

# Polymer Self-Assembly as a Novel Extension to Optical Lithography

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Advances in the ability to define integrated circuit (IC) elements at ever-higher resolution have largely fueled more than 40 years of persistent performance improvements in semiconductor electronics. The engine of this unparalleled technological progress is a robust process called photolithography, wherein ultraviolet light affects chemical changes in a photosensitive polymer resist material to create a latent image (Figure 1a), a process similar in concept to print photography. Steady improvements in the photolithography process have resulted in scaling of minimum printed feature sizes from tens of micrometers during the 1980s to sub-50 nm transistor gate lengths in today's state-of-the-art ICs. The impressive history of semiconductor technology scaling is chronicled in detail in a document entitled the *International Technology Roadmap for Semiconductors* (ITRS).<sup>1</sup> As well, the ITRS Lithography Roadmap provides a forecast of resolution requirements for future IC generations, anticipating a daunting set of scientific and engineering challenges with no presently known solutions for patterning at sub-30 nm dimensions. Technological difficulties

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persist across nearly all aspects of the photolithography process, including development of suitable short-wavelength optical sources and lenses, synthesis of polymer imaging materials meeting resolution, sensitivity, and etch-resistance requirements, engineering of lithography masks, and manufacturing issues related to wafer throughput.

The complexities associated with continued dimensional scaling of the photolithography process for future IC generations have created opportunities for alternative patterning approaches, and one inviting prospect from the world of nanotechnology involves using *self-assembling materials* to define the features of IC elements. Self-assembly is an attractive concept because the underlying mechanisms in principle permit scaling to atomic-scale dimensions; however, any legitimate IC patterning option necessarily involves much more than high resolution. Other important factors include extreme demands for pattern uniformity, minimal pattern roughness, and low defectivity levels; a need for precise pattern alignment and registration; the ability to pattern a wide variety of shapes; rapid parallel processing across large wafer areas; and materials/process compatibility with the semiconductor manufacturing infrastructure. Because this long list of stringent requirements is well-met by photolithography (and really nothing else), the semiconductor industry will likely never abandon the process as its primary patterning approach but will rather increasingly seek symbiotic techniques for augmenting lithographic resolution capabilities. It is in this spirit of technological compatibility that polymer self-assembly has recently emerged as an unconventional approach for extending the photolithography process to finer patterning dimensions.

In their article in this issue, Prof. Paul Nealey and colleagues report exciting

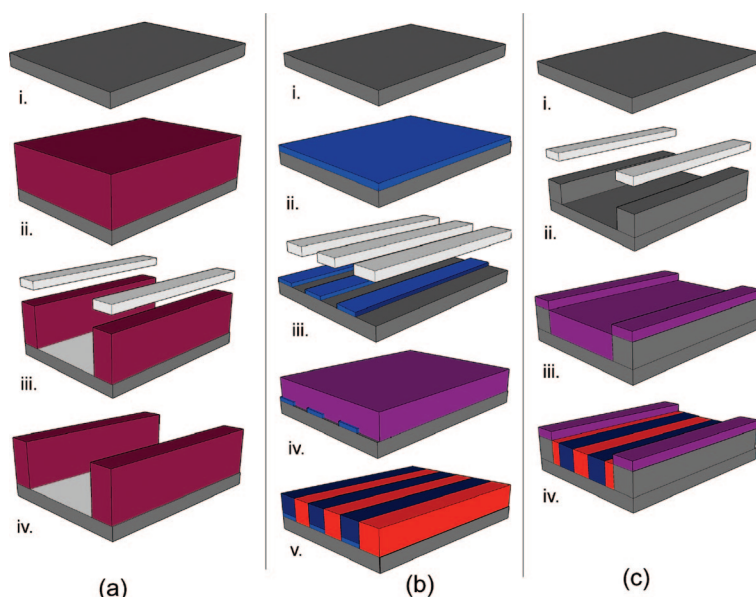
**ABSTRACT** The extreme technological complexity associated with continued dimensional scaling of the photolithographic patterning process to sub-50 nm dimensions has forced the semiconductor industry to seek increasingly innovative alternative approaches. One unconventional method under preliminary consideration involves using self-assembling block copolymer films as high-resolution patterning materials for defining integrated circuit (IC) elements. While these materials are attractive because of their ability to define nanometer-scale dimensions, their ultimate utility as a viable patterning method remains in question because of issues relating to pattern roughness and defectivity. In this issue, Prof. Paul Nealey and co-workers at the University of Wisconsin present compelling first demonstrations of experimental methods by which polymer self-assembly can generate the pattern elements essential for IC fabrication.

See the accompanying Article by Stoykovich *et al.* on p 168.

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**Figure 1.** Schematic process flows. (a) The photolithography process involves (ii) coating a substrate with photosensitive polymer and (iii,iv) creating a pattern by exposure to ultraviolet light through a mask and a chemical develop. (b) Self-assembly using chemical surface patterning involves (ii) coating a substrate with a chemical surface layer, (iii) creating a chemical pattern by exposure to ultraviolet light through a mask and a chemical develop, and (iv,v) self-assembly of a block copolymer film onto the chemical pattern. (c) Self-aligned self-assembly involves (ii) lithographic patterning of topographic surface pattern and (iii,iv) self-assembly of a block copolymer film onto the topographic pattern.

progress in demonstrating the ability of block copolymer thin films to serve as patterning materials for future IC generations.<sup>2</sup> These block copolymer materials form patterns *via* a thermally driven phase separation process wherein the two chemically distinct polymer blocks comprising each polymer molecule minimize their interaction volume. Geometric constraints imposed by the intrinsic material properties of polymer molecular weight and constituent block weight ratio determine both the morphology of the resulting self-assembled pattern and its dimensions, with typical feature sizes in the range of 10–30 nm—the size scale at which photolithography encounters serious challenges.<sup>3</sup> The block copolymer self-assembly process is similar to photolithography in that the latent image is formed in a polymer material; however, unlike photolithography, the image formation process is free from limitations imposed by optical diffraction effects. Since polymer self-assembly is driven by free energy minimization, the pro-

cess can only easily generate patterns of high symmetry, such as close-packed arrays and equal line/space patterns—a far cry from the complex patterns associated with state-of-the-art integrated circuits. Even so, these simple self-assembled patterns have been shown to be useful in nonlithographic aspects of IC fabrication,<sup>4</sup> including their incorporation into high-surface-area decoupling capacitors,<sup>5,6</sup> FLASH memories,<sup>7,8</sup> field-effect transistors (FETs),<sup>9</sup> and porous dielectric materials.<sup>10</sup> Materials integration of self-assembling polymers with the rest of the semiconductor electronics infrastructure has been an essential first step toward their adoption into IC manufacturing.<sup>4</sup>

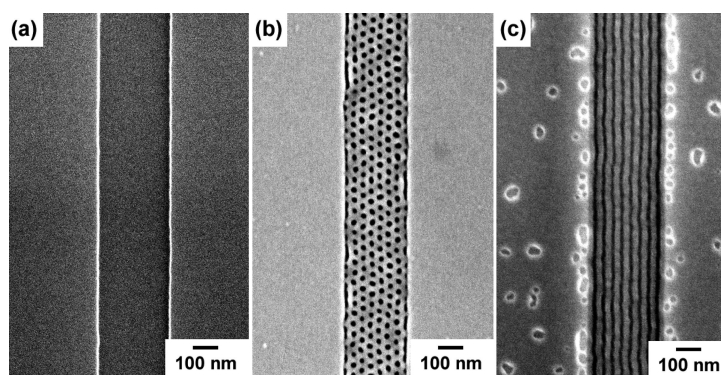
Prof. Nealey's group, working together with that of Prof. Juan de Pablo at the University of Wisconsin at Madison, has made a series of seminal research contributions in this field through their development of lithographic chemical surface patterning methods for directing block copolymer

self-assembly.<sup>11–14</sup> Their patterning scheme exploits the important quality of surface wetting and its impact on controlling self-assembled block copolymer pattern orientation.<sup>15,16</sup> They have previously shown that surface chemical patterns provide a strong driving force for polymer microphase separation and can thus impart degrees of uniformity, alignment, and low defect levels in self-assembled patterns that are unachievable on unpatterned surfaces. The approach combines high-resolution lithographic patterning of a chemical surface layer before subsequent self-assembly of the block copolymer material (Figure 1b). Skeptics of this technique point to the necessity of lithographic patterning at or near the dimension of the block copolymer material—meaning that the approach does not obviously provide *improved lithographic resolution*, but this criticism fails to acknowledge several important advantages. The foremost benefit, as shown in the results reported in Nealey's article,<sup>2</sup> is that chemical surface patterning allows design of complex geometries beyond simple high-symmetry patterns. As a practical matter, lithographic patterning of a chemical brush layer is much easier technologically, compared to patterning thicker photoresist materials, because of reduced depth-of-focus issues, meaning that state-of-the-art optical lithography tools may in fact be capable of printing dimensions in chemical surface layers that are not possible in conventional resists. Experimental data from Nealey's group have hinted at the potential for the block copolymer self-assembly process to smooth out roughness present in the patterned underlying chemical layer—an attractive prospect in microelectronics applications, where minimizing pattern roughness is paramount.

The experiments described in Nealey's article<sup>2</sup> provide experimental approaches to augmenting the limited range of achievable self-

assembled patterns that result from free-energy minimization. In demonstrating a wide variety of more complex self-assembled geometries enabled by chemical surface patterning and subtle changes to the block copolymer blend compositions, the authors take guidance from a prescribed set of essential IC pattern elements recently delineated by a group of semiconductor industry representatives working with the Semiconductor Research Corporation (SRC) in conjunction with the ITRS.<sup>17</sup> The catalog of essential shapes includes both long and short segmented lines, bends, junctions, hole arrays, and isolated features. In demonstrating these methods for enhancing the capabilities of the polymer self-assembly process, Nealey's group has provided a key step for those considering polymer self-assembly as a technique for extending optical lithography to higher resolutions.

Several groups, including our own, have been investigating a complementary approach for using block copolymer self-assembly to augment the optical lithography process. This technique operates on the principle that topographic features tend to nucleate block copolymer microphase separation, resulting in self-alignment of self-assembled patterns to predefined surface structures.<sup>18–22</sup> Under appropriate conditions, polymer films applied to surfaces with lithographically predefined topography will form self-assembled domains whose orientation is fixed along



**Figure 2.** Lithography subdivision by self-aligned polymer self-assembly. (a) Lithographically defined line patterns can be subdivided using self-assembly. (b) A 0.25  $\mu\text{m}$  wide lithographic line is subdivided by seven rows of a hexagonal hole array. (c) A 0.3  $\mu\text{m}$  wide line is subdivided into eight periods of a lines/space pattern.

the topographic pattern directions (Figure 1c). Two key benefits of this approach (sometimes referred to as “graphoepitaxy”) are that the lithographic features provide a means for self-registration of self-assembled polymer patterns to existing structures, and that the self-assembly process can subdivide larger prepatterned lithographic features into sublithographic units and thereby provides *resolution enhancement*. Unfortunately, the self-assembly process does not appear to heal roughness in the lithographic pattern, as is the case for patterned underlying chemical surfaces.

Our research has focused on self-aligned self-assembly of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer thin-film patterns of both hexagonal hole arrays and line/space patterns (Figure 2)—a thin-film material system originally

researched by Prof. T. P. Russell and Dr. C. J. Hawker in a collaboration between the University of Massachusetts at Amherst and the IBM Research Division.<sup>15,16</sup> Nealey's group has also worked primarily with PS-*b*-PMMA materials, although many other interesting block copolymers provide their own unique advantages.<sup>18,19,21,23</sup> We create surface topography by photolithographic patterning and reactive plasma etching of either silicon or silicon dioxide surfaces (Figure 2a). Polymer self-assembly onto such prepatterned surfaces results in subdivision of the lithographic patterns into defect-free hexagonally packed hole arrays or parallel line/space patterns, depending on the choice of block copolymer material. In Figure 2b, the lithographic pattern width is 0.25  $\mu\text{m}$ , with self-assembled hole diameters of 20 nm and pitch 40 nm, while in Figure 2c the lithographic pattern width is 0.3  $\mu\text{m}$ , with self-assembled line pitch of 37 nm. The power of the self-aligned self-assembly process is in subdividing larger-scale lithographic structures into sublithographic units.

While this self-aligned technique provides subdivision of lithography patterns into units of smaller dimension, it does not afford a means of increasing self-assembled pattern complexity beyond the high-symmetry geometries of close-packed arrays

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and line/space patterns. Another challenge for this technique for lithography applications is controlling pattern defectivity,<sup>24</sup> because unlike Nealey's chemical patterning approach, there is less preferential surface wetting providing a strong local force to impose pattern order. Nevertheless, there are many aspects of IC fabrication requiring only simple pattern geometries, such as the transistor gates, transistor contact holes,<sup>25</sup> and advanced FET channel elements.<sup>9</sup> One may envision a self-aligned polymer self-assembly process working hierarchically in concert with advanced optical lithography to define only the highest resolution IC elements.

Among the many nanometer-scale materials and processes under active investigation throughout the nanotechnology research community, polymer self-assembly has emerged as the most viable candidate for contributing to the continued resolution scaling of optical lithography for semiconductor manufacturing. Although technology adoption remains uncertain, these materials have a natural compatibility with the semiconductor manufacturing infrastructure. Moreover, innovative research demonstrations, such as those described by Nealey and co-workers in this issue, have begun to illuminate their patterning capabilities and provide a vision for how these materials may work in concert with the photolithography process. Many serious issues relating to pattern roughness, dimensional scalability, and ultimately manufacturability all remain open research questions; however, the diligent efforts of both Nealey's group and many others in this active field have moved self-assembly from the research laboratory into the discussion of viable approaches for future extensions of the optical lithography process.

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