

can be resolved with a spatial resolution of ~ 20 nm. Furthermore, the potential for high-resolution magnetic imaging is demonstrated by resolving Abrikosov vortices with 120 nm minimum lateral distance in a Nb thin film at $B \sim 0.2$ T (Fig. 1b). The combination of high spatial sensitivity with high bandwidth suggests the approach could have a range of exciting applications including the nanoscale investigation of dissipation and noise due to vortex dynamics in superconductors.

Despite their impressive performance, SQUID-on-tips still have room for further improvement. Vasyukov and colleagues have shrunk the SQUIDs to unprecedented values, but at this scale it becomes increasingly difficult to use conventional flux bias and feedback routines for maintaining optimum device performance while an external field is swept. This causes an oscillation of the sensitivity with magnetic field for the devices and loss of sensitivity on approaching zero field. The latter might be avoided by implementing asymmetries in the SQUID-on-tips.

Moreover, the comparison between lead-based devices and (less sensitive) niobium-based devices indicates that a careful choice of material with proper characteristic parameters, such as the superconducting coherence length, may further improve device performance. In this context, a better understanding of the properties of the constriction junctions should allow for further systematic optimization. And in this regard, it still remains to be seen whether other types of nano-SQUID, such as those based on the cuprate superconductors that can operate in huge magnetic fields, may be able to compete. Another open issue is the experimental determination of the coupling strength of a tiny magnetic dipole to a nano-SQUID; so far, the spin sensitivity is usually derived by measurements of the flux noise and estimates of the coupling strength, which together yields $S_n^{1/2}$ as an important figure of merit for these devices.

The work of Vasyukov and co-workers is an important step towards quantitative nanoscale magnetic imaging. Furthermore,

the ability to easily control the nanoscale position (and orientation) of the SQUID-on-tip relative to a magnetic nanoparticle (fixed on a surface), will most likely boost future investigations on individual magnetic nanoparticles and improve the understanding of their properties, which are very hard to access at present. \square

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References

1. Vasyukov, D. *et al.* *Nature Nanotech.* **8**, 639–644 (2013).
2. Clarke, J. & Braginski, A. I. (eds) *The SQUID Handbook: Fundamentals and Technology of SQUIDs and SQUID Systems* Vol. 1 (Wiley, 2004).
3. Voss, R. F., Laibowitz, R. B., Broers, A. N. *Appl. Phys. Lett.* **37**, 656–658 (1980).
4. Special Section: Focus on NanoSQUIDs and their Applications *Supercond. Sci. Technol.* **22**, 064001–064013 (2009).
5. Kirtley, J. *et al.* *Appl. Phys. Lett.* **66**, 1138–1140 (1995).
6. Wernsdorfer, W. *Adv. Chem. Phys.* **118**, 99–190 (2001).
7. Finkler, A. *et al.* *Nano Lett.* **10**, 1046–1049 (2010).

NANOLITHOGRAPHY

Painting with block copolymers

A combination of self-assembly and jet printing can be used to create block copolymer films with complex structures and tunable periodicities across a large substrate.

Richard A. Register

Block copolymer nanolithography — a process in which self-assembled polymeric nanodomain patterns are transferred into a substrate or replicated in an inorganic material — can be used to create precise nanoscale structures, and can potentially augment or replace traditional top-down lithographic methods in the fabrication of electronic devices¹. The simplest block copolymer, an AB diblock, consists of a chain of polymer A covalently end-linked to a chain of polymer B. The chemical dissimilarity between the A and B blocks, such as that arising when polystyrene (PS) is covalently linked to polymethylmethacrylate (PMMA), drives spatial separation between the two. However, because the blocks are covalently linked, this separation can occur only on the size scale of the polymer coil (typically about 10–100 nm). As a result, the material adopts an internal nanodomain structure

(Fig. 1) whose symmetry depends on the relative lengths (volume fractions) of the A and B blocks, and whose periodicity depends on the total length of the block copolymer chain (molar mass). Similar self-assembled structures can also form when the block copolymers are confined to thin films with thicknesses on the order of the nanodomain periodicity. These thin-film structures can be used as lithographic masks.

For any given block copolymer, there is a pronounced free energy minimum associated with a particular symmetry and periodicity. This thermodynamic driving force ensures that, after a brief anneal, the polymer will reproducibly adopt a particular structure across even a large substrate. However, this uniformity is also a weakness, because obtaining more complex patterns, comprising different nanoscale structures at different points across a substrate, becomes difficult.

Writing in *Nature Nanotechnology*, John Rogers, Heejoon Ahn and colleagues — who are based at the University of Illinois at Urbana-Champaign, the University of Chicago, Argonne National Laboratory and Hanyang University — now show that complex block copolymer patterns containing different symmetries and locally tunable periodicities can be created by using a combination of self-assembly and jet printing².

In the approach, PS-PMMA block copolymers are deposited on a silicon wafer substrate from solution using electrohydrodynamic jet printing (Fig. 1). The process can rapidly ‘paint’ lines of block copolymer ‘inks’ with widths of less than 500 nm and edge roughnesses of less than 50 nm over wafer-scale distances. Films as thin as these dry quickly, so different parts of the pattern can be written sequentially using inks containing PS-PMMA block copolymers of different block

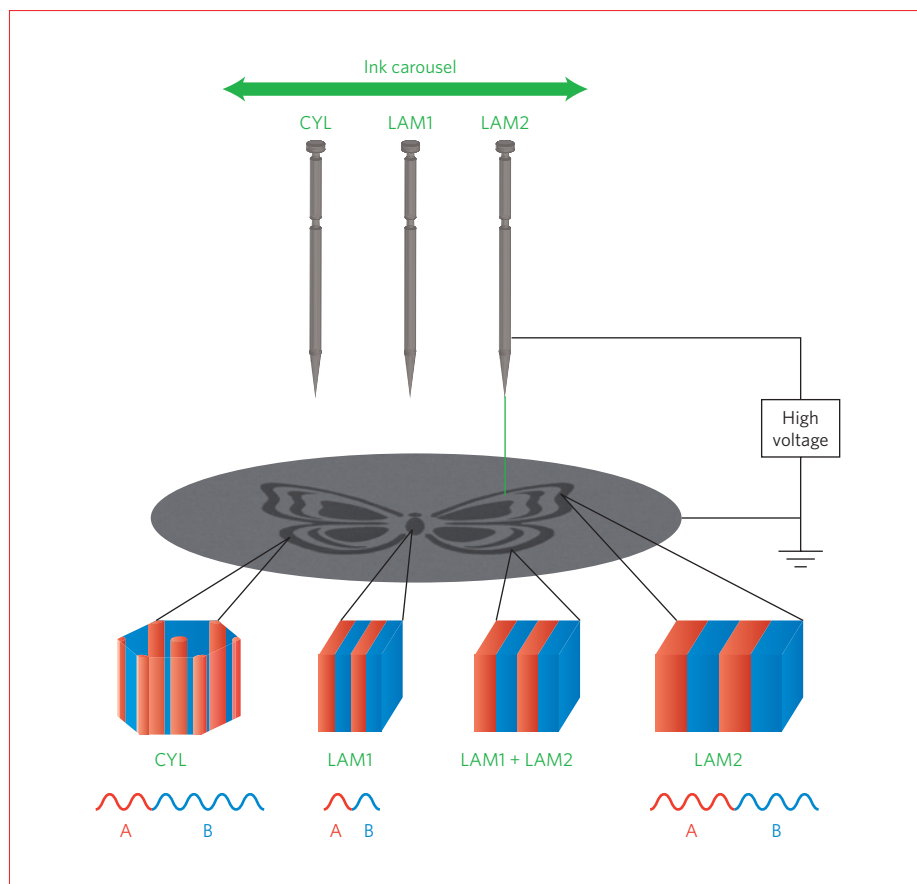


Figure 1 | Schematic of the electrohydrodynamic jet printing process used to paint hierarchical micrometre-to-wafer-scale-sized patterns with block copolymer inks, where the block copolymer structure and periodicity (typically 20–50 nm) can be varied locally². A high voltage is applied to a fine capillary through which the block copolymer ink is pumped, to draw it into a fine continuous stream (green line), which is deposited on the substrate in the shape of the desired pattern (here, a butterfly). By sequentially depositing layers from different inks rotated through a carousel, the resulting nanodomain structure can be cylindrical (CYL), a short-period lamellar structure (LAM1), a longer-period lamellar structure (LAM2), or an intermediate-period lamellar structure (by blending LAM1 and LAM2).

volume fractions or molar masses; a brief thermal anneal then allows the chains to self-assemble into nanodomains.

The researchers show that by sequentially depositing two different inks over the same spot on the substrate, followed by annealing, it is possible to obtain any domain spacing that is between the nanodomain spacings of the two pure inks, provided the two are fully miscible. Blending block copolymers to tune morphology and periodicity is a well-established idea³, and it has recently been refined to allow the width of one type of domain to be varied (for example, in a lamellar structure) while holding the other constant⁴. But blending by sequential deposition, with control over the relative thicknesses of the deposited films, allows the researchers to vary the periodicity

continuously at any point on the substrate, much like an artist who can achieve any shade of green by mixing the proper ratio of blue and yellow. This method is far more robust and high-throughput than earlier versions in which block copolymers with various different compositions needed to be premixed before deposition.

On unmodified silicon substrates, the preferential interaction of the substrate with the PMMA, rather than with the PS block, drives the nanodomains (lamellar or cylindrical) to lie parallel to the substrate. Building on an established approach⁵, Rogers and colleagues deposited a random copolymer mat on the substrate to impart a non-preferential wetting character, inducing the domains to stand perpendicular to the substrate. In the future, the same electrohydrodynamic jet

printing set-up could perhaps be used to pre-pattern the substrate with the random polymer mat as well, and therefore achieve control of both the nanodomain orientation (parallel versus perpendicular) and the nanodomain spacing in a single step. This method would be a versatile alternative to the lithographic processing⁶ applied to polymer mats in the present work to spatially vary the wetting character of the substrate.

Although through-film orientation is critical, achieving control of in-plane nanodomain alignment is equally important⁷ because most future devices will require a preferred nanodomain alignment at every position on the substrate. The process described by Rogers and colleagues is particularly appealing because it is compatible with established techniques of directed self-assembly, in which either extreme ultraviolet lithography is used to generate a chemical pattern on a crosslinked polymer mat⁶, or electron-beam lithography is used to fabricate a topographic pattern in the wafer substrate. However, it would be far simpler if the printed features could themselves act as templates for the nanodomains. Preliminary work in this regard⁸ has suggested that the curved cross-section of the printed lines, dictated by the contact angle of the block copolymer with the substrate, can drive the nanodomains to orient perpendicular to the contact line. Variations in film thickness can also be used to align the planes defining the two-dimensional hexagonal array of dots formed by cylindrical nanodomains standing perpendicular to the substrate⁹. Clearly numerous opportunities and challenges lie ahead, but Rogers and colleagues have for now provided new colour to the field of block copolymer nanopatterning. □

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References

- Kim, H.-C., Park, S.-M. & Hinsberg, W. D. *Chem. Rev.* **110**, 146–177 (2010).
- Onses, M. S. *et al. Nature Nanotech.* **8**, 667–675 (2013).
- Sivaniah, E. *et al. Macromolecules* **41**, 2584–2592 (2008).
- Park, S.-B. & Zin, W.-C. *J. Polym. Sci. B* <http://dx.doi.org/10.1002/polb.23353> (2013).
- Han, E. & Gopalan, P. *Langmuir* **26**, 1311–1315 (2010).
- Liu, C.-C. *et al. Macromolecules* **44**, 1876–1885 (2011).
- Marencic, A. P. & Register, R. A. *Annu. Rev. Chem. Biomol. Eng.* **1**, 277–297 (2010).
- Kim, B. H. *et al. Adv. Funct. Mater.* **19**, 2584–2591 (2009).
- Park, S. *et al. Science* **323**, 1030–1033 (2009).

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