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Directed Self-Assembly of Liquid-Crystalline Molecular Building Blocks for Sub-5 nm Nanopatterning

Koen Nickmans and Albert P. H. J. Schenning

The thin-film directed self-assembly of molecular building blocks into oriented nanostructure arrays enables next-generation lithography at the sub-5 nm scale. Currently, the fabrication of inorganic arrays from molecular building blocks is restricted by the limited long-range order and orientation of the materials, as well as suitable methodologies for creating lithographic templates at sub-5 nm dimensions. In recent years, higher-order liquid crystals have emerged as functional thin films for organic electronics, nanoporous membranes, and templated synthesis, which provide opportunities for their use as lithographic templates. By choosing examples from these fields, recent progress toward the design of molecular building blocks is highlighted, with an emphasis on liquid crystals, to access sub-5 nm features, their directed self-assembly into oriented thin films, and, importantly, the fabrication of inorganic arrays. Finally, future challenges regarding sub-5 nm patterning with liquid crystals are discussed.

1. Introduction

The last half century has witnessed a systematic exponential increase in the density of transistors on integrated circuits. This trend, commonly referred to as “Moore’s law,” has enabled the onset of personal computers and the advent of today’s powerful mobile devices. With the onset of human-level artificial intelligence, a data-driven society, and the internet-of-things, the hunger for further scaling beyond the current state of the art remains insatiable. Traditionally, advances in photolithography have been the driver behind the ability to print increasingly smaller features at a lower cost. According to the Rayleigh criterion, the smallest feature that can be patterned with acceptable control, i.e., the resolution, is proportional to the wavelength of the light used for imaging ($\lambda$), and inversely proportional to the numerical aperture (NA) of the projection lens. Over time, there has been a continuous shift to shorter wavelengths, from visible wavelengths (436 nm), to UV (365 nm), and deep-UV (248 and 193 nm). At the same time, the NA has increased dramatically by placing a liquid medium in the air gap between the lens and the wafer. Today, using a 193 nm immersion tool, minimum feature sizes have shrunk down to ≈36 nm.$^{[2]}$ In order to facilitate the production of even smaller features, extreme-UV (EUV) lithography, utilizing radiation of wavelength 13.5 nm, is currently being pursued on a global scale, even though it is tremendously complex and expensive.$^{[1,4]}$ Considering the rising cost of optical lithography tools, alternative patterning technologies must be considered to enable the manufacturing of next-generation integrated circuits, flash memory, and hard disk drives. Electron beam lithography (EBL), which involves scanning a beam of electrons in a controlled fashion across a resist, is not constrained by the optical diffraction limit. Unfortunately, EBL is considered prohibitively slow and expensive. Nanoimprint technology (NIL) is a contact rather than a projection-based technology in which features are replicated directly onto surfaces using a stamp process. However, in addition to concerns associated with the physical contact process such as alignment and contamination, the economical creation of an imprint template remains a challenge.$^{[5]}$

The length scales attainable by top-down lithography are approaching that of bottom-up self-assembly found in polymers and small molecules. For this reason, bottom-up patterning technologies based on self-assembly are becoming increasingly attractive.$^{[6–10]}$ The utilization of organic building blocks as self-assembled etch masks is particularly attractive since the lithographic information is contained in the self-assembling material itself, rather than provided in an exposure step.

The International Technology Roadmap for Semiconductors (ITRS) has identified the directed self-assembly (DSA) of block copolymers (BCPs) as a candidate for next generation nanopatterning. BCPs form nanostructures through microphase separation of incompatible blocks. Depending on the relative volume fractions of the blocks ($f_A$), lamellae, gyroid networks, hexagonally packed cylinders, and spheres can be obtained (Figure 1). The periodicity of the features is typically in the 10–100 nm regime.

In block copolymer DSA, the self-assembly of a block copolymer thin film is guided using top-down processes to result in a regular and oriented nanostructure array.$^{[10,12,13]}$ DSA is typically achieved using topological$^{[12]}$ or chemical$^{[13]}$
guiding patterns, known as graphoepitaxy and chemoepitaxy, respectively. The major advantage of DSA techniques involving patterned surfaces is that they allow the generation of addressable features (i.e., the circuit elements) by precisely placing the nanostructures across the wafer. Other alignment techniques, such as solvent annealing,[14,15] electric fields,[16] and magnetic fields,[17] have also been applied. In recent years, BCP DSA has emerged as a well-developed field, as exemplified by the appearance of numerous recent review articles.[9–11,18,19]

In order to fabricate circuit components such as inorganic nanowires[20,21] or nanodots,[22] a BCP pattern must be aligned in a monolayer, and subsequently used as an etch mask to convert the organic pattern into an inorganic one. For pattern transfer, “wet” and “dry” processes have been applied. In the wet approach, one of the BCP blocks is degraded and removed by rinsing in a selective solvent.[13,22,23] In contrast to wet etching processes, “dry” plasma etching makes use of reactive gaseous species or physical ion bombardment to degrade polymers into volatile segments. The etch contrast arises from the difference in etch rates between constituent blocks to an appropriate plasma treatment. The etch contrast arises from the difference in etch rates between constituent blocks to an appropriate plasma treatment. These materials are of particular interest since they can yield patterned inorganic nanostructures in a single etching step.[18,25,26] Among hybrid organic–inorganic BCPs, poly(styrene)-b-poly(dimethylsiloxane) (PS-b-PDMS) is the most widely investigated.[14,27–32] For example, Ross and co-workers demonstrated the fabrication of nanowires using a cylinder-forming PS-b-PDMS template.[29] A monolayer of planar PDMS cylinders in a PS matrix was deposited within topological guiding features to provide a uniaxial planar alignment. In a subsequent plasma etching process, the PS domains were degraded while the PDMS domains were oxidized, resulting in an array of parallel lines of oxidized PDMS with a feature size of 8 nm. By sputtering tungsten onto the oxidized PDMS template, and subsequently removing the oxidized PDMS, a nanostructured tungsten array of 9 nm features was fabricated with the reverse image. Since this process is applicable to other metals including titanium, platinum, tantalum, cobalt, and nickel,[33] these PDMS-based materials are excellent materials for device fabrication.

According to the ITRS, there are several issues currently preventing the integration of DSA with microelectronics fabrication processes. The first is related to concerns regarding the extendability of the DSA process to smaller feature sizes. For BCPs, the characteristic dimensions are controlled by the molecular weight of the polymer. The inverse relationship between molecular weight and the Flory–Huggins interaction parameter (χ) required for self-assembly places a lower limit of ≈10 nm on the minimum periodicity that can be realized through typical BCP self-assembly.[34] Second, an immediate challenge for DSA is to show low enough levels of defects for manufacturing use (<0.01 cm²). In contrast to top-down fabrication methods, soft organic building blocks have the tendency to form arbitrarily oriented poly-domain structures when left unguided, prohibiting their use in the fabrication of

Figure 1. Mesophase morphologies formed by diblock copolymers and rod–coil liquid-crystalline (LC) molecules. Abbreviations: Lam, lamellae; Gyr, bicontinuous gyroid; Hex, hexagonally packed cylinders; Sph, spheres. 3D renders: Reproduced with permission.[13] Copyright 2007, Elsevier.

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Figure 2. Schematic representation of directed self-assembly of LC small molecules, involving a) tailored interfacial interactions, b) topologically structured interfaces, and c) external fields.

addressable media. To date, work has been published showing defect levels for pilot line processes (<100 cm²), but defect levels are not yet low enough for manufacturing.

The use of patterning materials consisting of liquid-crystalline (LC) small molecules could address both of the aforementioned challenges, which caused it to recently attract attention of the scientific community. LC phases are formed by rod-coil molecules and are driven by a combination of molecular shape and noncovalent interactions. Similar morphologies to BCPs, but with significantly smaller characteristic dimensions, can be achieved with these materials (Figure 1). Most well-known for their use in the display industry, LC materials are now finding applications as functional nanostructured materials for lab-on-a-chip systems, responsive coatings, nanoporous membranes, templated synthesis, organic semiconductors, and photovoltaic devices. In addition to self-assembly at smaller length scales, LCs are highly customizable with regard to morphology and chemical functionality. Moreover, due to their low molecular weight, LCs show a fast response to stimuli and a straightforward alignment over device length scales. Importantly, the “soft” nature of LCs makes them amenable to DSA processes involving (1) tailored interfacial interactions, (2) topologically structured interfaces, and (3) external fields (Figure 2).

To date, the thin-film directed self-assembly of small molecules has hardly been explored for nanolithography applications. However, other applications based on liquid crystals have been envisioned that require functional thin films with sub-5 nm features, most notably organic electronics, nanoporous membranes, and templated synthesis. Figure 3 schematically depicts these applications alongside nanopatterning, and the required alignment configurations for discotic LCs (similar for smectics). Since these applications require the fabrication of thin-film nanostructure arrays with sub-5 nm features, a high level of perfection, and a unidirectional alignment over large areas, the developed methods provide opportunities for nanolithography applications.

Here, we discuss recent advancements, opportunities, and challenges in the field of sub-5 nm patterning using small molecules as building blocks. First, different strategies in the preparation of organic building blocks which form sub-5 nm patterns are discussed, including high-χ, low-N block copolymers (Section 2.1) and small molecules (Section 2.2). Through examples from the well-established field of organic electronics, the directed self-assembly of organic sub-5 nm patterns in thin films is discussed, together with their implications for nanolithography (Section 2.3). Then, suitable fabrication techniques for the conversion of organic sub-5 nm patterns into inorganic nanostructured arrays are considered (Section 3). Two approaches are discussed: i) the selective infiltration of inorganic precursors in nanoporous materials (Section 3.1) and ii) hybrid organic/inorganic small molecules with inherent etch contrast (Section 3.2). Finally, future challenges of sub-5 nm patterning using liquid crystals are discussed (Section 4).

2. Organic Building Blocks for Sub-5 nm Patterning

2.1. Limits of High-χ Block Copolymers

While reservations were expressed in the introduction regarding the feature size limitations of typical block copolymer self-assembly, novel BCPs with high interactions parameters are emerging that offer self-assembly beyond the current scaling barriers, i.e., the sub-10 nm regime. So-called “high-χ” BCPs with highly incompatible blocks typically consist of highly immiscible components, such as inorganic and organic segments. In principle, a large supramolecular toolbox is available to augment the block incompatibility through orthogonal noncovalent interactions that enhance phase separation.

For example, BCPs can be doped with small molecules, which interact selectively with one of the domains via hydrogen bonding or ionic interactions. Self-attractive noncovalent interactions may also be engineered directly into the polymer blocks, which avoids the use of additives. For example, ABC triblock polymers have been synthesized in which two of the blocks (e.g., A and B) interact favorably through π–π stacking or hydrogen bonding, resulting in a single nanodomain. The second domain is formed by the remaining noninteracting block (e.g., C). Shape anisotropy, for example through the incorporation of rod-like carbohydrate blocks, is another powerful means to access ultra-dense BCP nanopatterns.

Through the development of high-χ BCPs, it is estimated that features as small as 2 nm can be obtained. At this length scale, the borders between polymer and small molecules are convoluted. The molecules can no longer be considered BCPs, but rather co-oligomers, the properties of which more closely resemble small molecules such as low-molecular-weight lyotropic or thermotropic liquid crystals.
2.2. Small-Molecule Self-Assembly

Further lowering the molar mass of the soft building block brings one into the field of small-molecule self-assembly, where the intrinsic length scale is the molecular length, between 2 and 10 nm. Remarkably, the phase behavior of small-molecule lyotropic and thermotropic liquid crystals is similar to that of AB diblock BCPs (Figure 1, Figure 4), albeit at a smaller length scale. Amphiphilic molecules\cite{36,85} spontaneously form lyotropic liquid-crystalline phases of varying geometry depending on the solvent concentration. It is noteworthy that only dense lyotropic phases\cite{36} in which limited amounts of solvent are present, provide the necessary morphologies for long-range nanostructured materials (lamellae, cylinders). Molecules based on a rigid-flexible motif\cite{40–42} form thermotropic LC phases in bulk. In thermotropic phases, the distinct molecular shape in combination with supramolecular interactions such as electrostatic interactions, π–π stacking, and hydrogen bonding, results in thermodynamically stable structures.\cite{40} In contrast to BCPs, phase separation is no longer a prerequisite. The degree of order varies; from nematic phases with orientational order only, to higher order phases in which the periodicity of the nanopattern is approximate to the molecular length.\cite{86} The nematic phase does not provide the necessary bulk morphologies for nanolithography.

Rod-like molecules (calamitics), classically consisting of an aromatic core and a flexible tail, have the tendency to form lamellar structures (smectic mesophases, Sm). However, bicontinuous gyroidal, columnar, cubic, and other three-dimensionally ordered phases can be obtained by successively increasing the volume fraction of the alkyl chains in calamitics\cite{39,40,87,88} similar to varying the relative volume fractions in a diblock BCP (Figure 1). Disc-like molecules (discotics) tend to stack perpendicular to the disc plane, generally resulting in columnar

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Figure 3. Applications employing discotic LCs with uniaxial planar alignment (top) and vertical alignment (bottom), including a) nanolithography, b) organic electronics, and c) porous membranes and templated synthesis.

Figure 4. Mesophase morphologies formed by the self-assembly of rod-like and disc-like molecules, low-molecular-weight amphiphiles, and AB diblock copolymers. Abbreviations: nematic mesophase formed by rod-like molecules (N), disc-like molecules (ND), or columnar aggregates (N_{Col}), smectic A phase (SmA), bicontinuous cubic phase (Cub_b), hexagonal columnar mesophase (Col_{H}), and discontinuous (micellar) cubic mesophase (Cub). Reproduced with permission. Copyright 2001, Royal Society of Chemistry.
structures (columnar mesophases, Col). Discotic compounds are also known to exhibit lamellar and cubic phases. A distinct feature of LCs compared to BCPs is that their molecular shape can lead to molecular order within the lamellar or columnar structures. Many subtypes of Sm and Col phases have been allocated depending on the lattice and degree of positional and orientational order of the molecules. Figure 4 represents the most simple Sm phase in which the rod-like molecules are on average perpendicular to the lamellar structures (SmA), and the most simple Col phase (Colhex) in which the disc-like molecules are on average perpendicular to the columnar structure and the columns are packed in a hexagonal lattice. Higher order phases that include more complex 2D lattices (e.g., Colqu, Colqr, Coldd), and well-defined molecular tilt and spatial organization (e.g., SmC, SmB, SmE) can be achieved through specific molecular design. Such complex phase morphologies are unobtainable by amorphous BCP self-assembly, and they may offer both improved design flexibility and an improved pattern fidelity from a nanopatterning perspective.

2.3. Directed Self-Assembly of Organic Small Molecules

Since reports of DSA of sub-5 nm patterns in thin films for nanolithography are extremely rare, in this part, we will discuss examples from the well-established field of organic electronics, and highlight opportunities for nanolithography. For the design of higher-order LCs for organic electronic applications such as organic photovoltaics, organic light emitting diodes, and organic transistors, the reader is referred to many available reviews. In brief, LC materials are required with a high charge-carrier mobility for selective 1D charge transport (Figure 3b). High charge-carrier mobilities are achieved by using π-conjugated molecules, such as triphenylenes, phthalocyanine, and perylene bisimides. Separation between LC columns can be improved by using highly immiscible terminal tails, such as oligo(dimethylsiloxane) or a fluorinated alkyl tails. For applications in organic electronics, alignment of the LC phases into large-area domains with minimal structural defects is essential for efficient charge transport between electrodes. Both uniaxial planar and vertical alignments can be useful, depending on the envisioned application (Figure 3b).

Organic transistors require uniaxial planar alignment between source and drain. Scaling down of the uniaxial alignment of columnar π–π conjugated systems to the nanometer range, and ultimately to single columns, would permit the fabrication of high-density organic-transistors arrays. Mouthuy et al. demonstrated one of the earliest examples of uniaxial planar alignment using topological guiding structures (Figure 5a–e). The researchers studied a tetrasubstituted phthalocyanine, which forms a columnar LC mesophase at room temperature. For the confinement, 200 nm wide guiding structures were fabricated by e-beam lithography and subsequent etching into silicon oxide. After deposition of the LCs by spin-coating and short thermal annealing, the LC phase was found to form in-plane oriented multilayers with a periodicity of ~3 nm. AFM phase images revealed that LC columnar axis was perpendicular to the long axis of the guiding structures (Figure 5c), likely due to surface anchoring of the discotic core on the hydrophilic guiding surfaces. A strikingly low level of defects was observed. The researchers were also able to induce the parallel orientation of cylinders to the guiding structures by using a crisscross pattern. In subsequent work, the LCs were deposited within tangentially aligned spiral networks with variable curvature radii resulting in the controlled bending of the LC columns (Figure 5d,e). For this particular LC, tangential alignment of the LC columns was obtained down to a curvature radius of ~1 μm. At lower curvature radii, the LC columns followed a random alignment with respect to the spiral network, indicating that the bending energy of the columns overwrites the energy gain from the alignment at this limit.

Zhang et al. studied the self-assembly of columnar LCs in anodized aluminum oxide (AAO) pores. The researched among other LCs, a soft dendronized carbazole, which forms a hexagonal columnar phase at room temperature with a lattice spacing of 3.9 nm. It was found that the LC prefers to align parallel to substrate surfaces (Figure 5f), resulting in a circular concentric alignment inside the AAO pore. Incredibly, curvatures approaching the lattice spacing were tolerated for this “soft” LC (Figure 5h), which illustrates the amenability of these materials for directed self-assembly. Interestingly, axial alignment could be obtained over circular alignment by choosing an LC with a higher rigidity (Figure 5e). This finding exemplifies the importance of molecular design toward achieving the application-specific required orientation of the LC phase.

In the aforementioned studies, the confinement geometry was limited to several hundred nanometers (i.e., the size of the pore). Cattle al. demonstrated the alignment of a range of triphenylene and phthalocyanine-based discotic liquid crystals with widely spaced topological guiding structures. Using photolithography, SU8 channels of width 2–25 μm were fabricated on hydrophilic substrates. Among other LCs, the researchers investigated a substituted triphenylene which forms a Colhex phase at 85 °C, and a crystalline phase at room temperature (Figure 5j). For the alignment, a small amount of crystalline material was placed adjacent to the channels (Figure 5l, top left), heated to the isotropic phase to enable capillary filling, and cooled into the Colhex (0.5 °C min⁻¹). As a result, in-plane alignment was obtained, with the column director oriented across the microchannel (Figure 5k). The same observation was made for all investigated triphenylene and phthalocyanine compounds. The researchers concluded that the cooling rate, the width of the channel, and the strength of the anchoring interaction were critical for alignment. Under the investigated conditions, a slow cooling rate (0.1 °C min⁻¹), and channels of limited width (<5 μm), were optimal for the realization of monolithically oriented columnar structures. Even though the alignment of the sub-5 nm patterns was not investigated at the nanoscale, the results imply that the influence of the guiding channels extends to several micrometers, which is roughly three orders of magnitude larger than the periodicity of the patterns themselves.

Organic photovoltaics require the vertical alignment between electrodes of electron donor and acceptor moieties (red and blue columns). The distance between the columns should be
no greater than the exciton diffusion length, \( \approx 5-15 \text{ nm} \),\(^{59,102}\) which makes higher-order columnar LC phases ideally suited (Figure 3b). The most straightforward way toward obtaining vertical alignment for columnar LC phases is to confine them between parallel surfaces, while slowly cooling from the isotropic melt.\(^{56,103,104}\) In this process, the vertical alignment is driven by a nucleation and growth process, which is initiated at the interfaces. Hence, the process benefits from a slow cooling rate and depends on the film thickness. Kwon et al. recently demonstrated the general applicability of the confinement method to a range of supramolecular materials.\(^{100}\) The researchers investigated, among other LCs, a fluorinated tapered dendrimer containing a crown ether (Figure 5m). Via the fluorophobic effect, this material forms cylindrical...
dendrimers, which pack in a hexagonal lattice with a spacing of ≈4.5 nm (Figure 5n).[105] The crown ethers can be replaced with a large number of other functionalities, which become part of the core of these supramolecular columns (i.e., donors, acceptors, donor-acceptor complexes) to form complex electronic materials.[106] A 150 nm film of the fluorinated tapered monodendron was coated on a carbon substrate, covered with a PDMS top surface, heated to the isotropic phase (78 °C), and slowly cooled back to room temperature (Colinh phase) (Figure 5o). As indicated by TEM, a vertical alignment was achieved with high order (Figure 5p). Large-area, vertically oriented domains were not only found with carbon substrates and PDMS top surfaces, but also with any other combination of PDMS, Teflon, perfluoropolyether (PFPE), polyethyleneimine (PEI), and carbon. In contrast, polydomain structures were observed when single substrates were used, with varying vertical or planar orientation determined by the specific interaction between the dendrimer and supporting substrate. Hence, the face-on orientation of the planar aromatic moieties is likely due to contact at the top and bottom interfaces.

3. Fabrication of Inorganic Sub-5 nm Patterns

Owing to their small feature size and ease of alignment, small-molecule LCs make excellent candidates for the extension of BCP DSA processes to enable the patterning of sub-5 nm inorganic features, provided the small patterns can be converted into etch masks. The selective infiltration of inorganic material in organic films is a strategy worth pursuing since it has been readily applied to BCP materials.[24] Here we will discuss LC-based porous materials, which provide opportunities for the patterning of inorganic layers using related processes (Section 3.1). Alternatively, hybrid organic/inorganic patterning materials are highly desirable since they possess inherent etch contrast.[118] Here we will discuss the emerging class of hybrid organic/inorganic small molecules and their directed self-assembly (Section 3.2).

3.1. Selective Infiltration of Inorganics in Nanoporous Materials

For the construction of sub-5 nm porous membranes, most often lyotropic LCs[107,108] are utilized, but thermotropic LCs have also been employed.[52] LC monomers are highly suitable as template molecules for the fabrication of porous membranes since they can be crosslinked to form rigid polymeric materials.[109] Selective removal of a specific molecular component in a following step yields hollow channels with the dimensions of the template (1–2 nm). Given their monodispersity and customizable chemical functionality, LC materials could overcome the limitations of conventional membrane fabrication approaches with regard to pore size distribution, tortuosity, and selectivity.[53] Furthermore, the porous channels provide an opportunity to be filled with inorganic materials for the preparation of hybrid organic/inorganic nanostructured materials, which are interesting from a nanopatterning perspective.

In order to produce through-film channels for nanofiltration membranes, the LC columns must be vertically oriented and highly ordered with minimal defects throughout the thickness of the membrane (Figure 3c). Magnetic alignment is particularly well suited for the alignment of LC mesophases.[50,110] The great advantage of magnetic fields is their ability to penetrate homogeneously into the bulk from a distance, which allows the alignment of the entire sample in a noncontact manner. When LCs are placed in a magnetic field, they align preferentially with their most magnetically susceptible axis (“easy” axis) oriented parallel to the field. For calamitic LCs consisting of mostly aromatic groups, the easy axis is along the long axis of the molecule (positive diamagnetic susceptibility), resulting in the parallel alignment in the magnetic field (Figure 3c). For discotic LCs, the easy axis is typically in the plane of the aromatic rings (negative diamagnetic susceptibility), since the component of the diamagnetic susceptibility perpendicular to an aromatic ring is greater than the in-plane component.[41] For discotics in a static magnetic field, this results in a degenerate scenario in which all azimuthal orientations of LC columns are isoenergetic. The degeneracy can be lifted by use of a rotating magnetic field.[50,111,112]

Eng et al. investigated the magnetic alignment of a wedge-shaped amphiphilic monomer (Figure 6a).[50] Structural “freezing in” of the LC order is promoted by the use of multiple reactive groups per monomer. In this study, a dense lyotropic phase was obtained with hexagonal symmetry and a lattice spacing of 3.6 nm by combining the LC monomer with a small amount of water. For the magnetic alignment, the material was slowly cooled in a rotating magnetic field (achieved by rotating the sample in a static field). The mesophase was aligned such that the least magnetically susceptible axis (“difficult” axis) was oriented parallel to the axis of rotation (Figure 6b). By lifting the degeneracy, oriented structures were obtained that are impossible to obtain by using a static field only.[50,112] After crosslinking the mesophase by polymerization, TEM images were obtained of the polymeric films perpendicular (Figure 6c) and parallel (Figure 6d) to the rotation axis, providing direct evidence of the long-range persistence of vertically aligned nanopores. The resulting ionic channels had a diameter of ≈1 nm. Remarkably, ion conductivity measurements on the aligned membranes showed an 85-fold enhancement of conductivity over nonaligned samples.[50]

The nondestructive nature of magnetic fields over longer time periods enables their use in combination with slower self-assembly processes such as surface alignment.[113] Feng et al. recently demonstrated the preparation of vertically aligned nanopores based on conjugated linoleic acid (CLA) monomers. When combined in a 3:1 ratio with 1,3,5-tris(1H-benzo[d]-imidazol-2-yl)benzene (TBIB) core, these materials form a thermotropic Colinh phase at room temperature (Figure 6e) with a lattice spacing of 2.6 nm.[111] The LC phase is formed through triple hydrogen bonding interactions by acid–base proton sharing, which leads to a partially ionic character. For relatively thin films (<5 μm), vertical alignment was achieved using a polyelectrolyte poly(sodium 4-styrenesulfonate) (PSS) surface, which shows a strong affinity for the LC core. Therefore, anchoring of the core through ionic interactions resulted in a vertical alignment. For relatively thick films (>5 μm), surface alignment alone was insufficient for obtaining through-film vertically oriented channels. For this reason, the PSS surface
modification was combined with a rotating magnetic field (Figure 6f). The vertically aligned films exhibited optical extinction under crossed polarizers, thereby confirming their vertical alignment throughout the thickness of the film (Figure 6g). The TBIB core could be recovered by crystallization from solution, and subsequent adsorption experiments performed with model dye molecules demonstrated that the 1–1.5 nm ionic pores displayed size and charge selectivity. However, pattern collapse was observed upon drying of the films, which prohibits the use of these materials as an etch mask. Pattern collapse during the wet development of high-aspect-ratio features in lithography is a well-established phenomenon in BCP lithography, and is due to large capillary forces. The filling of the ionic LC channels with inorganic precursors could be an alternative route toward obtaining hybrid organic/inorganic sub-5 nm patterns. LC-derived porous materials can be employed for direct
templatting of inorganic materials by filling up the nanopores, which could be an interesting route toward lithographic etch masks. Our group has demonstrated the filling of porous materials formed by smectic hydrogen bonding LCs. The smectic LC formulation consisted of hydrogen bonding acrylate monomers, which form hydrogen bonds between the smectic layers by carboxylic acid dimerization, and 10% of a diacrylate crosslinker (Figure 6h). The interlayer crosslinks ensure that the structural integrity of the polymer is maintained after breakage of the hydrogen bonds in a basic solution (Figure 6i), which results in a stable polymer film, useful as a high-capacity adsorber material for cationic dyes. The 2D smectic porous polymer network was subsequently used to fabricate silver nanoparticles by the infiltration of silver nitrate and subsequent reduction of the silver ions within the pores (Figure 6j). The diameter of the silver nanoparticles could be controlled by the covalent crosslinker. Moreover, the process was amenable to other metal precursors, such as zinc ions. Further investigation of the silver nanoparticle polymer film by peak force tapping atomic force microscopy revealed a layered morphology over a large area (Figure 6j). The periodicity of the hybrid organic/inorganic features was ≈4.3 nm.

3.2. Hybrid Organic/Inorganic Building Blocks

Since hybrid organic/inorganic small molecules with high etch contrast have emerged only very recently, an overview is provided below.

3.2.1. Polyhedral Oligomeric Silsesquioxanes

Polyhedral oligomeric silsesquioxane (POSS) is a popular building block for the preparation of hybrid organic/inorganic small molecules. POSS consists of a 3D crystalline silicon–oxygen cage with the formula (RSiO1.5)n. The cubic POSS cage has a size of 0.53 nm, and there are eight available vertices on which to place substituents. Wang et al. obtained hybrid organic/inorganic layered structures by monosubstituting a POSS cage with varying number and length of alkyl tails (Figure 7a). These materials showed various crystal–crystal and crystal–isotropic phase transitions, and formed crystalline structures at room temperature. By varying the amount of alkyl tails and their lengths, lamellar structures were obtained in the range of 3.4–5.3 nm. Long-range order was promoted by slowly decreasing the temperature from the isotropic state to 30 °C at the rate of 0.1 °C min⁻¹. Under these thermal annealing conditions, long-range ordered lamellar structures with sharp boundaries were observed (Figure 7b). The length of this long-range ordered structure formed within a single grain was ≈200 nm. Unfortunately, the crystalline nature of the reported phases will make the application of DSA processes extremely challenging, for the tendency of crystalline materials to nucleate and grow in into arbitrarily oriented domains. In order to grow single crystal films in an epitaxial process, the substrate would require the same crystal structure as the layer and a close match of lattice parameters. For this reason, smectic and discotic LC phases would be preferred for their mobility in combination with their high order.

Various LC phases utilizing POSS cages have been obtained by attaching different mesogens of varying shape and spacer length, and by varying the number of substituents on the POSS cage. For example, Wang et al. reported a series of octameric POSS-based LCs. Smectic phases were achieved when the mesogens were substituted with single flexible chains (R¹ = R³ = H, R² = –OC12H25), as exemplified by the formation of large birefringent domains under crossed polarizers (Figure 7d). When the mesogens were substituted with two or three flexible chains, no LC phases were formed, indicating the importance of the number and length of flexible chains on the phase behavior. While fully substituted (octameric) POSS materials are easy to synthesize, their transition temperatures remain relatively high, with LC phases being achieved over 100 °C. However, Kim et al. recently showed that smectic phases can be induced by the addition of a nematic LC (4-cyano-4′-heptyloxybiphenyl) (7OCB) to a POSS cage monosubstituted with a cyanobiphenyl (POSS-CB) (Figure 7e). A 30/70 POSS-CB/7OCB composition induced a room-temperature smectic phase in which the nematic LCs crawl into the space between the POSS cages. As evidenced by TEM (Figure 7f), the layered structure had a periodicity of 5.2 nm. Unfortunately, the composition range of the induced smectic phase was very narrow, and the phase diagram was rather complex with several coexisting phases, including various crystalline and nematic regions, which is highly undesirable from a processing standpoint.

3.2.2. Oligo(dimethylsiloxane)

Oligo(dimethylsiloxane) (ODMS), with the formula (Si(CH3)2O)n, can also act as a precursor to inorganic silicon oxides through plasma oxidation, making it an attractive etch mask. In contrast to POSS, ODMS is a flexible silicon-containing moiety, which makes it a favorable “coil” moiety in LC design. Due to the chemical incompatibility and large surface tension mismatch of ODMS with most organic materials, nanophase segregation is promoted, which leads to the formation of highly ordered nanostructured morphologies. In the case of rod-coil motifs, smectic, discotic, or more complex LC phases are observed, rather than nematic phases, which is a requirement for the preparation of sub-5 nm hybrid organic/inorganic patterns. Although many ODMS-based LCs have been reported, their ODMS content has been generally restricted to 2–4 repeating units due to an unavailability of commercial ODMS of longer lengths. For nanopatterning applications, higher ODMS fractions are desirable (~50% of the molecule).

Recent progress in the synthesis of discrete ODMS by the group of Meijer has led to the generation of a range of ODMS block molecules with interesting self-assembly behavior. For example, an ureidopyrimidinone (Upy) end-capped ODMS was shown to follow a BCP-like self-assembly behavior, while benzyl-protected derivatives always exhibits a lamellar organization, independent of the molecular composition. It was hypothesized that crystallization of the benzyl-protected Upy
moiety in the UPy–ODMS conjugates was the reason for the generation of the lamellar morphologies. Subsequent investigations of block molecules consisting of naphthalenediimides (NDIs) and ODMS revealed that the synergy of high incompatibility and crystallization of the NDIs drives the formation of conformationally disordered crystal phases characterized by a crystalline-type order and very low mobility. When a centrally placed NDI moiety was flanked by two ODMS chains, granular textures were observed. Figure 8a,b shows the case where the length of the ODMS chain consisted of 15 DMS units. According to XRD, this material forms a ColHex phase with a lattice parameter of 6.6 nm. The grainy textures (Figure 5b), together with the large number of sharp reflections observed in the XRD scattering (beyond fourth order), indicate the combination of high order with low mobility, typical for conformationally disordered crystal phases. When NDI moieties were placed on the periphery of an ODMS bridge, this generally gave rise to low-contrast birefringent textures, indicating limited order. An exception was seen for a compound with limited ODMS content, (8 DMS units) (Figure 8c), which formed lamellar crystallites (Figure 8d) with a lattice parameter of 4.4 nm.

While the high order observed in these materials is a suitable characteristic for nanolithography applications, the high crystallinity and associated low mobility of conformationally disordered crystal phases are likely undesirable for DSA processes.

By making use of discrete ODMS developed in the Meijer and co-workers, our group recently prepared ODMS-based LCs consisting of an azobenzene core and ODMS side tails (Figure 9). Based on a traditional rod-coil design, these materials form smectic and columnar liquid-crystalline phases at room temperature, with lattice constants between 3.0 and...
Figure 8. a) Chemical structure of Si15-NDI-Si15 which forms a Col_{hex} phase. b) POM image of Si15-NDI-Si15 showing granular texture. c) Chemical structure of NDI-Si8-NDI which forms a lamellar morphology. d) POM image of NDI-Si8-NDI showing a spherulitic texture. POM images obtained under crossed polarizers after slow cooling from the isotropic melt. a–d) Reproduced with permission.[137] Copyright 2017, American Chemical Society.

Figure 9. a) Chemical structure of photoresponsive oligo(dimethylsiloxane) liquid crystal LC-22Si. b) Room-temperature POM image obtained under crossed polarizers. The polarizer axes are indicated by the cross. Scale bar: 100 µm. c) High-resolution AFM phase image of a 40-nm-thin film confined within 100 nm graphoepitaxial guiding structures. The inset shows a 2x magnification. Scale bars: 50 nm. d) High-resolution AFM phase image of a photoaligned thin film of 40 nm thickness. The direction of E is indicated by the arrow. The inset shows a 2x magnification. Scale bars: 50 nm. a–c) Reproduced with permission.[37] Copyright 2016, Wiley-VCH. d) Reproduced with permission.[139] Copyright 2017, Wiley-VCH.
5.1 nm. Figure 9a shows the chemical structure of LC-22Si, which consists of 11 DMS units on either side of the molecule. This material exhibits room-temperature POM textures (Figure 9b), which typify the self-assembly into large domains (≈100 µm). In thin films, LC-22Si self-assembles into planar-oriented cylinders with a lattice spacing of 4.3 nm.[37] Due to the high mobility of the LC phase, large-area ordered thin films were readily obtained by directed self-assembly methods such as graphoepitaxy and photoalignment. For example, Figure 9c shows the confinement of LC-22Si within channels of 100 nm width, in which highly ordered line structures were observed with a 4.3 nm periodicity, without the need for thermal annealing. Moreover, due to the incorporation of the central azobenzene moiety (Figure 9a), these materials were amenable to photoalignment methods.[139] While photoalignment was initially developed for the alignment of nematics in the liquid-crystal-display-panel industry, it is currently finding applications for a broad range of functional materials including higher order LC phases.[140–142] When exposed to linearly polarized light, an in-plane alignment of cylinders was achieved in which the cylinder axis was parallel to the polarization vector of the linearly polarized light (⃗{E}). High-resolution AFM imaging indicated the total absence of defects in aligned samples (Figure 9d). When exposed to unpolarized light, the nanocylinders were aligned out-of-plane. However, the out-of-plane morphology was unstable, likely due to the surface energy disparity between the molecular components. Importantly, this result highlights an important difference between BCPs and LCs; while the removal of defects is facilitated by the low glass-transition temperature of the LCs, the retention of the metastable out-of-plane morphology is hampered. In principle, photoalignment could be used for the manufacturing of complex circuits by performing multiple mask exposures to selectively orient features in the thin film, or be applied in combination with other alignment methods such as those described in Section 2.3.

4. Future Challenge of Sub-5 nm Patterning Using Liquid Crystals

With respect to feature sizes, the sub-5 nm features reported here are far ahead of the scaling curve pursued by the semiconductor industry. This observation implies that several critical challenges must be overcome for these materials to be integrated into existing patterning technologies. Most notably, the critical challenges are related to the development of suitable pattern transfer techniques, mechanical stability of the ultrathin features, the application of appropriate metrology tools, and the integration of the required processing operations into fabrication facilities.

4.1. Integration

As shown in Section 3, liquid crystals are highly compatible with geometric alignment techniques, which is the most well-established alignment and pattern registration method in block copolymer directed self-assembly.[14] In principle, this allows the integration of LC materials with existing patterning techniques for their extension through directed self-assembly. However, the graphoepitaxial features produced by optical lithography are not perfect, but contain their own variations known as line edge roughness (LER). LER is caused by a number of statistically fluctuating effects at small dimensions such as photon flux variations, statistical distributions of chemical species in the resist, and the nonzero size of polymers being dissolved during development. For the precise registration of LC patterns within a trench of varying width, the LER must be smaller than the feature size (<1 nm). Currently, the LER tolerance for logic patterning (transistors) is ≈1.5 nm (3σ), which is set to decrease to 0.7 nm by 2025.[143] enabling integration with LC materials.[144] The LER requirement for extension of DSA to LC materials might be met by optical immersion lithography, EUV lithography, or e-beam lithography.

4.2. Pattern Transfer

Pattern transfer is by far the most widely recognized bottleneck for sub-5 nm patterning. Common pattern transfer methods, such as plasma etching, become more precarious at these length scales, since the processing requirements become increasingly stringent and the processing windows are narrowed.[24] These processes will have to be severely optimized to allow high-fidelity pattern transfer, which represents a formidable challenge. Fortunately, there is still room for etch optimization of the self-assembled materials through molecular design, or through the selective incorporation of inorganic precursors after the self-assembly.

For block copolymers, the latter method has established itself as a promising technique to improve pattern transfer.[24,144–147] The method, commonly referred to as sequential infiltration synthesis (SIS), is related to atomic layer deposition (ALD). It is a cyclic, gas phase process based on self-limiting chemical reactions of a metal precursor with a specific domain after infiltration into a block copolymer thin film. Darling et al. first demonstrated SIS on a PS-b-PMMMA block copolymer film using alternate cycles of tetramethylethynylmum (TMA) and water vapor. TMA forms localized Al-OH and Al-CH₃ sites on the PMMA carbonyl moieties, while water produces layers of Al₂O₃. After the SIS process, sufficient etch contrast was embedded in the film to allow the production of high-aspect-ratio features by plasma etching. More recent work by Hillmyer and co-workers demonstrated the extension of the SIS process with a high-γ BCP with sub-10 nm feature sizes.[22] To date, SIS has not been demonstrated for sub-5 nm phases.

In order to obtain inorganic nanostructure arrays at the sub-5 nm scale, it is essential for pattern transfer processes such as plasma etching and SIS to proceed in a controlled fashion with high selectivity, and at defined positions within the self-assembled building blocks. The key herein will be the preparation of well-defined supramolecular architectures with a one-to-one registration of molecular components or reactive sites, and extremely sharp interfaces.[148–150] LC materials are ideally suited to address these challenges because, besides the sub-5 nm periodicities, control over the chemical functionality allows for site-selective chemistry such as crosslinking, selective.
Supramolecular interactions such as hydrogen bonding may direct individual reactive sites, positively impacting the processes of selective plasma etching or inorganic material growth with sub-nanometer resolution. Moreover, the multiple orthogonal supramolecular interactions at the root of the self-assembly, in combination with a chemical monodispersity, result in highly ordered mesophases with well-defined lattices and sharp interfaces. This stands in contrast with low-molecular-weight BCPs, which exhibit ill-defined interfaces due to composition fluctuation effects in the weak segregation regime ($\chi N \approx 10.5$).

Mechanical stability of the sub-5 nm patterns is required for their utilization as templates for pattern transfer. For LCs, this is typically achieved by chemical crosslinking of reactive molecules to form a nanostructured polymer, usually by UV-polymerization, since it can be performed at the temperature corresponding to the desired mesophase. For pattern transfer in nanolithography, the in situ polymerization of reactive LC monomers is highly challenging since defects can originate from the multicomponent nature of the reactive thin films (LC, photo initiator, inhibitor), and the polymerization shrinkage effect. An alternate approach consists of engineering an appropriate glass transition into the LC material through molecular design. Unfortunately, while glass transition behavior is observed in some LCs, it is not well understood, and additional fundamental research is required. From this perspective, the complexion of LCs with glassy polymers through supramolecular interactions could be a more practical method to fabricate systems with tunable dimensions.

4.3. Defect Density and Alignment

Defect densities are another major concern for the semiconductor industry. While defects like dislocations and disclinations become thermodynamically more favorable with low-molecular-weight materials, the kinetic barrier associated with defect annihilation is greatly reduced. In practice therefore, low-molecular-weight materials display long-range order, even when undirected, as typified by POM birefringence experiments of thermotropic liquid crystals. In addition, low defect densities are observed as a result of the improved ability to anneal away defects and direct the self-assembly. Particularly near the order–disorder transition, where the barrier associated with defect annihilation becomes $<< k_B T$, fast self-assembly dynamics are observed. For liquid crystals, a common method to obtain monolithically oriented samples is by transitioning through several phases from a low to high order. The design of materials with nematic phases (orientational order only), in addition to higher-order phases at lower temperatures, may therefore aid in obtaining monolithic alignment. The extension of computer simulation methods currently applied to BCP systems would enable both further understanding of the mechanisms of defect annihilation and optimal LC design for high order and minimal defectivity.

Obtaining vertically oriented features becomes increasingly challenging for soft building blocks with highly immiscible components, such as high-$\chi$, low-N BCPs or hybrid organic/inorganic LCs. Since the respective surface energies are increasingly disparate, the development of interfaces which are neutral to both components is increasingly difficult. The development of surface active components, in the form of additives or built-in components, may help to achieve this goal, although they will need to be tailored to each supramolecular system. It would further be beneficial to develop the graphoepitaxy approach for the vertical orientation of sub-5 nm features. Studies show that control over the surface energy of the template bottom and sidewall is crucial for achieving vertically oriented features, which can be achieved by selectively modifying the surfaces with a polymer brush.

4.4. Metrology

The need persists for appropriate metrology tools for the characterization of sub-5 nm patterned thin films where near-atomic resolution is required to accurately image features and defects. It is currently highly challenging to obtain structural information at this length scale using common top-down imaging techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). In brief, SEM is limited by its ability to discriminate individual domains through lack of contrast, while AFM is limited by the dimensions of the probe tip. Scanning tunneling microscopy (STM), has an extremely high lateral resolution ($\approx 0.1$ nm), enabling the visualization of individual molecules (Figure 3) or even atoms, but it is limited to the imaging of conductive monolayers on extremely flat, conductive surfaces. Helium ion microscopy (HIM) is a relatively new technique, which could be of significant value in the analysis of sub-5 nm patterns, HIM has a resolution between that of SEM and TEM ($\approx 0.3$ nm), and an improved material contrast. The technique has been applied to obtain high-resolution BCP images but it has not been applied to LC thin films. In order to fully understand the complexity of the thin-film structures, it is essential that the 3D morphology is studied in addition to the 2D surface arrangement. The indirect technique of grazing-incidence X-ray diffraction (GIXRD) can be used to probe the average domain structure over large areas ($\text{mm}^2$), but it is relatively insensitive to defects, the domain interfaces, and structural deviations that occur at specific locations within the film (for example at the substrate and air interfaces). Direct 3D visualization can be achieved by transmission electron microscopy (TEM), but this method is restricted by challenging sample preparation (such as embedding and cross-sectioning).

5. Conclusion

Recent advances in precise morphological control present unique opportunities for obtaining highly ordered, hybrid organic/inorganic sub-5 nm nanostructured morphologies. Coupled with directed self-assembly for 3D orientational control and large-area alignment, this exciting class of materials could lead to a broad range of impending nanotechnologies, most notably nanopatterning. Given the impact of these technologies, it is foreseeable that this thrilling field will continue to expand at a rapid pace.
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Conflict of Interest

The authors declare no conflict of interest.

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