Nanostructured Surfaces with Long-range order for Controlled Self-Assembly

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A variety of applications for self-assembled systems (e.g. block copolymers, quantum dots, or pores in anodic alumina) have been proposed. For example, self-assembled arrays of magnetic nanoparticles may be useful as data storage media, while arrays of quantum dots could be used in semiconductor lasers. Although self-assembled systems typically have good short-range order, they lack long-range order, which limits their usefulness in some of these applications. The aim of our work is to achieve templated self-assembly, i.e. to control the position and geometry of arrays of nanostructures over large areas with precise long-range order.

We are studying several self-assembled systems, including the growth of SiGe quantum dots by chemical vapor deposition, the formation of porous alumina films by anodization, the phase separation of thin films of block copolymers, and the agglomeration of thin metal films. In each case the self-assembly process is carried out on substrates that have been patterned with periodic modulation (topographic or chemical). These substrates are prepared using interference lithography, which allows large areas to be patterned with periodic structures using the interference of laser beams to expose resist on the substrate. We are looking in particular for methods to control nanoscale self-assembly by larger length scale substrate features, for instance using 250 nm wide substrate grooves to template the formation of 25 nm block copolymer domains. These methods will allow the hierarchical assembly of nanostructures, by combining 'top-down' (interference lithography) and 'bottom-up' (self-assembled) structures, to obtain sub-lithographic features.

1. Substrate preparation by interference lithography

At present we can produce large-area arbitrary period gratings with periods down to ~180 nm using a Lloyds mirror interference lithography system, and a single grating period of 100 nm with AIL (achromatic interference lithography). These structures have been used for a variety of experiments described below. More recently we have been working on materials issues and designs towards spatial frequency doubling with an on-wafer scheme called an integrated thin film interferometer (Fig. 1). This would allow us to generate gratings with arbitrary periods down to 85-90 nm, while opening the door to periods down to ~65 nm or even 45-50 nm using a 193 or 157 nm laser. The ability to generate periods well below λ/2 is one of the key benefits of the thin film interferometer, and is possible because the diffracted orders from the parent grating are propagating inside a high index material, effectively reducing the wavelength. Critical to the success of this process is the suppression of the zero-order diffracted beam from the parent grating. In order to do this, the material from which the gratings are made must be highly transparent such that the parent

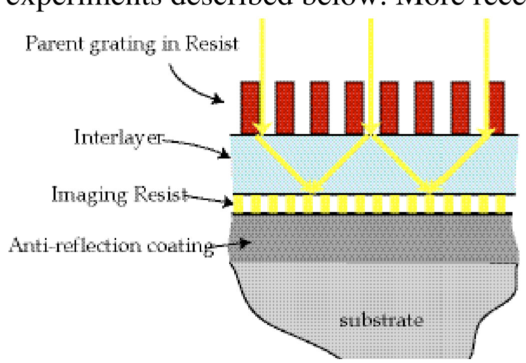

Fig. 1: An integrated thin film interferometer. Near-field spatial-frequency doubling from a parent photoresist grating is captured in a second layer of resist lower in the stack. The parent grating and interlayer can be washed away to reveal the daughter grating.

is a phase rather than amplitude grating. Thus, one requirement of the photoresist used for the parent grating is that it be sensitive enough to expose at 325 nm, while being transparent enough to suppress the zero-order diffraction at 193 nm. This unusual set of properties turns out to be unavailable in commercial resist products, but we have been modifying a commercially available 193 nm resist so that it becomes sensitive at 325 nm without losing the transparency at 193 nm. We are currently working on optimizing the processing parameters to achieve the best resist profiles.

2. Templating of block copolymers

Block copolymers self-assemble to form small-scale domains whose size and geometry depend on the molecular weights of the two types of polymer and their interactions. The domains have a very uniform distribution of sizes and shapes. We have been using block copolymers as templates for the formation of structures such as 35 nm diameter Co/Cu/NiFe magnetic particles, by selectively removing one type of domain and using the resulting template to pattern a magnetic film. To induce long-range order we use graphoepitaxy, i.e. the polymer is templated by artificial topographical patterning. Block copolymers have been spin-cast on shallow silica grating substrates made by interference lithography. For block copolymer PS/PFS 33/10, well-ordered structures form in the grooves of the gratings with all the close-packed rows aligned within the grooves (Figure 2), provided the groove width is less than about 300 nm wide. We have found that the number of rows within the groove, the spacing of the rows, and the deliberate introduction of defects such as vacancies and dislocations, can be controlled by adjusting the groove dimensions (Ref. [2]).

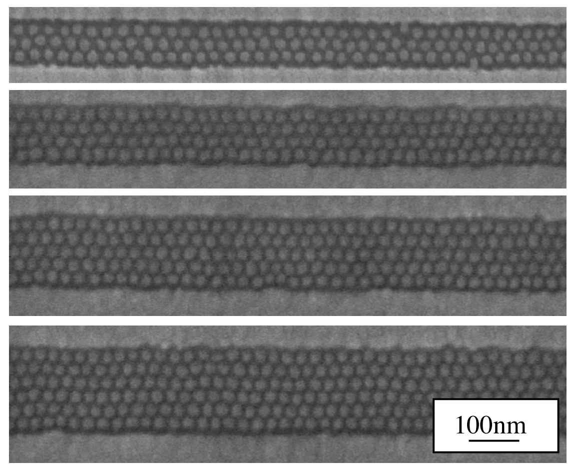

Fig. 2. Orientation of spherical block copolymer domains occurs by confining the polymer within shallow grooves, to give 3,4,5 or 6 rows of domains.

3. Growth of anodic alumina

When aluminum is anodized, the resulting oxide film contains a hexagonal arrangement of pores or channels running through the film. The pores are locally close packed, but lack long range order. We have developed a way of ordering the pores, for instance to form a regular square or hexagonal array. This is done by etching an array of shallow holes into a silicon wafer, coating the wafer with an aluminum film, then anodizing the film to form alumina. The pores in the alumina film form in places determined by the pattern originally etched into the silicon. Additionally, by changing the anodization conditions the periodicity of the structure can be halved (Figure 3). Regular porous films could be useful as lithographic masks, or as templates for growing structures such as nanowires or “antidot arrays” (films with regular hole patterns), all of which have properties very different from their bulk counterparts. For example we have coated the top of the alumina with a magnetic film; the resulting holes in the magnetic film change its coercivity and magnetoresistance and the behavior has been modeled. We have grown magnetic nanotubes within the pores using a chemical reduction process, and we have also filled them by electrodeposition of Cu. (Ref. [3])

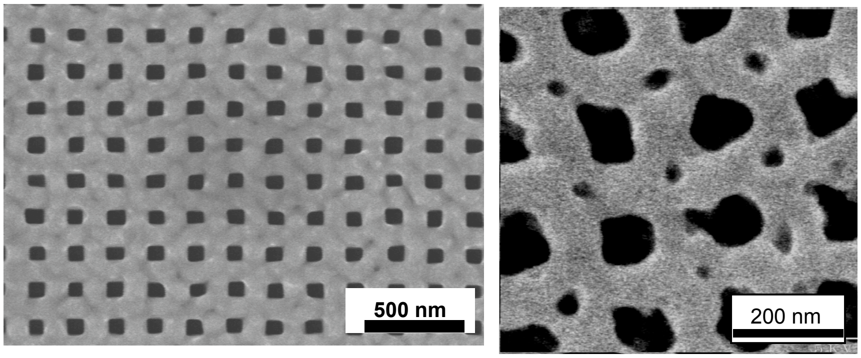

Fig. 3. left: An example of an array of pores in alumina with a square arrangement, made by coating a silicon substrate with aluminum then anodizing it. The silicon contained a square array of indentations made by etching, and these templated the formation of the pores. Right: by changing the anodization conditions, additional small pores are nucleated on a sub-lithographic length scale.

4. Agglomeration of metal films

We have begun experiments to study how initially continuous thin films agglomerate (i.e. they break up into islands on annealing). We are using the Au/silica system as an example because Au wets silica poorly and agglomerates readily. We have already examined agglomeration in films deposited onto smooth silica as a function of annealing time, temperature and Au thickness. We are now looking at the effect of substrate topography on this process. For example, agglomeration occurs with a very different morphology on substrates patterned with shallow grooves or pyramids. Related to this work, we have begun to consider faceting of MgO substrates on annealing, in collaboration with J. Floro (Sandia National Lab.). The aim is to create arrays of metal islands on facetted MgO surfaces and examine their optical properties.

5. Quantum dot growth

In collaboration with F. Ross of IBM, we have examined how topographic substrates affect the growth of quantum dots that form via Stranski-Krastanov growth. We have used in situ electron microscopy to observe the nucleation of Ge islands on lithographically patterned Si(001) mesas. Images were obtained at video rate during chemical vapour deposition of Ge, using a reflection electron microscopy geometry which allows nucleation to be observed over large areas. Figure 4 shows one image, where the white dots indicate the positions of islands that form preferentially on the 140 nm wide valleys. By comparing the kinetics of nucleation and coarsening on substrates modified by different annealing conditions, we find that the final island arrangement depends on the nature of the mesa sidewalls, a suggest that this may be due to changes in diffusion of Ge across the non-planar surface. (Ref. [4])

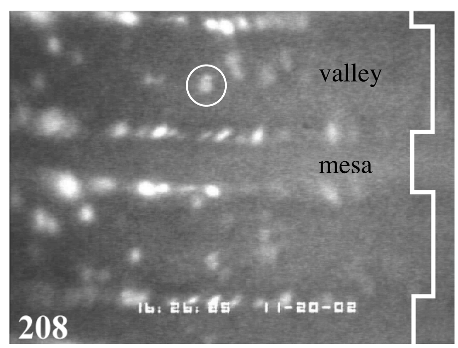

Fig. 4. Islands, such as the one shown inside a circle, form in the 140 nm wide valleys, instead of on the 60 nm wide mesas of this patterned substrate. (The substrate steps also show as the lines of brighter dots)

6. Future research plans

As we study these diverse self-assembly phenomena, we aim to develop an understanding of general principles that underly the templating process. For example, what sorts of substrate modulation (topographic, strain or chemical) are most successful in controlling the self-assembly processes, how reliably does sub-lithographic patterning work for different systems, and what factors control defect generation in the ordered arrays.

7. Educational activities and Outreach

We began a pilot outreach project with one of our undergraduate students to design animations to communicate the concepts of self-assembly and templating in block copolymers. Just as writing a science article encourages one to create an order of comprehension, so it is for the visual expression of the same ideas. The aim is to illustrate the following:

- the process of thinking of how to visually represent science and engineering *for the purpose of communication* enhances the understanding of scientific concepts for the creator, in this case our undergraduate student.
- discovering an accessible visual language to communicate science to the adult and young public emphasizes to the next generation of researchers the importance of communicating to the public, making it a part of their education.

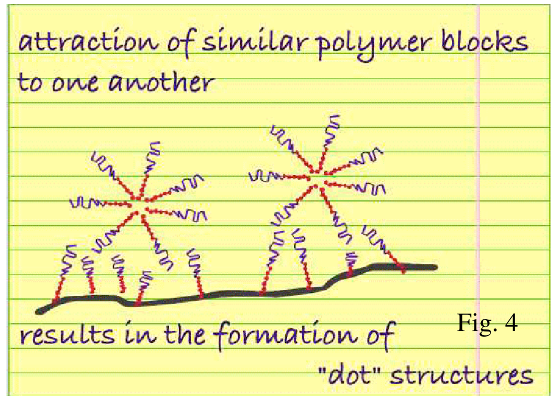

Fig. 4

Animations have been developed and will be placed on a web site and used in other outreach activities. An example of a still from the animation is given in Figure 4. (Ref. [5])

References

[1] For further information about this project contact caross@mit.edu

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[4] F. M. Ross, M. Kammler, M. E. Walsh and M. C. Reuter, *In situ* reflection electron microscopy of Ge island nucleation on mesa structures, in press, Microscopy and Microanalysis

[5] Contact felicef@mit.edu for more information.