Imaging Layers for the Directed Assembly of Block Copolymer Films: Dependence of the Physical and Chemical Properties of Patterned Polymer Brushes on Brush Molecular Weight

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Patterning nanoscale features requires advanced lithographic techniques that involve redesigning the traditional photolithographic process. As feature dimensions shrink below 30 nm, the fidelity of the transferred information using current resists may not meet manufacturing requirements, particularly with respect to control over the size and shape of the patterned features (e.g. critical dimension control and line edge roughness). We are investigating the integration of self-assembling block copolymers into the lithographic process such that the materials themselves contribute valuable information towards the desired ends. At the same time we retain essential process attributes such as pattern perfection, registration and the ability to pattern non-regular device-oriented structures. Previously, we have shown the assembly of block copolymer films into nanometer scale patterns with long-range order using chemically nano-patterned surfaces (Figure 1) [1]. The imaging layer that records the chemical pattern on the substrate is a critical part of the process. This layer must be molecularly thin, highly uniform, and have a chemical composition that can easily be modulated with high pattern fidelity and contrast. One solution is to use a polymer brush as the imaging layer, since it is easy to produce and can be synthesized with a range of compositions [2]. Previously, we found that a polystyrene brush with nano-patterned regions selectively modified with oxygen plasma forms a robust chemical surface pattern for the assembly of overlying films of poly(styrene-block-methylmethacrylate) [3]. In this study we investigate the effect of the molecular weight of the polystyrene imaging layer on the assembly of block copolymer films. Brushes of end-grafted polystyrene of various molecular weights were prepared, analyzed with ellipsometry, AFM, water contact goniometry and FTIR, and patterned with Extreme-Ultraviolet Interferometric Lithography for the assembly of block copolymer films. As shown in Figure 3, we achieved the best assembly of block copolymer films using brushes with molecular weights of 3 kg / mol or less. Contact angle measurements, as in Figure 2, indicate that the best surface energy contrast in the chemical pattern is achieved with a brush of approximately 3 kg / mol, and that the chemical pattern has higher fidelity during annealing in the low molecular weight brushes. We conclude that the higher molecular weight brushes form poor imaging layers because of their low grafting density and higher chain length that allows for the migration of functional groups within the film and the scissioning of large chain segments during oxygen plasma treatment. The results of this study motivate the development of new imaging layer materials that are thin and have a high surface grafting density [4].

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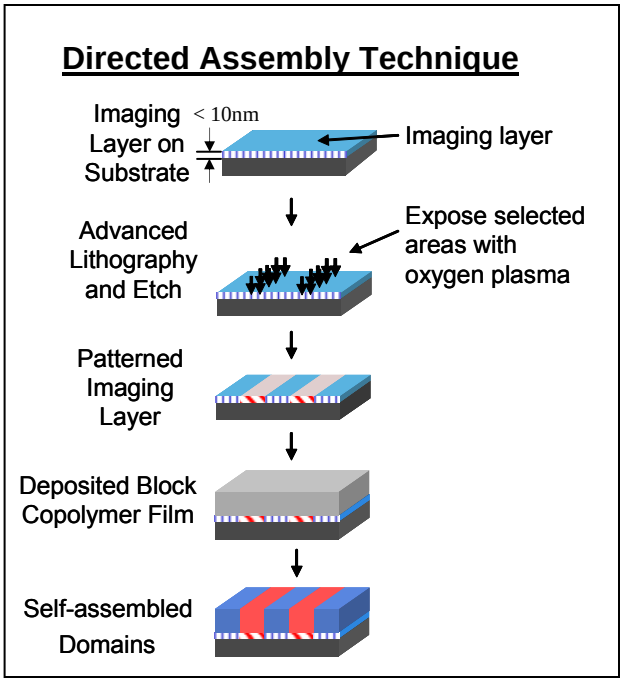

Figure 1. The directed assembly of a block copolymer film on a chemically patterned surface. In the second step, a photoresist layer is patterned with Extreme-Ultraviolet Interferometric Lithography and used as a mask to protect selected areas during oxygen plasma treatment.

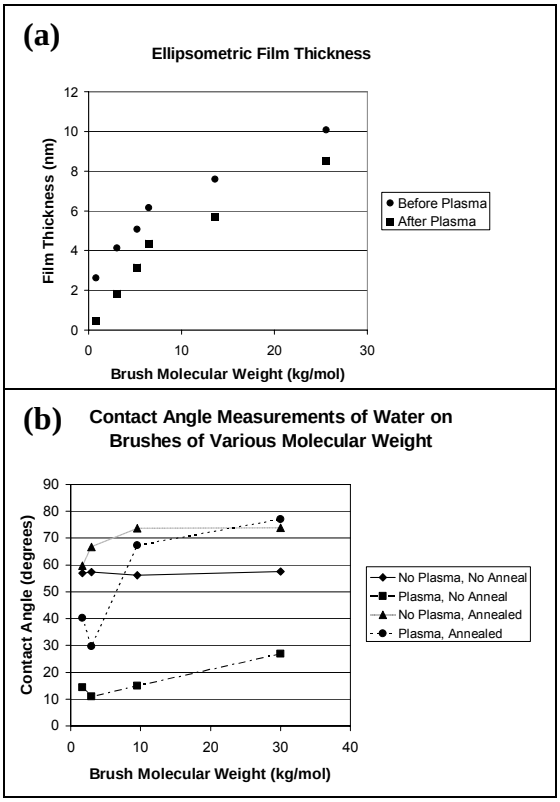

Figure 2. (a) Brush thickness as a function of molecular weight before and after oxygen plasma etching. (b) Receding contact angle of water on various brushes. Curves are shown with and without plasma treatment and annealing. Annealed samples were annealed at 190°C for 3 days. The angle difference between plasma treated and untreated brush is greatest for the 3 kg/mol molecular weight sample.

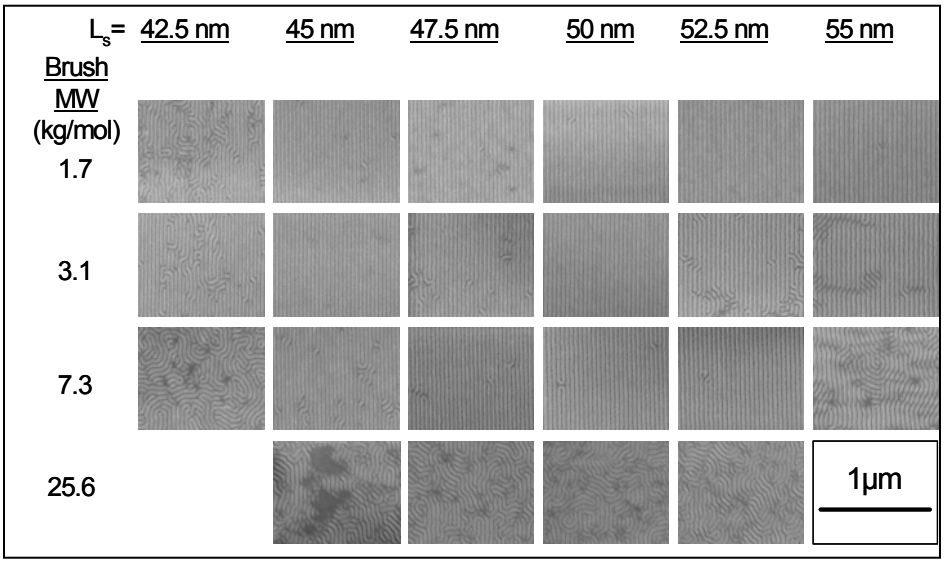

Figure 3. Top-down SEM images of PS-b-PMMA assembled on brushes of various molecular weights. The repeat period of the polymer ~ 48nm. Ls is the repeat period of the chemical pattern. The lower molecular weight brush provides better assembly, especially at extreme Ls values.