

BLOCK COPOLYMERS

With a little help from above

Complex nanoscale patterns can be generated by combining the self-assembly of block-copolymer thin films with minimal top-down templating.

Justin E. Poelma and Craig J. Hawker

An important goal in nanofabrication is to develop a robust low-cost technique that can create arbitrary, complex structures with feature sizes of less than 20 nm. Top-down approaches, such as electron-beam lithography, can generate such structures, but they tend to be time consuming and expensive, which restricts their use in the large-scale production of devices. In contrast, bottom-up self-assembly techniques offer a high-throughput low-cost alternative that can generate 5–20 nm features over large areas. However, until recently, the range of patterns that could be created using these self-assembled strategies has been limited.

For block-copolymer lithography — a self-assembly approach that uses covalently linked chains of different polymer blocks — the choice of patterns was, for a long time, restricted to either vertical lamella or hexagonal cylinders, which limited the industrial appeal of this approach. However, the need for features smaller than those obtained through traditional photolithography is real, and block-copolymer lithography is now beginning to find its way into industrial applications. For example, IBM's Air Gap technology relies on photolithographic processes combined with steps involving hexagonal arrays of cylindrical 20-nm holes prepared from self-assembled layers of poly(styrene)-*b*-poly(methyl methacrylate)¹. This application illustrates the tantalizing opportunities of combining the best features of top-down photolithographic techniques with bottom-up block-copolymer strategies. Of equal importance is the demonstration that block-copolymer lithography is compatible with standard manufacturing techniques and can be used in modern fabrication plants with minimal re-tooling. Hence, the stage is set for innovative approaches that can control and manipulate block-copolymer self-assembly, and so address the grand challenges of nanofabrication.

Writing in *Nature Nanotechnology*, Caroline Ross, Karl Berggren and colleagues at Massachusetts Institute of Technology² now show that a sparse array of nanoscale features can be used to accurately dictate

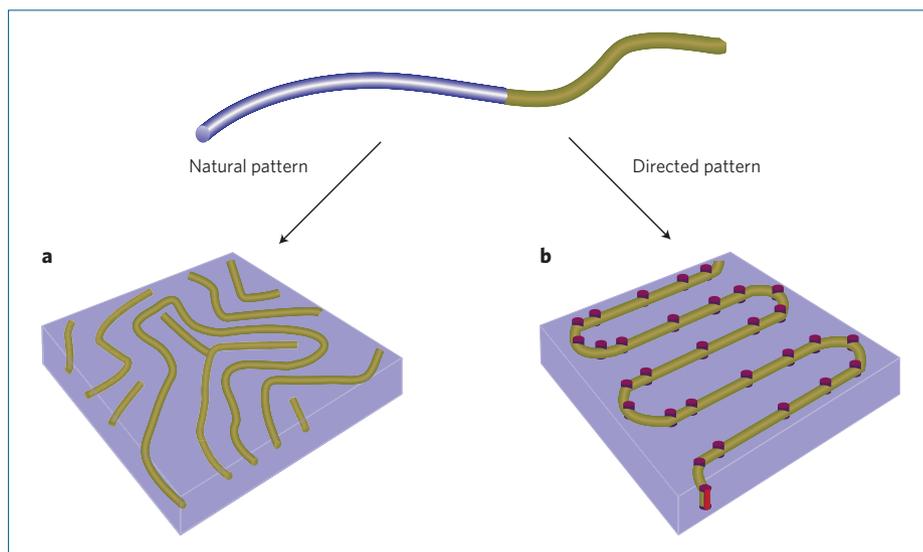


Figure 1 | Pattern generation with block copolymers. The natural self-assembly of diblock-copolymer thin films leads to poorly defined patterns (a). (The majority block-copolymer phase is depicted in light purple and the minority block-copolymer phase is depicted in brown.) However, by using a sparse template — an array of posts prepared by electron-beam patterning of an inorganic resist (depicted here in dark purple) — highly organized and asymmetric patterns can be obtained (b).

the assembly of a diblock copolymer into a wide assortment of complex, unsymmetrical features (Fig. 1). The natural domain length of the block copolymer can be controlled by its molecular weight, and the array of nanoscale features — prepared by electron-beam patterning of an inorganic resist — act as a template that occupies a few per cent of the overall wafer area. Together this allows the researchers to create parallel 20-nm features that can be variably rotated through 90° with excellent registration and minimal defects. In a potentially more far-reaching finding, the authors were also able to demonstrate that certain template features, easily accessible with electron-beam lithography, could direct the assembly of diblock copolymers into a complex array of periodic and aperiodic features on the same wafer. One of the most visually striking examples is a tight, meandering serpentine structure (Fig. 1b). This ability goes a long way to fulfilling the initial demands of the International Technology Roadmap for Semiconductors³,

which calls for a robust, commercially viable nanopatterning technique.

In combination with a number of other recent advances in block-copolymer lithography, such as the use of chemical patterning⁴, graphoepitaxy⁵ and supramolecular diblock-copolymer mixtures⁶, it is becoming increasingly clear what the focus of future research should be. By exploiting the ability to accurately control the molecular weight and chemical functionality of block copolymers, a degree of molecular engineering can now be directed towards pattern generation. Through a combination of supramolecular interactions, molecular topology, surface chemistry and structure control, in association with judicious use of top-down techniques, the design of defect-free registered systems containing sub-10-nm features with multiple sizes and patterns in the same layer may be possible.

A greater fundamental understanding of processing conditions and phase separation will also enhance the preparation and pattern

transfer of these systems. The ultimate goal being the fabrication of 12-inch wafers, with an average net throughput of ~1 wafer every 1–2 minutes by means of single wafer or batch processing. If successful, these next-generation block-copolymer lithographic systems could make a dramatic impact on one of the world's largest and most important industries, and its continued adherence to Moore's Law.

Given the potential impact, one of the most lasting outcomes from this latest work may in fact be its influence on the general top-down versus bottom-up argument. This intellectually stimulating and visually

appealing result from the MIT researchers clearly illustrates that success may actually be a compromise incorporating aspects of top-down and self-assembly strategies. The challenge is to intelligently exploit the advantages of each, using expensive and time consuming top-down strategies only when necessary to direct and control the self-assembly strategies. With the proper combination of techniques, researchers will be able to develop simple and powerful self-assembling lithographic platforms for patterns and feature sizes that can at present only be imagined. □

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ORGANIC CONDUCTORS

A dash of salt is superconducting

In an experimental *tour de force* involving ultrahigh vacuum and low-temperature scanning probe techniques, researchers have created organic nanostructures that show evidence of unconventional superconductivity.

James S. Brooks

It is the opinion of some researchers in the organic-conductor community that organic charge-transfer salts — structures that come in one-, two- and three-dimensional forms — embrace most of the possible physical ground states of matter. Naturally, these researchers hope that it will be possible to exploit the marvellous properties of these materials in devices, ideally as single- or few-layer crystalline films. However, it may be that the impressive ability of organic charge-transfer salts to self-assemble into three-dimensional structures has, so far, kept them away from the atomically flat world occupied by epitaxial thin films. Now, writing in *Nature Nanotechnology*, Saw-Wai Hla and co-workers report that they have succeeded in opening up what might be a new route to the epitaxial-like growth of these materials¹. Moreover, they have found new physics along the way.

Hla and colleagues worked with a single-crystal charge-transfer salt called λ -(BETS)₂GaCl₄, where BETS is a molecule called bis(ethylenedithio) tetraselenafulvalene that donates electrons to GaCl₄, which accepts them (Fig. 1). It is this transfer of charge from donors to acceptors that stabilizes charge-transfer salts and is responsible for many of their unique properties. For example, below a critical temperature these compounds lose their resistance to electric current and become superconducting. Alternatively, when the gallium atom is replaced with an iron atom, which is magnetic,

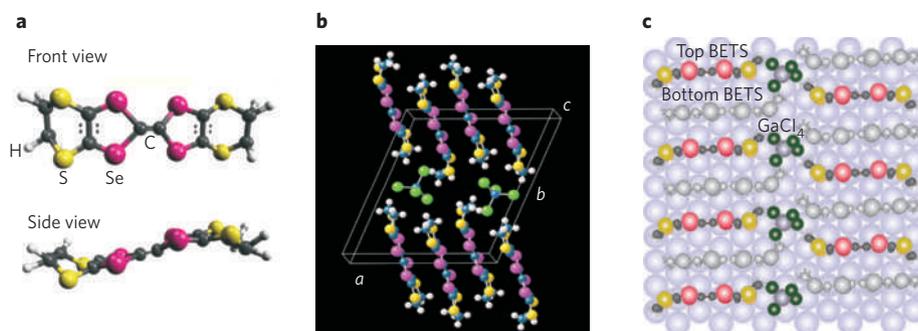


Figure 1 | The different faces of (BETS)₂-GaCl₄. **a**, BETS molecules are nearly planar, and contain five- and six-sided rings made of carbon (black), sulphur (yellow) and selenium (pink) atoms; hydrogen atoms are shown in white. **b**, BETS molecules and GaCl₄ molecules crystallize into the λ -(BETS)₂GaCl₄ bulk structure shown here. (In this panel the carbon atoms are blue, as are the gallium atoms; chlorine atoms are shown in green.) In simple terms, there are two face-to-face BETS molecules in contact with each GaCl₄ molecule; this structure is repeated (stacked) along the *a*, *b* and *c* axes, forming the crystal. **c**, These bulk crystals can be evaporated and deposited onto an ultraclean atomically flat Ag(111) surface to form this nanoscale (BETS)₂-GaCl₄ structure in which one BETS molecule (shown in grey) is close to the silver surface, with the other molecule (shown in colour) farther away. The BETS molecules form stacks along the vertical direction, separated by GaCl₄ molecules in (BETS)₂-GaCl₄ pairs, mimicking the bulk crystalline molecular arrangement. All panels reproduced from ref. 1.

the system can show a combination of antiferromagnetism and field-induced superconductivity. Moreover, unconventional superconductivity in organic superconductors — including the possibility that the Cooper pairs of electrons that are responsible for the superconducting state do not show the *s*-wave symmetry found in conventional superconductors — has been reported in some experiments^{2–4}.

In many cases, efforts to produce high-quality single-crystal thin films of charge-transfer salts by the co-deposition of the donor and acceptor components on silicon or similar substrates have resulted in low-quality polycrystalline films that do not have the useful physical properties found in bulk samples. To overcome this problem Hla and co-workers — who are based at Ohio University in the US and laboratories in Japan and Germany — used