Direct Patterning of Polymer Brushes by Electron Beam Lithography

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Abstract:

We have studied the possibility of patterning polymer brushes directly using electron beam lithography. Conventionally patterned polymer brushes are fabricated by patterning the initiator layer, followed by the surface initiated polymerization of the desired monomer. However, contamination or loss of activity of the initiator is always a concern. Also, growth of patterned brushes in this way can lead to lower resolution features when the brush height is comparable in length to the pattern width, due to chain relaxation into the voided regions during growth. We have synthesized poly(methyl methacrylate) (PMMA), poly(2-hydroxyethyl methacrylate) (PHEMA), and PMMA-block-PHEMA brushes via atom transfer radical polymerization (ATRP) and successfully patterned them using a 0.5-1 nA beam current with doses ranging from 10 to 1500 µC/cm². We have shown that feature sizes close to 20 nm (for PMMA brushes) and close to 50 nm (for PHEMA brushes) can be achieved using e-beam lithography. The sensitivity curves of these brushes have also been studied.

Summary:

Patterned polymer brushes have attracted great interest because of the need for systems in the fields of molecular-scale electronics, magnetic storage, biosensing and other areas of nanotechnology [1,2]. We have studied the possibility of patterning polymer brushes directly using electron beam lithography. Conventionally, patterning of polymer brushes is done by first patterning an initiator layer on the substrate, followed by surface initiated polymerization of a suitable monomer [3,4]. However, it would be favorable to make this a single step process as this would reduce the possibility of surface contamination. In addition, direct patterning of brushes could help prevent pattern collapse which may occur during polymerization of patterned initiator sites due to chain relaxation into the voided regions [5].

To investigate the feasibility of patterning polymer brushes in a single step, brushes of poly(methyl methacrylate) (PMMA) and poly(2-hydroxyethyl methacrylate) (PHEMA), known electron beam resists [6], were prepared via atom transfer radical polymerization (ATRP) and direct patterning was carried out using electron beam lithography. The brushes were patterned using 0.5 nA to 1 nA beam currents, with doses ranging from 10 to 1500 µC/cm². Development was done using 1:3 ratio of methyl isobutyl ketone and isopropyl alcohol mixture for 90 seconds. Figure 1 shows an scanning electron microscopy (SEM) image of a patterned PMMA brush. Atomic force microscopy
(AFM) images of the e-beam patterned PMMA and PHEMA brushes are shown in Figure 2.

“Direct” patterning of PHEMA brushes by e-beam lithography was carried out after pre-baking at 160°C for 5 minutes. A 0.5 nA beam current was used with doses ranging from 10 to 120 µC/cm². The patterned brushes were developed in 0.9 N TMAH solution for 60 seconds.

We also investigated the sensitivity of these polymer brushes. Figure 3 shows the sensitivity curves for a 45.3 nm thick PMMA brush and a 50 nm thick PHEMA brush. Line edge roughness can be improved if the development conditions are optimized. Typical development conditions used for spun coat samples are not adequate enough as chain lengths are much shorter in the brushes than the high molecular weight polymers used in spun coat samples, which can lead to chain relaxation into the patterned areas. This phenomenon is noticeable in the patterned PHEMA sample in Figure 2b.

Currently, we are looking to explore the use of other monomers for brushes to pattern directly. We will study their electron beam resist behavior and also incorporate them into a study of patterning other block copolymer brushes other than PMMA-b-PHEMA. We are also very interested in the patterning of block copolymer brushes in order to combine top-down lithography with bottom-up self-assembly of the block copolymers. By studying the patterning of various block copolymer brushes with differing molecular weight ratios, and by working with various monomers, we expect the convergence of the top-down and bottom-up methods to result in smaller periodic structures than what is currently achievable with current lithographic techniques. Lastly, we believe it to be possible to create “nano-channels” with the direct patterning method. Using diblock copolymer brushes where the top block crosslinks to electron beam exposure while the bottom block depolymerizes, nano-channels of various sizes can be achieved.

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References: