

Functional Nanostructures Based On Polymeric Templates

NSF Functional Nanostructures Grant 9871782

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Project Objectives. The molecular self-assembly of diblock copolymers provides a simple, robust route to create well-defined arrays of functional nanostructures. In recent work, funded by the *NSF Partnership in Nanotechnology: Functional Nanostructures* program, we developed techniques by which diblock copolymer thin-films can be transformed into robust nanoporous array templates, and then with subsequent chemical modifications, into arrays of functional nanostructures. This simple approach offers rapid fabrication of nanoscale elements with characteristic dimensions that can be chosen from the 5-100 nm range — a scale that is likely to impact nanotechnology with applications ranging from magnetic data storage to chemical sensing to microelectronics.

Template formation. These experiments have centered on the use of thin films of asymmetric diblock copolymers of polystyrene and polymethylmethacrylate P(S-b-MMA) to create the nanoporous array templates. The template can be made to any chosen thickness in the range of 20 nm to 10 μm , since the polymer is initially applied by spin-coating. We have developed two methods to orient the PMMA cylinders *perpendicular* to the substrate — using either controlled interfacial interactions¹ or an external electric field.² Subsequent UV or electron-beam irradiation followed by an acetic acid rinse facilitates removal of the PMMA while simultaneously cross-linking the PS. This results in a film with a periodic hexagonal array of nanopores as shown schematically in Figure 1. These geometric parameters can be controlled and tuned by the copolymer molecular weight and block fraction.

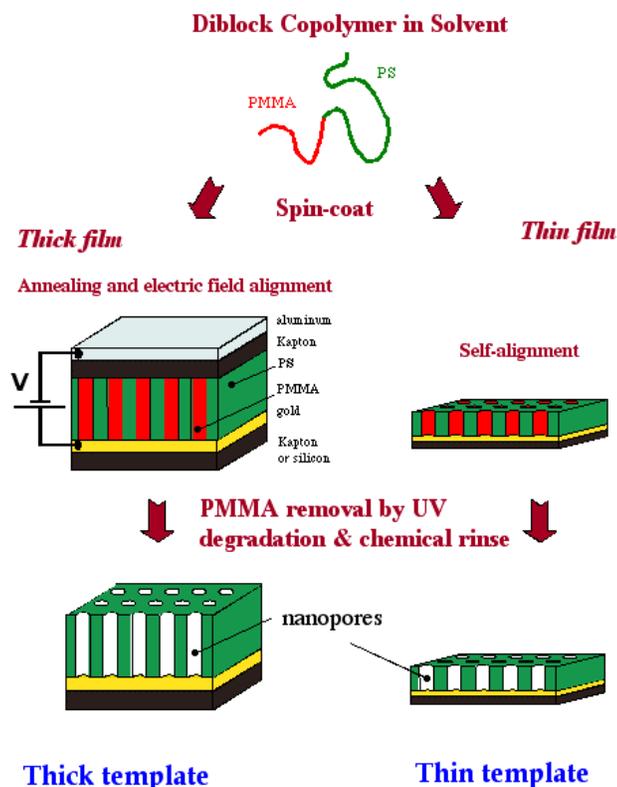


Figure 1. Copolymer template formation.

Functional Nanostructure Arrays. Since the underlying substrate is exposed at the base of each pore, we are able to use surface-selective chemical techniques to fill the pores with other materials to create functional nanoarrays. In the case of a metallic underlayer, electrochemical deposition is used to fabricate

nanowire arrays. With silicon oxide substrates chlorosilane hydrolysis is used to make glass nanopillars. The processing is inexpensive, amenable to integration, and has been performed on both rigid and flexible substrates.

Figure 2 illustrates several different avenues that we are pursuing in using these arrays. In particular, these arrays are being used to: fabricate an array of nanowires by metal electrodeposition;³ as a transfer mask to pattern the substrate beneath by chemical etching;^{4,5} as a scaffold to create patterned magnetic media with element densities in excess of 1.2 terabits per square inch;³ as a nanoelectrode array for use in electrochemical sensing; and as a membrane having well-defined pore size, pore arrangement, and surface properties. These nanoarrays can be patterned into arbitrary designs using conventional lithography in selective regions, thereby creating a means to bridge structural scales from the molecular to the macroscopic.

This copolymer nanoarray template fabrication technique is now developed to the point where it has become a routine fabrication process, used in varied types of experiments. For example, it has been recently adopted by our collaborators at IBM T.J. Watson Research Center as a means to create nano-etched silicon.⁵ In a separate study, the diblock templates were used as an etch-mask to tailor the exchange bias in magnetic bilayers by way of nanoscale structuring.⁴

Terabit-Density Nanowire Arrays. As shown in Figure 3, cobalt metal can be electrodeposited into the pores of a diblock template to create an ultrahigh density nanowire array.^{3,6} The polymer templates are hydrophobic, necessitating the use of an alcohol surfactant in the plating bath. These magnetic arrays may offer a simple route to future ultrahigh density data storage media with capabilities of 1.2 terabits/in² — two orders of magnitude more dense than the best available commercial media. The perpendicular coercivity of the cobalt nanowire array is much enhanced as compared to bulk or thin film cobalt, a direct result of a nanowire diameter smaller than magnetic domain size. These single-domain nanowires and their enhanced coercivity make this system a strong candidate for patterned perpendicular media data storage applications.

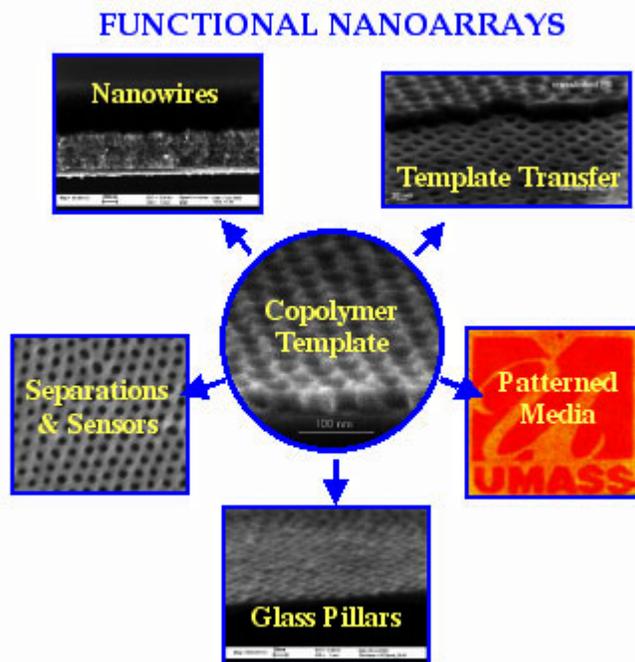


Figure 2. Some research areas enabled by diblock copolymer templates.

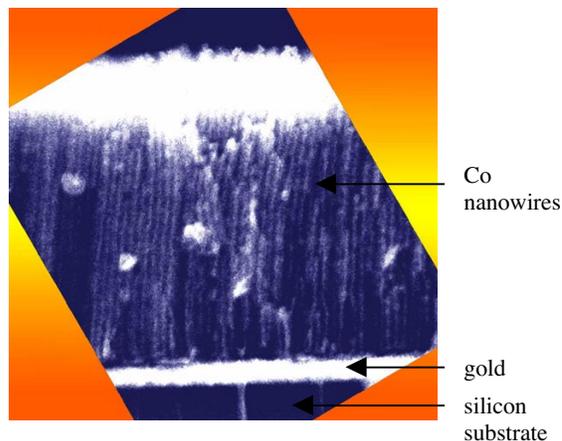


Figure 3. SEM micrograph of 14 nm diameter x 500 nm long cobalt nanowires grown in a copolymer nanoarray template.

Laterally Patterned Nanoarrays. Since electron-beam or UV irradiation is used to “expose” the virgin copolymer film, such films can be patterned laterally to produce nanoarrays in select regions (Figure 4). Experiments have been carried out to optimize the final pattern structure parameters (e.g., lithographic contrast) with respect to exposure conditions and determine design margins. Small-angle x-ray scattering and atomic force microscopy provide crucial structural characterization of the array structure at every processing step. Complementary multilayer electrodeposition experiments have been carried out to help develop full multiscale control of the array architecture — on length scales which range from molecular to macroscopic. Combining self-assembly with conventional lithography enables both lateral and 3D control of integrated structures based on the nanoarray fabrication technology.

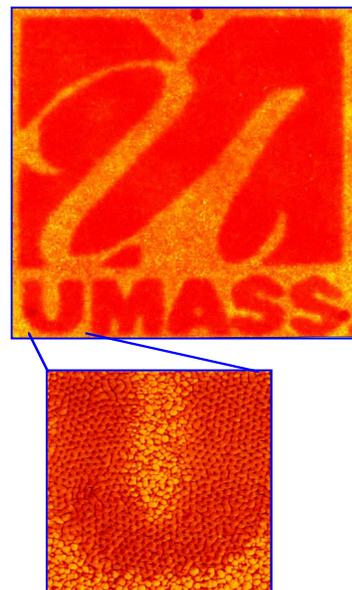


Figure 4. A nanoporous copolymer template, laterally patterned by electron-beam exposure and internally patterned by diblock copolymer assembly.

Future. These studies to date have only begun to explore the intrinsic versatility of these self-assembling materials. New avenues of polymer manipulation are being pursued to extend the range of these materials, including a designed variation of the molecular weight of the copolymer, the volume fraction of components, the chemical composition of the copolymer, mixtures of the copolymer with homopolymers and the use of multiblock, as opposed to diblock, copolymers. The impact of this advanced level of control will affect all of the application areas mentioned above. As an example, to optimize the properties of the magnetic nanowire arrays, new templates will allow tuning of the dipolar magnetic coupling by using smaller pore diameters, larger pore-to-pore spacing, and optimized wire length. Improvements in the long-range order of the arrays will enhance the signal-to-noise performance of the media, and further, allow for the possibility of addressing single nanowires (one-wire, one-bit) for future terabit technologies.

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