Copolymer Templates: A Self-Assembling Route to High-Density Arrays of Functional Nanostructures

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Introduction. The self-assembling microphase separation of diblock copolymers provides a simple, convenient route to well-defined arrays of functional nanostructures. This project overview describes recent techniques developed to transform diblock copolymer thin-films into robust nanoporous array templates, and with subsequent chemical modification, into functional arrays of nanowires, patterned surfaces, or integrated devices. Nanofabrication by diblock copolymer lithography is a massively-parallel, fast processing technique. Moreover, since it uses polymers already familiar to the microelectronics industry, it is compatible with many conventional process steps and amenable to integration. This new approach offers rapid fabrication of nanoscale elements with dimensions that can be tailored by the molecular weight of the copolymer in the 5-100 nm range — the scale that is likely to impact nanotechnology in applications ranging from magnetic data storage to optics to microelectronics. Project objectives focus on advancing the capabilities of nanoporous templates through polymer engineering and using these templates for the creation new functional materials and devices that exploit nanoscale structure.

Template formation. A diblock copolymer molecule is comprised of two chemically-distinct polymer blocks covalently linked to each other at one end. Whereas a homopolymer mixture of the two polymers would macroscopically phase separate (like oil and water) the diblock copolymer exhibits a "microphase" separation. Here, the molecules self-assemble into arrays of nanoscopic spheres, cylinders, or lamellae, depending on the volume fraction of the two blocks. The NIRT group has developed techniques that use thin films of asymmetric "cylindrical phase" diblock

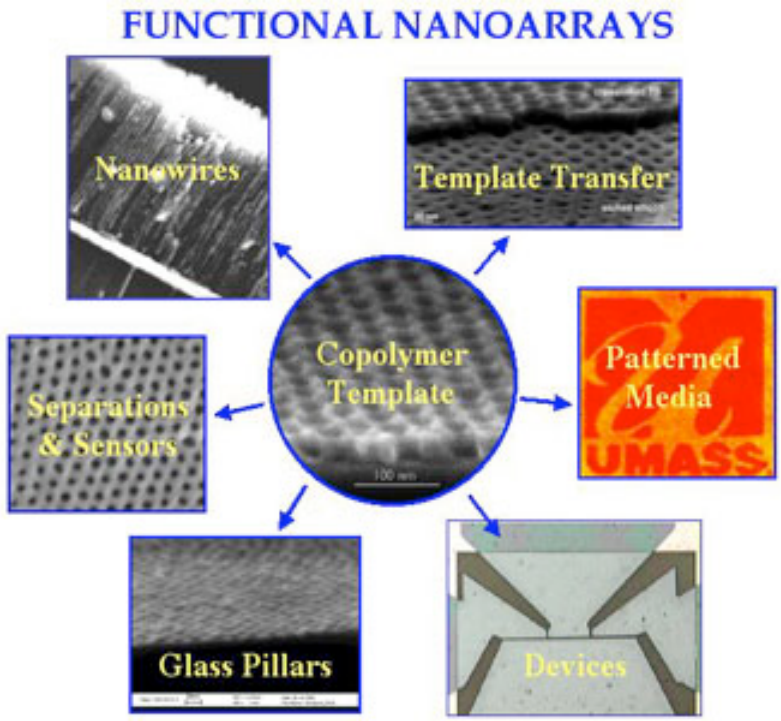

Figure 1. Several application areas enabled by the diblock copolymer nanoporous template fabrication method.

copolymers of polystyrene and polymethylmethacrylate P(S-b-MMA) to create nanoporous array templates. To form the nanofabrication template, the polymer is spin-coated in solution onto a substrate to produce a polymer film of any chosen thickness in the range of 20 nm to 10 μm. Two methods have been developed to orient the PMMA cylinders *perpendicular* to the substrate — using either controlled interfacial interactions or an external applied electric field. Subsequent UV or electron-beam irradiation followed by an acetic acid rinse remove the PMMA while simultaneously cross-linking the PS. This results in a polymer film with a periodic hexagonal array of nanopores (Fig. 1, center and left) — a robust template for nanofabrication. Ongoing research includes the development of long-range ordering of microphase structure, tuning pore diameter and period dimensions, and the synthesis of chemically functional polymer surfaces.

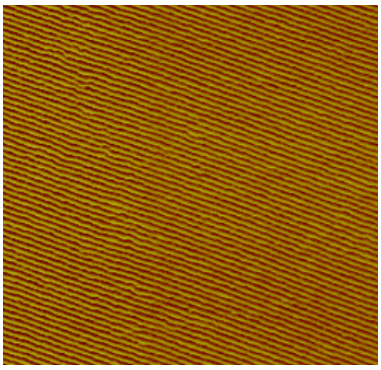

Figure 2 Long range ordering of PS-PBD lateral cylinders over tens of microns, induced by solvent flow.

Arrays of Nanowires. Surface-selective chemical techniques are used to fill the pores with other materials to create arrays of nanoscale elements. For example, starting with a gold-coated silicon substrate, cobalt can be electrodeposited within the pores to create an ultrahigh-density array of 13 nm diameter magnetic nanowires, laterally positioned on a ~25 nm array period (Figure 1, upper left). Producing nanowires of desired length can be achieved easily through control of the electrodeposition process. These magnetic nanowire arrays may offer a simple route to future ultrahigh density data storage media with capabilities of 1.2 terabits/in^2 (roughly 25 DVD's worth of data on a disk the size of a quarter). Under appropriate fabrication conditions, the perpendicular coercivity of the cobalt nanowire array exceeds 1.7 kOe at 300K, due to cylindrical shape anisotropy and nanowires of diameter producing single magnetic domain behavior. The cylindrical shape of the nanowires helps to stave off the onset of superparamagnetism while retaining a high packing density. The close spacing of the wires makes magnetostatic interwire interactions, and the modeling thereof, an important consideration in potential applications. Through manipulation of electrodeposition conditions c-axis oriented cobalt can be grown, which results in alignment of magneticrystalline anisotropy and shape anisotropy axes.

Laterally Patterned Nanoarrays. These nanoarrays can be patterned into arbitrary designs using conventional lithographic exposure in selective regions, thereby creating a means to bridge structural scales from the molecular to the macroscopic. To do so, the virgin diblock copolymer film can be exposed laterally by writing with an electron beam, or by UV irradiation through a mask (Fig. 1, right). This enables the fabrication of functional nanoarrays in selected areas such that the polymer template can be used as one-step in a multi-step lithographic device fabrication scheme. For example, a unique type of giant magnetoresistance device has been made (Fig. 1, lower right), which consist of a magnetic nanowire array atop a gold film patterned in a 4-wire configuration. This device is used to investigate spin-dependent scattering in a "current-in-plane" geometry where the scattering interface is spatially periodic. This device was fabricated by integrating electron-beam lithography with copolymer template lithography in two subsequent steps. Electrodeposition of cobalt results in nanowires (seen as black in the figure) within the exposed square region, but only atop the gold underlayer. The magnetoresistance behavior of

these devices can be easily manipulated by geometric changes: the length of the nanowires, their diameter and their spacing. This has now been extended to facilitate electronic transport measurements through nanowires with top and bottom electrode contacts, enabling the use of anisotropic magnetoresistance as a tool to investigate the magnetization reversal in magnetic nanowires.

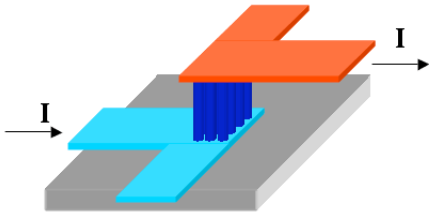

Figure 3 Schematic of vertical nanowire electron transport device.

Education. A graduate course in Nanostructure Physics is currently offered and an interdisciplinary course in Nanoscience is in development. Research students receive training in new laboratory technique with the aid of web-based digital video tutorials. REU and RET grants are used to supplement the educational objectives with hands-on training for undergraduate and teachers.

Future. These studies to date have only begun to explore the intrinsic versatility of this self-assembly based fabrication technique. This copolymer nanoarray fabrication technique is now developed to the point where it has become routine and is used in varied types of experiments. For example, it has been recently used as a means to create nano-etched silicon, as an etch-mask to tailor the exchange bias in magnetic bilayers by way of nanoscale structuring, as an electrochemical nanoelectrode array, to grow silicon oxide glass posts, and for field emission arrays.

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