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Directed self-assembly of block copolymers for universal nanopatterning

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Bong Hoon Kim, Ju Young Kim and Sang Ouk Kim*

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Block copolymers (BCP) are self-assembling polymeric materials that have been extensively investigated for several decades. Recently, directed self-assembly (DSA) of BCPs has received enormous research attention from both academia and industry as next-generation nanolithography technology. This article provides a brief introduction to (i) the spontaneous and directed self-assembly of BCPs, (ii) the orientation and lateral ordering of BCP nanopatterns and their relationships with DSA strategies, (iii) various potential applications of BCP nanopatterning, and (iv) mussel-inspired BCP nanopatterning for arbitrary substrate materials including low surface energy materials.

1 Self-assembly *vs.* directed self-assembly of BCPs

Molecular self-assembly is an efficient nanostructure formation mechanism widespread in natural and artificial soft materials.[1] The subtle interplay of weak intermolecular interactions, such as van der Waals force, hydrogen bonding, and hydrophobic interaction, triggers the spontaneous ordering of molecular building blocks and generates an ultrafine nanoscale structure in a parallel manner. Meanwhile, self-assembly frequently suffers from retarded structure formation and dense defects, which are attributed to the weak intermolecular interactions among molecular building blocks. Those limitations do not matter significantly in a living system with a sufficiently long lifetime and self-healing mechanism. In contrast, when self-assembly is employed for the production of nanostructures, those limitations would significantly degrade the throughput and yield of desired nanostructures. In order to address these inherent limitations, directed self-assembly (DSA) is of particular research interest. DSA approaches employ external stimuli to promote a self-assembly. Prepatterned substrates or external fields can be employed in conjunction with a self-assembly such that the overall nanostructure formation can be accelerated with minimized defect formation.

Among various self-assembling materials, BCPs are representative polymeric materials that have been extensively investigated for several decades.[2–7] Currently, BCPs are utilized in technological fields, such as thermoplastic elastomers, compatibilizers for polymer blends, and drug delivery. It is well-known that the self-assembly of BCPs is driven by microphase separation behaviour. The chemically distinct macromolecular blocks covalently linked within BCP chains undergo spontaneous segregation into dense, periodic nanoscale domains.

Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Department of Materials Science and Engineering, KAIST, Daejeon, 305-701, Republic of Korea. E-mail: sangouk.kim@kaist.ac.kr; Fax: +82 42 350 3310; Tel: +82 42 350 3339

Dr Bong Hoon Kim obtained his Ph.D from the Department of Materials Science and Engineering at KAIST, Republic of Korea, in 2012 under the supervision of Prof. Sang Ouk Kim. The thesis title is "Fabrication of Functional Nanomaterials Using Block Copolymer Molecular Assembly". He is currently a Research Fellow at the Applied Science Research Institute at KAIST.

Ju Young Kim received his M.S. from the Department of Materials Science and Engineering at KAIST in 2011 under the supervision of Prof. Sang Ouk Kim. The thesis title is "Block copolymer lithography upon reduced graphene film substrate". He is now studying toward a Ph.D degree. His current research is focused on nanolithography using block copolymer self-assembly for functional nanomaterials.

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While the relative volume fraction of macromolecular blocks determines the shape of nanodomains (nanospheres or nanocylinders or nanolamellae), the overall molecular weight of the BCP chain determines the characteristic size of nanopatterns. The typical domain size of BCP self-assembly (ranging from 3 to 50 nm) is beyond the resolution limit of conventional photolithography.[8,9] Since the pioneering work by Register *et al.*,[10] BCP self-assembly has attracted a great deal of research attention as an alternative or complementary nanopatterning method for conventional photolithography. Presently, nanopatterning technology relying on the DSA of BCPs is actively exploited both in academia and industry. It is noteworthy that the International Technology Roadmap for Semiconductors (ITRS) regards the DSA of BCPs as a strong complementary technology for the nanopatterning process of semiconductor device fabrication.[11,12]

2 Orientation and lateral ordering of self-assembled nanodomains in BCP thin films

The nanopatterning application of BCP self-assembly requires the controllability of orientation and lateral ordering of the self-assembled nanodomains in a thin film geometry.[13,14] When a thin film of BCP is deposited on a substrate and self-assembled by thermal or solvent annealing, the orientation of BCP microdomains is strongly influenced by the interfacial energies at the air/polymer and polymer/substrate interfaces. Because the interfacial energies of chemically different macromolecular blocks are inconsistent at an arbitrary surface, a particular macromolecular block with a lower interfacial energy preferentially segregates at the interfaces. The resultant substrate parallel nanostructure without any nanoscale structure in the film plane is generally inappropriate for nanopatterning applications. This technological hardship could be overcome by surface modification for a chemically neutral surface, as firstly demonstrated by Hawker and Russell *et al.*[15,16] A carefully chosen self-assembled monolayer (SAM)[17,18] or polymer brush monolayer[15] or ultrathin crosslinked polymer layer[16,19] can modify a substrate surface to have a balanced identical interfacial energy for both components of a block copolymer. On this neutrally modified surface, lamellae or hexagonal cylinders in a BCP thin film are spontaneously oriented in the substrate perpendicular direction due to the preferential alignment of stretched block copolymers in the substrate plane direction (Fig. 1A(a)). The resultant thin film morphology with nanoscale line or dot array in the film plane is highly useful as nanopatterning templates. In this regard, the universal surface modification method generally applicable to arbitrary substrates is a crucial technological demand for the broad applications of BCP nanopatterning.[20] As discussed below, our research group developed surface treatment methods employing a 'mussel-inspired' adhesive for the effective nanopatterning of chemically inert and low surface energy materials, such as Au, graphene and even Teflon.[21]

Another significant technological issue in the BCP based nanopatterning is the lateral ordering of self-assembled nanodomains. When a self-assembled BCP thin film is formed on a planar surface with homogeneous surface energy, the self-assembled nanodomains are randomly oriented in the film plane along with dislocation and disclination defects (Fig. 1A(b)). As such, this multi-grain morphology with a high density of defects is inappropriate for nanopatterning applications. Here, the lateral ordering of nanodomains can be controlled in a desired way with a minimized defect formation by DSA principles. To date, various DSA strategies have been developed for highly ordered BCP nanopatterns. Among them, the most successful approaches are 'epitaxial self-assembly' and 'graphoepitaxy'.

'Epitaxial self-assembly', firstly introduced by Kim and Nealey *et al.*,[18] utilizes chemically pre-patterned surfaces to direct BCP self-assembly (Fig. 1B(a)).[22–26] The surface energy modulation usually engraved in a surface organic monolayer by extreme ultraviolet (EUV) or e-beam lithography (SAM or polymer brush layer) registers the lateral ordering of self-assembled nanodomains in BCP thin films. The commensuration of the periods between surface pattern and BCP self-assembled morphology is the critical parameter for highly ordered nanopatterns. Fig. 1B(b) and (c) show the SEM images of defect-free lamellae and hexagonal cylinder morphologies in PS-*b*-PMMA thin films achieved by epitaxial self-assembly.[18,26] It is noteworthy that our research group recently demonstrated that chemically prepatterned surfaces prepared by conventional photolithography including 193 nm ArF lithography or I-line lithography, whose pattern periods are much larger than BCP pattern periods, can successfully direct BCP self-assembly.[27] Those works are good examples demonstrating that BCP self-assembly can be synergistically integrated with conventional photolithographic processes for semiconductor or other commercial device fabrication.

'Graphoepitaxy', firstly developed by Kramer *et al.*, utilizes a topographically patterned substrate to guide the self-assembly of BCP thin films (Fig. 1C(a)).[28–35] The topographical confinement from the side walls of trenches enforces the lateral ordering of BCP nanodomains within the trenches. Fig. 1C(b) and (c) show the SEM images of highly ordered surface parallel

Prof. Sang Ouk Kim obtained his Ph.D from the Department of Chemical Engineering at KAIST, South Korea, in 2000. In 2001, he joined the Department of Chemical and Biological Engineering, University of Wisconsin-Madison, as a postdoc. At the end of 2004, he accepted an assistant professor position at KAIST. He is now a full professor and his main research interest focuses on the 'Directed Molecular Assembly of Soft Nanomaterials', which includes (i) block copolymer self-assembly, (ii) carbon nanotubes and graphene synthesis and assembly, and (iii) soft optoelectronics and energy devices. Detailed information can be found at http://snml.kaist.ac.kr.

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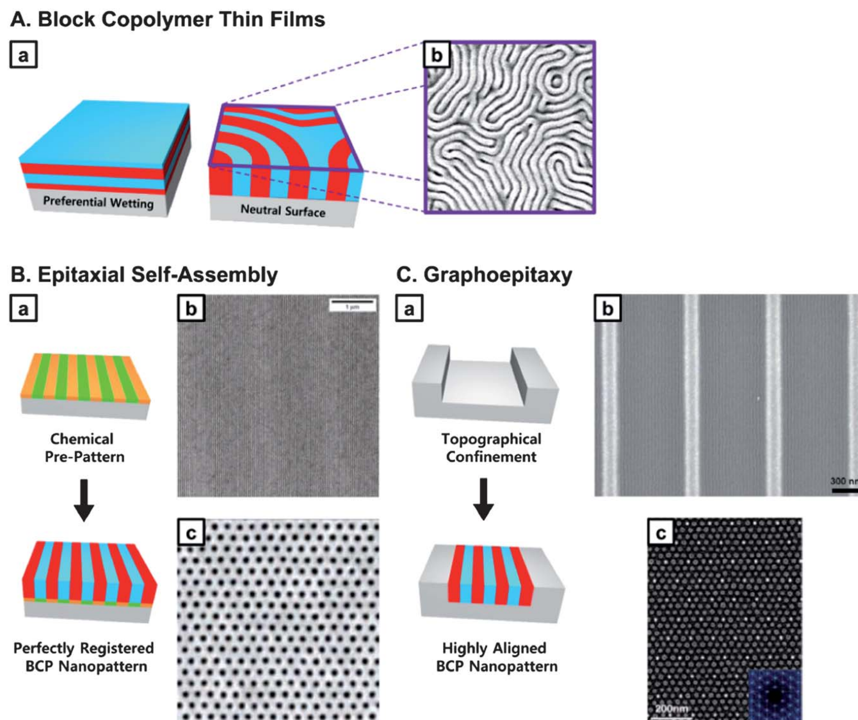

Fig. 1 (A) (a) Surface parallel (left) and perpendicular (right) lamellar nanostructures self-assembled in BCP thin films on preferential and neutral substrates, respectively. (b) SEM image of randomly oriented BCP lamellar morphology self-assembled on a homogeneous neutral substrate. (B) (a) Schematic illustration of epitaxial self-assembly. SEM images of defect-free (b) lamellar and (c) hexagonal cylinder patterns attained by epitaxial self-assembly.[18,26] (C) (a) Schematic illustration of graphoepitaxy. SEM images of highly aligned (b) lamellar and (c) hexagonal cylinder patterns prepared by graphoepitaxy.[36,37]

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and surface perpendicular cylinder morphologies of BCP thin films, PS-*b*-PMMA and PS-*b*-PDMS, respectively, prepared by graphoepitaxy.[36,37] In those approaches, the substrate pattern frequently remains even after pattern transfer and prevents a further overlay process for multilayered device architecture. Our research group introduced the 'soft-graphoepitaxy' method, where an organic negative tone photoresist pattern can be employed as a disposable topographic pattern.[38–41] Various metallic or semiconductor nanowire arrays could be produced on a substrate surface without any trace of a structure directing topographic pattern.

3 Emerging applications of BCP nanopatterning

The potential application of BCP nanopatterning is growing in various technological areas. In the early days, semiconductor devices and magnetic storage media were the major target applications. Recently, new areas are emerging, including photonics and membranes. Fig. 2 summarizes the relevant technological fields. As shown in Fig. 2A, BCP self-assembly can enhance the pattern density of conventional photolithography.[27,39] The synergistic integration of BCP self-assembly with ArF lithography was firstly demonstrated by our research group[27] and successfully reproduced by others.[41,42] Fig. 2A shows the highly ordered double arrays of 20 nm-scale metal and oxide nanodots generated from the 140 nm-scale ArF lithography. In the near future, effective integration with other advanced light sources, such as EUV, is anticipated for sub-10 nm scale nanopatterning.

Pattern size shrinkage is another interesting application of BCP self-assembly in semiconductor device fabrication.[43] BCP self-assembly can effectively reduce the local dimension of contact holes or other photoresist patterns into a desired size. The shape uniformity of target features can also be greatly enhanced by this process. Owing to the relative technological simplicity, this application is sometimes considered as the most urgent target in semiconductor areas. Fig. 2B(a) and (b) show silicon contact holes fabricated with 193 nm ArF immersion photolithography and the corresponding contact hole shrinkage result, respectively.[43] Statistical analysis of the patterned contact hole size distribution revealed that this DSA process has high tolerance for guiding template defects and the ability to heal template defects.

Fig. 2C shows the patterned magnetic storage media fabricated by BCP nanopatterning.[44] The DSA of BCP combined with e-beam lithography achieved highly uniform rectangular nanopatterns with a critical dimension of 16 nm, a full pitch of 27 nm, and an arbitrary aspect ratio. This ultrafine nanoscale pattern can be employed as a pattern master for a high throughput nanoimprint.[26] These highly uniform arrays of dense rectangular features are particularly attractive for fabricating magnetic bit patterned media with a high bit aspect ratio.

Fig. 2D shows ultrahigh-density resistive memory devices, *e.g.* the memristor nanostructures on metal and graphene

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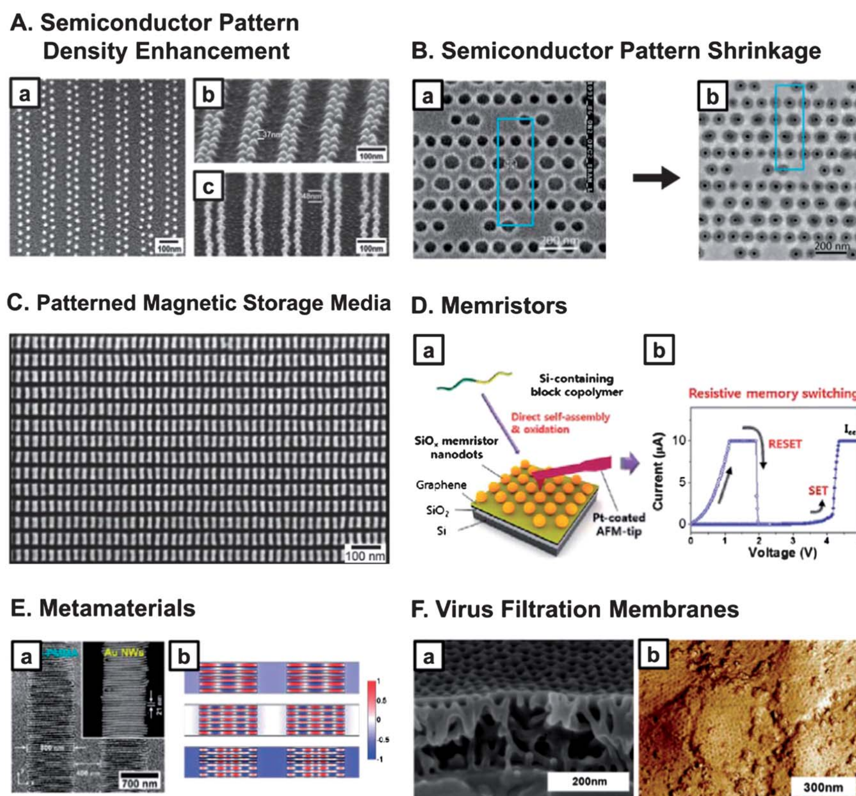

Fig. 2 (A) SEM images of double arrays of (a) Al nanodots and (b) silica nanopillars prepared by synergistic integration of BCP nanopatterning with conventional ArF photolithography.[27] (B) (a) Silicon hole pattern prepared by 193 nm ArF immersion photolithography and (b) hole size shrinkage by BCP self-assembly.[43] (C) SEM image of the nanoscale rectangular array for magnetic storage prepared by BCP nanopatterning integrated with e-beam lithography.[44] (D) (a) Nanoscale silicon oxide memristors fabricated from silicon-containing BCP nanopatterning. (b) The current–voltage measurement shows a unipolar operation.[45] (E) (a) SEM images of Au nanowire arrays fabricated from one-dimensional block copolymer lamellar templates. (b) Normalized nearfield profile of the *y* component of magnetic fields on the horizontal plane 3 nm above the wire. From the top, the wavelength of the incident light is 2308, 1607, and 1304 nm, respectively.[49] (F) (a) SEM image of a nanoporous membrane prepared by BCP nanopatterning. (b) AFM phase image of the nanoporous membrane after filtration of HRV 14 virus.[50]

electrodes, obtained by BCP nanopatterning.[45] The nanodot memristors, fabricated from silicon-containing BCP thin films, presented unipolar switching behaviors for resistive memory applications.

Nanoscale photonics,[46,47] such as plasmonics[48] or metamaterials,[49] are new emerging application fields of BCP nanopatterning. Unlike semiconductor or other electronic devices requiring extremely high controllability of defect formation, nanoscale photonics allow a large tolerance for defect density. However, the desired pattern shape is more complicated particularly for metamaterials. Fig. 2E shows the metamaterials consisting of linear metal nanowire arrays prepared from graphoepitaxy of BCP self-assembly.[49] Owing to the nanoscale dimension, the metamaterials are anticipated to interact with the visible light spectrum.

Another emerging application of the BCP thin film is the nanoporous membrane for selective filtration, which was firstly introduced by J. K. Kim *et al.*[50] Highly selective virus filtration was demonstrated with a good dimensional stability under high pressures (Fig. 2F).[50] The BCP based membrane did not leak even at a high pressure (~2 bar). Moreover, this nanoporous BCP membrane showed excellent resistance to all organic solvents due to the crosslinked porous matrix.

4 Mussel-inspired BCP nanopatterning

As mentioned above, various methods for surface modification *e.g.* self-assembled monolayer (SAM),[17,18] polymer brush,[15] and ultrathin polymer mat,[16,19] have been exploited for the chemically neutral surface formation. The substrate vertical cylinder or lamellar morphology self-assembled on the neutral surfaces provides nanotemplates with a high aspect nanopattern ratio and vertical side wall profile, which are greatly advantageous for further precise pattern transfer.[20] Recently, our research group introduced several novel approaches for neutral surface modification.[21,51] Firstly, we reported that chemically modified graphene can be employed as a surface neutral layer for PS-*b*-PMMA block copolymers.[51,52] While pristine graphene with a low surface energy is generally incompatible with BCP film formation, chemically modified graphene prepared by substantial reduction of graphene oxide provided a chemically neutral surface for PS-*b*-PMMA BCPs. Taking advantage of the atomically flat surface geometry, mechanical flexibility, high thermal/chemical stability and solution processability over an arbitrary surface, chemically modified graphene enabled the surface modification without covalent bonding to the underlying target substrate. Secondly, we recently reported

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'mussel-inspired surface modification' based on polydopamine adhesives.[21] Previous neutral surface modification methods for BCP nanopatterning commonly require spin casting of an ultrathin organic layer and thermal treatment for chemical modification of a target substrate. Those steps are intrinsically incompatible with low surface energy substrates, such as Teflon, Au, and graphene. Due to the low surface energy, the spin casting of uniform nanoscale thick organic films onto those materials is a formidable challenge. Moreover, thermal or solvent annealing, which is generally required for self-assembly, readily causes the dewetting of the organic layer. Here, 'mussel-inspired polydopamine treatment' is introduced as a universal adhesive layer to address the technological challenges. As presented in Fig. 3A, the polydopamine coating process is inspired by the adhesive proteins secreted by marine mussels.[53–57] Dopamine, a molecular building block having both amine and catechol groups for polymer coatings, can provide a universal route to modify virtually all types of material surfaces, including Teflon, gold and graphitic surfaces, regardless of their chemical functionality or surface energy. The simple immersion of any target substrate in an aqueous solution of dopamine generates an ultrathin polydopamine layer having a sufficiently high

Fig. 3 (A) (a) Mussel attached to the Teflon surface. (b and c) Schematic illustrations of Mefp-5 and amine and catechol groups. (d) The amino acid sequence of Mefp-5. (e) Dopamine having both amine and catechol groups found in Mefp-5.[54] (B) Schematic illustration of mussel-inspired BCP nanopatterning. After the polydopamine coating and neutral polymer brush treatment, PS-*b*-PMMA thin films were spin-cast and thermally annealed to form surface perpendicular lamellar or cylinder nanopatterns.[21] (C) (a) Optical and SEM images of the Teflon nanowire array, (b) TEM image of the cylindrical PS-*b*-PMMA thin film on CVD graphene and (c) optical and SEM images of the CNT array grown on Au substrates attained by mussel-inspired BCP nanopatterning.[21]

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surface energy. Significantly, the polydopamine layer supplies dense surface reaction sites for the additional ad-layer formation. We demonstrated that adhesive polydopamine coating can be synergistically combined with neutral polymer brush layer formation such that BCP lithography can successfully be applied to low surface energy substrates. Therefore, we demonstrate various unconventional nanostructures, including Teflon nanowires (Fig. 3C(a)), nanopatterned graphene (Fig. 3C(b)), and vertical carbon nanotubes (CNTs) directly grown on Au (Fig. 3C(c)).[21] It is obvious that novel surface chemistry inspired by natural biological system greatly strengthens the potential of BCP nanopatterning.

5 Conclusions and future perspectives

As mentioned in the introduction part, BCPs have thus far been used in chemical industry for polymer blends, thermoplastic elastomers, drug delivery and so on. Now, this one of the oldest synthetic nanoscale materials is becoming close to the utilization in semiconductors and other relevant industry fields. To this end, there are a few significant issues to be addressed. The most urgent issue is the low cost, large scale supply of photoresist grade block copolymers. Current research studies are relying on either lab-scale synthetic samples or expensive commercial samples with limited supply, which is a severe bottleneck for industrial scale research and development. Second, the judicious selection of the target device structure is highly significant. Since BCP self-assembly intrinsically generates periodic patterns, it is hard to envisage BCP nanopatterning as a completely alternative method to the current lithography method, which can generate arbitrarily shaped patterns. In this regard, synergistic integration with other patterning technologies, such as optical lithography, EUV lithography and nanoimprinting, may offer optimal solutions.[27,36,38] Third, further controllability of defect density must be attained to satisfy the defect tolerance allowed in the commercial device fabrication. If those issues are appropriately addressed in the near future, BCP nanopatterning can be one of the rare examples that the nanoscale self-assembly principle is indeed implemented in the commercial device manufacture.

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