

Spontaneous Alignment in Self-Assembled Block Copolymers for Nanolithography

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Abstract

Block copolymers were used to create self-organizing templates for pattern transfer. The goal of the templates was to exceed 10^{12} features per square inch for use in magnetic media. The cylinder forming diblock copolymer polystyrene-poly lactide (PS-PLA) has been observed to spontaneously align with cylinders of PLA oriented perpendicular to the substrate in a PS matrix after thermal annealing. The project examined spontaneous alignment of PS-PLA thin films of varying thickness on silicon (Si) and nickel-iron / gold (NiFe/Au) substrates without thermal annealing, and compares PS-PLA thin films with previously characterized polystyrene-polyisoprene-poly lactide (PS-PI-PLA) triblock terpolymer thin films. In addition, the project included general observations of the pattern transfer process. One hypothesis was that PS-PI-PLA forms a perpendicular cylindrical pattern because of the energetic preference for PI for the film surface, thus there should be no perpendicular alignment with PS-PLA.

Introduction

The capacity of magnetic media is approaching an upper limit with current optical lithography techniques. In order to create new media with capacities in the terabit range, novel techniques must be found. Pattern transfer is one such technique, but there remain some obstacles with the block copolymer method, such as attaining long-range order (on the scale of $\sim 1 \text{ cm}^2$), choosing the ideal block copolymer for its feature size and chemical properties, and perfecting the pattern transfer process to reproducibly create the desired pattern on a magnetic film. The ideal block copolymer has an average feature size of approximately 10 nm, with the minority component(s) self-assembling into a hexagonal pattern of cylinders aligned perpendicular to the substrate. Optimizing the pattern transfer process means, first and foremost, ensuring that the pattern is transferred. This is accomplished by trying to make the template an etch resist. Eliminating unnecessary steps in the process is also important, as this can increase reproducibility and minimize costs.

Experimental Procedure

The synthesis of PS-PLA is described elsewhere [1-3]. The sample (labeled MDR-II-85) we used had an average molecular weight of 60 kg/mol, determined from GPC, with a 2:1 mass ratio of PS to PLA and a polydispersity of 1.05. The substrates were Si/SiO₂ wafers of approximately 1 cm². Six were left as naked Si/SiO₂ and the other six were prepared with 5 nm NiFe (80:20 Ni:Fe) and a 5 nm Au endcap sputtered on at room temperature. Six PS-PLA solutions of varying concentration were created by

adding 2 mL of chlorobenzene to varying masses of PS-PLA, from 15 mg to 35 mg. Then the solution was spin-coated onto the wafers at a constant spinning speed of 2000 rpm.

Film thickness was measured with grazing angle x-ray reflectivity (GIXR). Other characterization was performed with a Nanoscope III atomic force microscope in tapping mode. After initial characterization, the samples underwent a 45-minute 0.5 M NaOH bath followed by a 5-minute rinse in distilled water and argon drying to degrade and remove the PLA component. The samples were characterized again with the atomic force microscope (AFM).

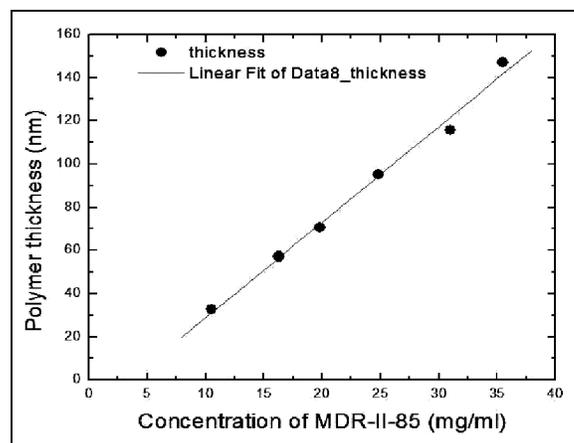


Figure 1: Thin film thickness in nm as a function of polymer solution concentration in mg/ml, as determined by GIXR.

Results And Conclusions

The thin film thickness as a function of solution concentration showed a linear relationship (Figure 1). The first round of AFM images taken of the samples as spun showed majority perpendicular cylindrical orientation for all samples but the 147.0 nm film. Perpendicular alignment looked particularly good in medium thickness samples such as the 57.1 nm and 70.5 nm samples (Figures 2 and 3). This observation undermined the hypothesis that a third component, polyisoprene, would be necessary for spontaneous perpendicular alignment.

There was no strong long-range ordering in the samples, which we determined from the lack of regular hexagonal patterning. On the other hand, initial results from the PLA-degraded samples showed more parallel cylindrical ordering in samples that appeared to have perpendicular ordering with the PLA component present. All the samples need to be further analyzed before any solid conclusions can be drawn.

Future Work

First and foremost, the remaining PLA-degraded samples need to be further characterized. Then, the images taken will be further analyzed to determine the average feature size of the perpendicular holes (i.e. from the PLA cylinders). If PS-PLA turns out to be a viable option for pattern transfer, further work will be required to determine how to create a pattern of freestanding cylinders, i.e. degrading the majority matrix. One option is to stain the PLA with a metal, which would make it an etch resist. The group is also currently pursuing techniques to hard mask the pattern. This helps to preserve the pattern while the magnetic film is etched.

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References

- [1] Zalusky, A.S.; "Mesoporous polystyrene monoliths"; J. Chem. Soc., 123, 1519-1520 (2001).
- [2] Zalusky, A.S.; "Ordered nanoporous polymers from polystyrene-poly lactide block copolymers"; J. Chem. Soc, 124, 12761-12773 (2002).
- [3] Mao, H.; "Control of pore hydrophilicity in ordered nanoporous polystyrene using an AB/AC block copolymer blending strategy"; Faraday Discussions, 128, 149-162 (2005).

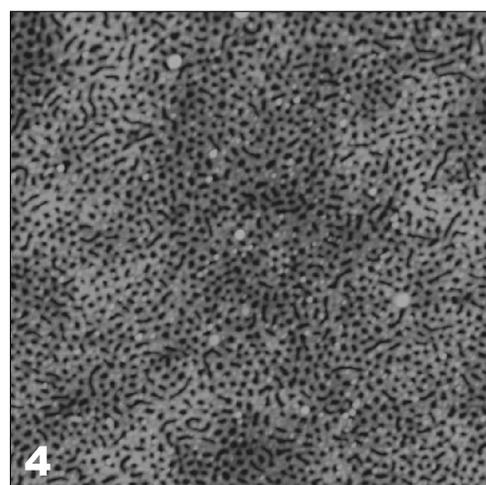
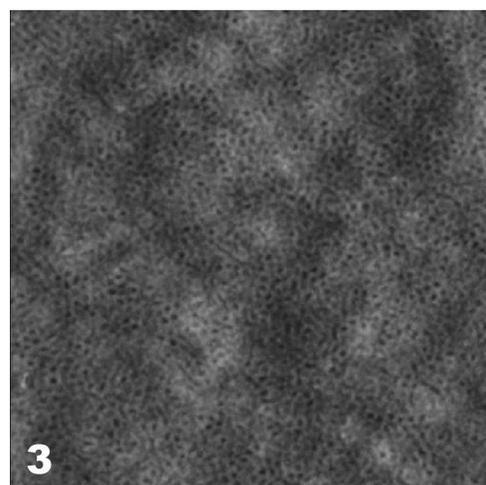
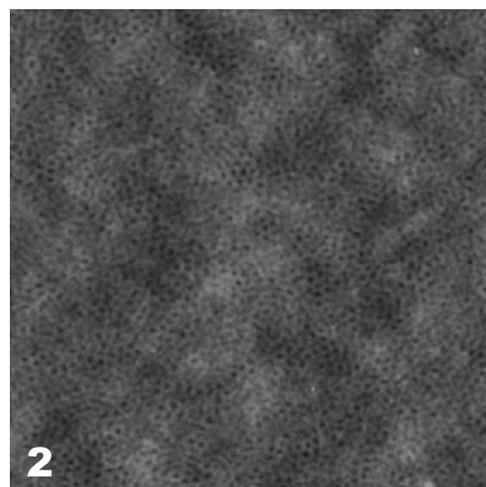


Figure 2, top: 57.1 nm thin film on Ni/FeAu substrate, as spun, $2 \times 2 \mu\text{m}$ image.

Figure 3, middle: 70.8 nm thin film on Ni/FeAu substrate, as spun, $2 \times 2 \mu\text{m}$ image.

Figure 4, bottom: 95.0 nm thin film on Ni/FeAu substrate, PLA degraded, $2 \times 2 \mu\text{m}$ image.