoming quite expensive as the size requirements for critical device features continue to shrink. At the time of the writing of this Perspective, IC devices with critical features of 32 nm were going into production at advanced semiconductor fabrication facilities. Not only do these patterning processes become much more difficult as molecular dimensions are approached, but the cost of acquiring, operating, and maintaining these advanced lithographic tools has become prohibitively expensive, already forcing many established manufacturers to exit the business. Consequently, there are numerous research efforts underway to develop alternative high-resolution patterning techniques.

Today, there are several contact patterning methods that have made significant in-roads in advanced technological applications: relief, intalglio, lithography, screen, and electrophotography.[1] Researchers have also explored the direct transfer of molecules to substrates using scanning probe microscopes to place molecules on substrates with nanometer precision.[2] This “molecular printing”, more commonly called dip-pen nanolithography (DPN), has shown great promise, but its limitations in throughput have prevented wide-scale adoption in commercial fabrication processes. Embossing and molding methods have also shown great promise. Generally termed nanoimprint lithography (NIL), these processes physically emboss into a thermoplastic layer or mold into a film of a thermosetting or photo-cross-linkable resin.[3] NIL has demonstrated accurate replication of features as small as 5 nm over large areas, and in just a decade after its introduction, NIL is being adopted by commercial manufacturing enterprises.

So-called “soft-lithographic” patterning approaches have attracted a great deal of attention due to their simplicity, reliance on conformal soft image transfer materials such as polydimethylsiloxane (PDMS), and effectiveness in patterning large areas.[4−6] A number of variants of soft lithography have been developed to pattern metallic structures, most notable of which are nanotransfer (nTP)[7] and microcontact printing (μCP).[5,8,9] Both of these methods rely on thiols, limiting these techniques to the patterning of gold or other noble metals. Furthermore, the patterning of specific materials can be complicated by interaction of the material with the PDMS stamp. For example, copper has been shown to adsorb siloxane oligomers and aluminum, which requires careful application of a release monolayer and water adhesion layer.[10,11] In particular, μCP can suffer from limited fidelity and lateral resolution due to thiol mobility on the metal-coated substrate after transfer from the mold surface and is hampered by the need for caustic wet chemistry to etch through a masked metallic film, which contributes to loss of lateral resolution due to the isotropic etch profiles.[12−14] Also, while nTP can be accomplished without employing thiols, it still requires considerable pressure and heating of the substrate to obtain effective transfer[15] and the metal layer must be deposited carefully on the PDMS surface prior to each imprint, a time-consuming and costly factor.

In their article in this issue, Nealey and co-workers report a new method that addresses many of the above-mentioned considerations and offers a route to robust, high-throughput nanofabrication.[16] They utilized the bottom-up, self-assembly of block copolymers to create new print templates. Block copolymers are composed of two or more chemically dissimilar polymer chains that are covalently linked. Due to their low entropy of mixing, different homopolymers typically are immiscible and will phase separate macroscopically if simply blended together. On the other hand, block copolymers will not undergo this large-scale separation since the dissimilar components are physically linked. In many cases, the phase separation is limited to the dimensions of the copolymer chains (5−20 nm). This effect has been studied in detail in bulk and thin films. By controlling the volume fraction of the block copolymer components, the rigidity of the segments, the strength of interaction between the segments, and the molecular weight, one is able to obtain specific nanoscale-segregated morphologies predictably.[17] These morphologies range from spherical to cylindrical to bicontinuous gyroid to lamellar. A great deal of work has been reported on the use of block copolymers as a lithographic mask and in obtaining high-resolution patterns; this topic has been reviewed elsewhere.[18]

Nealey and co-workers describe a new process called "molecular transfer printing" (MTP), where the ordered block copolymer layer essentially serves as patterned molecular-scale ink reservoirs that will transfer their ink to suitable substrates upon contact. In many ways, this process is not much different than Senefelder's 200 year old stone lithography, where a smooth limestone surface is divided into (1) hydrophilic regions that accept a film or water and reject ink while damp, and (2) hydrophobic (water-repelling) regions which accept ink because the surface tension is higher on the greasier image area and remains dry because the water will part and runoff this area. When placed into contact with paper, the ink is transferred from the stone, resulting in pattern replication.

In fact, MTP is remarkably similar to the original lithographic technique; a phase-separated block copolymer surface acts as the stone where the two dissimilar regions are selectively wetted or inked by selected homopolymer "inks". As described in their paper, MTP starts with the self-assembly or directed assembly of a blend film of a block copolymer and inks on a substrate (Figure 3). During assembly, ink molecules are segregated into their respective block copolymer domains. A receiving substrate is then placed in contact with the surface of the assembled film. Upon thermal annealing, the ink molecules are transferred to and react with the receiving substrate, creating a dense covalently bound pattern of ink molecules that mirrors the domain structure of the block copolymer film at the interface. After MTP, the block copolymer and unreacted or excess ink molecules are dissolved in solvents to recover the original master surface and the patterned replica surface.

> In many ways, the molecular transfer printing process is not much different than Senefelder's 200 year old stone lithography.

The simplicity of the process makes it attractive, as is often noted for processes utilizing self-assembling systems. They utilize poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) and two homopolymer inks: hydroxyl-terminated polystyrene (PS−OH) and hydroxyl-terminated poly(methyl methacrylate) (PMMA−OH). These hydroxyl-terminated homopolymer inks were selected because they will both segregate fully into the appropriate PS or PMMA domains and will not swell the block copolymer domains. Whereas the old lithographic techniques were two-step processes, where the stone surface needs to be written to make the two chemically dissimilar regions, followed by wetting with water and ink, the MTP process is done all at once. A suitable substrate is coated with the block copolymer loaded with ink, and upon annealing, the ordering is achieved with the inks segregating automatically into their respective domains of the block copolymer. When placed into contact with an oxide-coated wafer and heated, the hydroxyl-terminated homopolymers become covalently attached to the receiving oxide layer, forming a dense, brush-like layer. Any excess homopolymer ink or block copolymer can be washed from the receiving layer. Excellent pattern fidelity was observed with sub-50 nm features being accurately replicated. When using chemically patterned wafers to dictate the ordering of the block copolymer layer,[19−21] the MTP process can be used to reproduce these arbitrary patterns. Large-area MTP looks

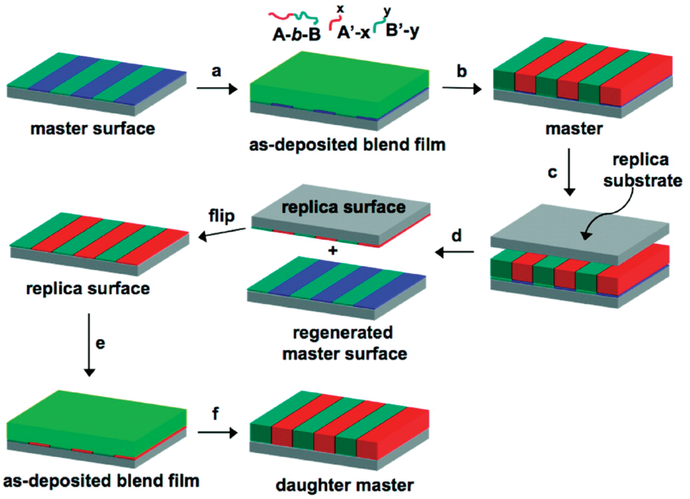

Figure 3. Schematic of the molecular transfer printing process. Reproduced from ref 16. Copyright 2010 American Chemical Society.

promising, and very good results were obtained using rather crude mechanical clamping.

To be sure, there are shortcomings and limitations to the new method. For one, the processing times at high temperature will need to be improved if the goal is to apply the process in a commercial manufacturing setting. The first block copolymer annealing step requires heating the samples to 190−250 °C for 24 h. The transfer step requires a 24 h annealing step at 160 °C. It is unlikely that many manufacturers will find 48 h of high-temperature processing attractive. Although the chemically patterned molds can be reused for additional MTP steps, each cycle requires performing all of the coating and annealing steps. The authors also acknowledge that the MTP process is limited in the geometries of the patterns that can be replicated. For some applications, like patterned magnetic media, this could be a true breakthrough processes; for others, like the complex structures required for complementary metal−oxide−semiconductor (CMOS) IC devices, it may have more limited applicability. Like many nanofabrication processes, MTP will likely find niche applications where it surpasses all other techniques, but it will not find universal application. This should not be considered a negative, but rather a challenge in identifying existing or new applications that can be enabled or improved by MTP. While electron-beam lithography, DPN, and other techniques may offer higher resolution, one must account for the cost of the process, materials, and equipment. MTP may be a good alternative when ultimate size reduction is not the primary goal.

Molecular transfer printing using block copolymers represents a clever advance in the field of nanopatterning. It takes a 200 year old concept and, through exploitation of polymer physics and dissimilar surfaces, enables the replication of nanostructures from a flat parallel surface. It is unlikely that Senefelder could have anticipated how his invention would revolutionize art and printing even 25 years after it was introduced, and it is fairly safe to say that he could not conceive that a multibillion dollar industry would be using a derivative of his simple invention 200 years later. This is no surprise since Antoine Lavoisier described the chemical term "element" only several years earlier in 1789; hence the concept of nanolithography would have no meaning for many generations. Similarly, will MTP grow and be refined? Only time will tell, but it shows great promise.

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