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Molecular Recognition in Self-Assembled Integrated Circuits: Getting Smaller while under Control**

*Yong-beom Lim and Myongsoo Lee**

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Necessity is the mother of invention. As the sizes of electronic devices get ever smaller, scientists and engineers are facing new challenges. They need to shrink the dimensions of electronic and storage devices, and therefore the devices must contain more information per square area. The conventional optical lithography (also called photolithography) technique, a process in which light is used to transfer a geometric pattern from a photomask to a light-sensitive chemical (photoresist) in the microfabrication of integrated circuits (ICs), has reached its economic and technological limits. Keeping pace with current demands requires that the lithographic pattern is further reduced down to below 30 nm. However, the microfabrication of such tiny patterns by such techniques is difficult and time-consuming. This is where self-assembly comes in.

Self-assembly is a spontaneous and cost-effective process where individual molecules (building blocks) are organized into ordered structures by noncovalent interactions.[1] These forces include hydrophobic forces, hydrogen bonding, van der Waals forces, π–π interactions, metal coordination, and electrostatic effects. Even if the noncovalent interactions themselves are rather weak, collectively they result in the formation of very stable aggregates. Among the many types of synthetic building blocks, block copolymers are one of the most popular and widely studied systems in the realm of self-assembly.[2–4] Block copolymers, which consist of two or more different polymers covalently linked together, form a wide range of microphase-separated nanostructures depending on the relative length and incompatibility of the polymer blocks, constraints in the connectivity, and the type of noncovalent interactions.

Since the power of self-assembly lies in the fact that "molecular-scale" control over the nanostructural morphology/pattern is possible, attempts have been made to utilize block copolymers in the microfabrication of ICs.[5,6] In block copolymer lithography, feature sizes are largely dictated by the molecular weight of the block copolymer and very small features, typically 10 to 30 nm, can be fabricated. There are several issues to overcome before the patterning methods based on this technique can find their way into industrial applications. One of them is to broaden the range of nanoscale patterns that can be made.

A recent study by Tang, Hawker et al. is a nice example that shows the versatility of the block copolymer lithography technique to address this issue.[7] In most cases, block copolymers adopt a close-packed hexagonal order when confined to a 2D thin-film monolayer. However, other types of ordered morphology, such as square arrays, are required to be fully compatible with the required semiconductor IC designs. To implement this while obtaining long-range orientational order, the authors employed a molecular recognition approach. This elegant approach begins with the blending of the two diblock copolymers A-B and B′-C. Such a blending approach, similar to that for the synthesis of ABC triblock copolymer systems, can result in the formation of much richer and more complicated structures than are present in simple AB diblock copolymer systems.[8] Uniform long-range order could previously not be achieved in thin-film blends of block copolymers because of the overwhelming tendency of such mixtures to exhibit macrophase separation. However, Tang, Hawker et al. made good use of attractive hydrogen-bonding forces to overcome this problem.[9]

The diblock copolymers poly(ethylene oxide)-*b*-poly(styrene-*r*-4-hydroxystyrene) [PEO-*b*-P(S-*r*-4HS); A-B] and poly(styrene-*r*-4-vinylpyridine)-*b*-poly(methyl methacrylate) [P(S-*r*-4VP)-*b*-PMMA]; B′-C] were synthesized, with the hydrogen-bonding donor (4-hydroxystyrene) or the hydrogen-bonding acceptor (4-vinylpyridine) randomly (*r*) incorporated into polystyrene blocks. Dramatic molecular recognition processes took place when the solution containing one acceptor- and one donor-substituted polymer at a 1:1 molar ratio was spin-coated onto a silicon wafer and further processed (Figure 1). A nanostructured morphology with little order and either hexagonal or square packing was observed when block copolymers containing different numbers of hydrogen-bonding donors and acceptors were mixed.

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[*] Prof. M. Lee
Center for Supramolecular Nano-Assembly
and Department of Chemistry
Yonsei University, Seoul 120-749 (Korea)
Fax: (+82) 2-393-6096
E-mail: mslee@yonsei.ac.kr
Homepage: http://csna.yonsei.ac.kr

Dr. Y.-b. Lim
Department of Materials Science and Engineering,
Yonsei University

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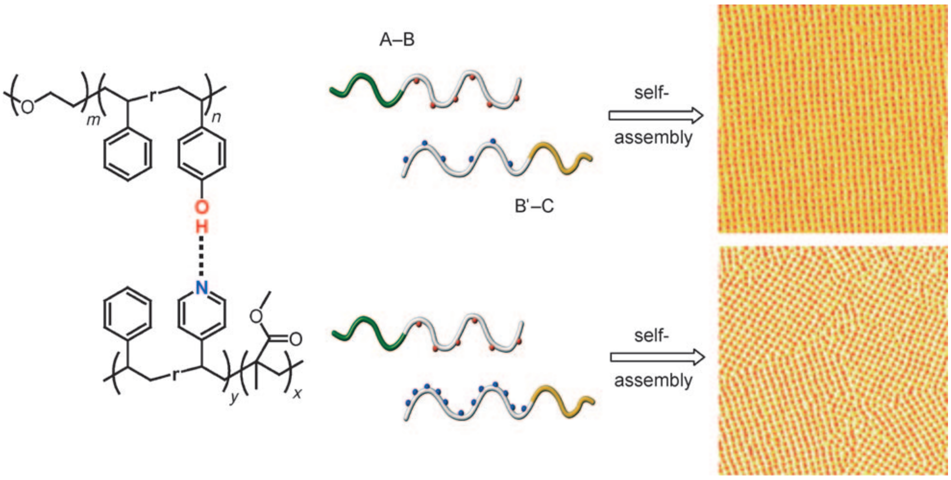

Figure 1. Self-assembly of A-B and B′-C diblock copolymer blends on silicon wafers. The AFM images show that well-ordered square arrays form only when equal numbers of hydrogen-bonding donors (red) and acceptors (blue) are present in the two block copolymers. Reprinted from Ref. [7] with permission; copyright 2008, American Association for the Advancement of Science.

However, for blends with approximately equal numbers of hydrogen-bonding donors and acceptors, the corresponding thin films exhibited only square arrays with an extremely high degree of in-plane order. Grains with the square-array morphology were larger than $5 \times 5\ \mu m^2$. Control experiments showed that hydrogen-bonding interactions are critical for both the square packing and the long-range ordering.

Similar molecular recognition processes have also been found in another diblock copolymer system with a different type of noncovalent interaction.[10] Harada and Kataoka prepared oppositely charged block copolymers, namely, poly(ethylene oxide)-*b*-poly(L-lysine) [PEO-*b*-PLL] and poly(ethylene oxide)-*b*-poly(L-aspartic acid) [PEO-*b*-PAA]. Molecular recognition was found to occur only in aqueous solution when block copolymers with the same polyanion and polycation block lengths were mixed, which led to the formation of a core–shell supramolecular assembly. These two examples suggest that, regardless of whether it is the bulk or the solution state, or if the interaction is hydrogen bonding or electrostatic, the key determinants in these molecular recognition processes are the strict and regular phase separations between the two interacting polymer blocks.

Tang, Hawker et al. further demonstrated that the square-arrayed self-assembled films can be used in microfabrication. Well-ordered square arrays of holes in the silicon substrate were revealed when the film was used as a lithographic mask to transfer the template image onto the underlying silicon substrate by standard etching techniques. The diameter and period of the holes (22 nm and 50 nm, respectively) in the substrate correspond well with the dimensions of the square arrays before transfer of the pattern, thus showing the high degree of fidelity in the lithographic process.

Simply broadening the range of patterns is not sufficient for block copolymer lithography to meet the industrial standards for semiconductors. For successful industrial usage, the film should be virtually defect-free and the features should be fully addressable. One solution to this can be found in the templated self-assembly of block copolymers, such as by chemical prepatterning[11] and graphoepitaxy.[12] Recently, two research groups independently reported the fabrication of defect-free and addressable hexagonal arrays of block copolymer films by using chemical pre-patterning or graphoepitaxy methods (Figure 2).[13,14] The strength of this technique lies in multiplication of the feature density and rectification of the pattern quality. In contrast to the square pattern, which is best suited for a semiconductor industrial standard based on a rectilinear coordinate system, the hexagonal pattern would require extensive and expensive reworking of the circuit design software, fabrication protocol, etc.[7]

In this sense, the approach delineated by Tang, Hawker et al. has great potential, as it provides a rational approach to create square arrays of block copolymers over a wide area. To

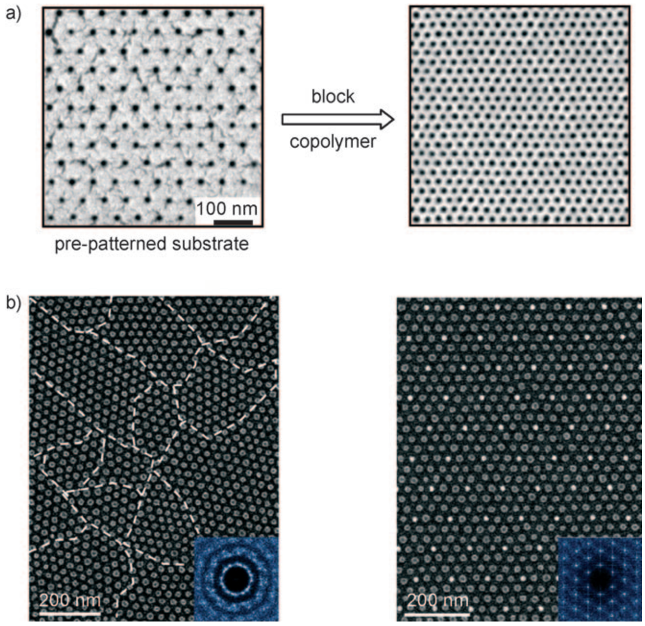

Figure 2. a) Directed self-assembly of a block copolymer (PS-*b*-PMMA) for multiplication of the feature density and rectification of the pattern quality on a chemically pre-patterned substrate. Reprinted from Ref. [13] with permission; copyright 2008, American Association for the Advancement of Science. b) Left: Poorly ordered monolayer of spherical domains of a block copolymer (polystyrene-*b*-polydimethylsiloxane; PS-*b*-PDMS) formed on a flat surface. The boundaries between different grain orientations are indicated with dashed lines. Right: Well-ordered PS-*b*-PDMS spheres formed within a sparse 2D lattice of posts (brighter dots). Reprinted from Ref. [14] with permission; copyright 2008, American Association for the Advancement of Science.

increase the current limit of the grain size (ca. 5 μm × 5 μm) and to fabricate more regular and fully addressable square arrays, this method can take advantage of the templated self-assembly method.[11–14] Furthermore, block copolymers may not be the sole type of self-assembling building blocks for patterning. Considering the fact that the pattern size can depend on the molecular weight of the building blocks, smaller features might be obtainable if one uses appropriate building blocks with smaller molecular weights than those of typical block copolymers (20–2000 $\text{kg}\,\text{mol}^{-1}$).[15–17] If the field advances further, it may not only be a dream that any type of desired pattern can be obtained simply by pouring out a block copolymer solution over a solid substrate and letting self-assembly occur.

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[1] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.

[2] A. C. Balazs, T. Emrick, T. P. Russell, *Science* **2006**, *314*, 1107.

[3] M. Lee, B. K. Cho, W. C. Zin, *Chem. Rev.* **2001**, *101*, 3869.

[4] M. Schappacher, A. Deffieux, *Science* **2008**, *319*, 1512.

[5] J. Y. Cheng, C. A. Ross, H. I. Smith, E. L. Thomas, *Adv. Mater.* **2006**, *18*, 2505.

[6] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, *276*, 1401.

[7] C. B. Tang, E. M. Lennon, G. H. Fredrickson, E. J. Kramer, C. J. Hawker, *Science* **2008**, *322*, 429.

[8] C. B. Tang, J. Bang, G. E. Stein, G. H. Fredrickson, C. J. Hawker, E. J. Kramer, M. Sprung, J. Wang, *Macromolecules* **2008**, *41*, 4328.

[9] J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke, O. Ikkala, *Science* **1998**, *280*, 557.

[10] A. Harada, K. Kataoka, *Science* **1999**, *283*, 65.

[11] M. P. Stoykovich, M. Muller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, P. F. Nealey, *Science* **2005**, *308*, 1442.

[12] R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, *13*, 1152.

[13] R. Ruiz, H. M. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. de Pablo, P. F. Nealey, *Science* **2008**, *321*, 936.

[14] I. Bita, J. K. W. Yang, Y. S. Jung, C. A. Ross, E. L. Thomas, K. K. Berggren, *Science* **2008**, *321*, 939.

[15] M. Lee, M. H. Park, N. K. Oh, W. C. Zin, H. L. Jung, D. K. Yoon, *Angew. Chem.* **2004**, *116*, 6627; *Angew. Chem. Int. Ed.* **2004**, *43*, 6465.

[16] C. Tschierske, *Chem. Soc. Rev.* **2007**, *36*, 1930.

[17] T. Shimizu, M. Masuda, H. Minamikawa, *Chem. Rev.* **2005**, *105*, 1401.