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Selective Laser Ablation in Resists and Block Copolymers for High Resolution Lithographic Patterning

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Previously, we demonstrated an all dry, selective laser ablation development in methyl acetoxy calixarene (MAC6) which produced high resolution (15-25 nm half-pitch), high aspect ratio features not achievable with wet development. In this paper, we investigate the selective laser ablation process as a means to create a block copolymer derived lithographic pattern through the selective removal of one block. Two block copolymer systems were investigated PS-*b*-PHOST, and P2VP-*b*-PS-*b*-P2VP. The selective laser ablations process on block copolymers offers an alternative to plasma etching when plasma etching is not effective.
Keywords: block-copolymer, ablation, lithography

1. Introduction

Block copolymer lithography (BCPL) offers an appealing option for patterning structures at the 3-30 nm size scale. Industrial applications for semiconductor chip manufacturing and hard drives are on the horizon, but as noted in a recent review by Bates, *et. al*.[1] will require overcoming challenges in many areas, including pattern transfer. As noted in the review by Gu*, et. al.,*[2] there are two critical steps in BCPL pattern transfer, selective removal of one block and then transferring the pattern left by the remaining block to the substrate. In this paper we focus on the first step, selective block removal.

Plasma based dry etching (*i.e.* reactive-ion etching, RIE) is typically used for block removal over wet etching because it avoids pattern distortion/collapse caused by capillary forces in the wet block removal approach, as shown in the polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) system.[3] However, not all block copolymer systems have selectivity in plasma- based chemistries and alternatives approaches need to be developed.

Here, we investigate the selective laser ablation process for BCPL in two systems where there is difficulty using RIE to remove one block selectively, specifically: polystyrene-b-poly hydroxy styrene (PS-b-PHOST), and P2VP-*b*-PS-*b*-P2VP, For these neat BCPs, even though they are microphase separated, the aromatic nature of the

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monomers makes the plasma etching rates similar.[4, 5] Two alternative methods have emerged to increase etch selectivity between blocks. One is selective infiltration synthesis, where one of the block copolymer domains is complexed with an metal organic prior to etching.[6] The other is to complex one of the domains with a metal via a solution process which not only can improves the etching resistance, but also can increase the ability to microphase separate the smaller domains. [7]. Laser ablation may be able to replace or complement these techniques. For instance, in PS-*b*-P2VP, where the PVP is complexed with metal to increase the etching resistance, the metal can phase segregate during etching, degrading the pattern transfer. Laser ablation may prove a gentler process for block removal.

As discussed in reviews by Lippert, [8, 9] laser-ablation has been used to pattern polymers down to the diffraction limit of the scanning laser since 1982.[10, 11] Typically the laser is in the UV range where the absorption of most polymers is high.[8, 9] More recently, a few authors have applied laser ablation to selectively remove blocks in block-copolymers.[12-15] In this case, the resolution of the pattern is not determined by the size of the laser beam or the masking pattern, but instead by the chemical pattern in the polymer. Ahn, *et. al.* used an eximer laser to selectively remove the more UV-sensitive block in the copolymer leaving behind, polystyrene dots. Overall, however, the final PS structure was thinner than the original. [12] Wang, *et. al.*[14, 15] doped the PVP block of a PS-*b*-P4VP block copolymer to induce visible light laser ablation at 532 nm.

In this work, we build on our success in selective laser ablation for dry development of a high-resolution resist material, methyl acetoxy calix(6)arene.[16, 17] In our selective ablation process, we expose the calixarene using electron beam lithography and replace the wet development step with laser ablation. We found there is a difference in absorption between the exposed and unexposed regions allowing selective development of the exposed region. This resolution is therefore is determined by the e-beam pattern, not by the laser spot size (~300 nm FWHM). We were able to laser develop the e-beam exposed calixarene down to 15 nm half-pitch features in films thicknesses of 100 nm. The performance of the ablation was superior to that achieved by wet development. Under identical electron beam exposure conditions, wet development caused pattern collapse in part due to capillary forces during drying [18] and, possibly, feature swelling.[19]

We studied the laser ablation mechanism through systematic analysis of this and other chemical systems and found two components that contribute to the increase in 532 nm absorption, the increase of extended conjugation and the appearance of –OH groups on the aromatic ring due to electron beam induced chemistry. The aromatic–OH group can form a long-lived proton adduct, aromatic-OH_2^+, when exposed to e-beam or lasers and this species has a 532 nm absorption.[20] We also verified, that working at 532 nm had and advantage over ultraviolet wavelengths in that there was much weaker absorption, due to a UV absorption shoulder in pristine, unexposed calixarene film. At 532 nm, thinning of the unexposed material could be minimized compared to the UV regime where both the exposed and unexposed film have significant absorption. Understanding the selective ablation mechanism in the studied calixarene system, we saw a clear opportunity to pattern block copolymers using visible wavelength lasers, especially in the PS-*b*-PHOST system which we expect to have a selectivity due to the presence of aromatic-OH's in the hydroxy styrene system.

In this work, we extend our studies of selective laser ablation. First we investigate polyhydroxy styrene with and without t-butoxycarbynyl.carbonyls to verify the mechanism for phenolic systems. Secondly, we move to block copolymers where we demonstrate conditions for selective ablation in the PS-*b*-PHOST system. Finally, we extend our study to the PS-*b*-PVP system although we expect the mechanism to be different.

2. Methods (Polymer film preparation)

Poly((t-butoxycarbonyl)oxy)styrene (BOCS) was diluted in ethyl lactate and spun coat to a thickness of 100 nm. Samples were baked one minute at 100 ºC after spinning. Triphenylsulfonium triflate (TPSOTf) was added as a photo-acid generator to promote the deprotection of BOCS//HOST-*b*-PS (29k) synthesis is described in another reference.[21] Silicon substrates were coated with a neutral underlayer as described previously.[21] The block copolymers solutions were made using PGMEA as a casting solvent and filtered through 0.2 um PTFE filters. BCP films were made by spin casting on neutral substrate. Spun films were baked at 120° C for 2 min to remove the casting solvent resulting in 20 nm films as measured by ellipsometry (Woollam M-1000V). BCP films were solvent annealed in sealed containers with atmosphere saturated acetone for 6 hours.

P2VP-*b*-PS-*b*-P2VP (47k) was dissolved in Toluene/THF (3:1) mixed solvent to prepare 10 mg/mL solution, and was filtered with 0.45 µm PTFE syringe filters before coated onto P(S-*r*-2VP-*r*-HEMA) grafted silicon substrates, to prepare films with thickness of 28 nm. The BCP thin films were then annealed in acetone vapor environment in a sealed chamber for 1 hour.

3. Results and Discussion

3.1 Studies of the ablation process in in PHOST: the role of the aromatic-OH

Our first step in the analysis was to confirm that aromatic-OH plays a role in the PHOST system analogous to the calixarenes. In figure 1, we compare ablation in the poly((t-butoxy-carbonyloxy)styrene (BOCS), the protected PHOST system, to the deprotected system. Deprotection is accomplished by exposing to 0.05 mC/cm^2 of 10 keV electrons with and without 10% by weight of photo acid generator (PAG). The addition of PAG allows deprotection via the mechanism shown in Figure 1.[22]

The deprotected sample shows an immediate onset of photoluminescence, while no luminescence is observed from the pristine BOCS. Furthermore, only a weak photoluminescence signal appeared in the e-beam exposed sample of pure BOCS after a

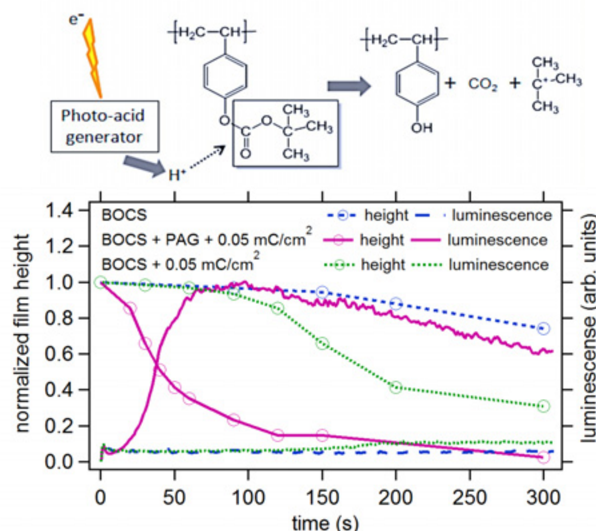

Fig.1. Laser Ablation for protected and deprotected poly((t-butoxycarbonyloxy)styrene (BOCS). High levels of deportection are achieved with the addition of a photo-acid generator (PAG). Below, luminescence together with the corresponding film thickness vs. time curves for BOCS with and without PAG. Prior to laser exposure 2 films were treated with flood electron beam at a dose of 0.5 mC/cm^2. Curves were measured upon irradiation with 3.7 mW, focused, 532 nm light.

significant laser exposure time. Like in calixarenes, this luminescence is directly correlated to the ablation ,as shown by measurements of the film height as a function of laser exposure time. As expected, thickness measurements show that ablation starts immediately for the deprotected sample. Ablation is virtually absent the pristine BOC sample. The e-beam exposed BOCS, without PAG, shows partial ablation (70 % of the film) but only after a significant incubation time (delay between initial laser exposure and the onset of ablation). The

dramatically accelerated ablation for the deprotected sample confirms the important role played by the hydroxyl groups in the ablation. Repeating the measurements with polystyrene, at this laser power, we saw a long incubation time and little evidence of photoluminescence.

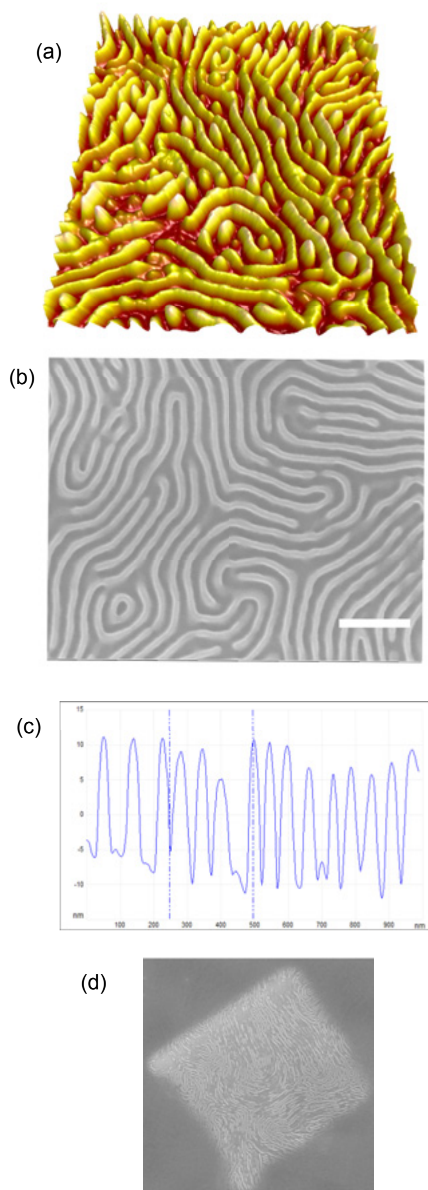

Fig.2. Images of selectively ablated PHOST from a PS-*b*-PHOST 46 nm in pitch (a) AFM image; (b) AFM line scan of (a); (c) SEM image. Scale bar is 200 nm. (d) SEM overview of an ablated area. Lighter area is where ablation occurs.

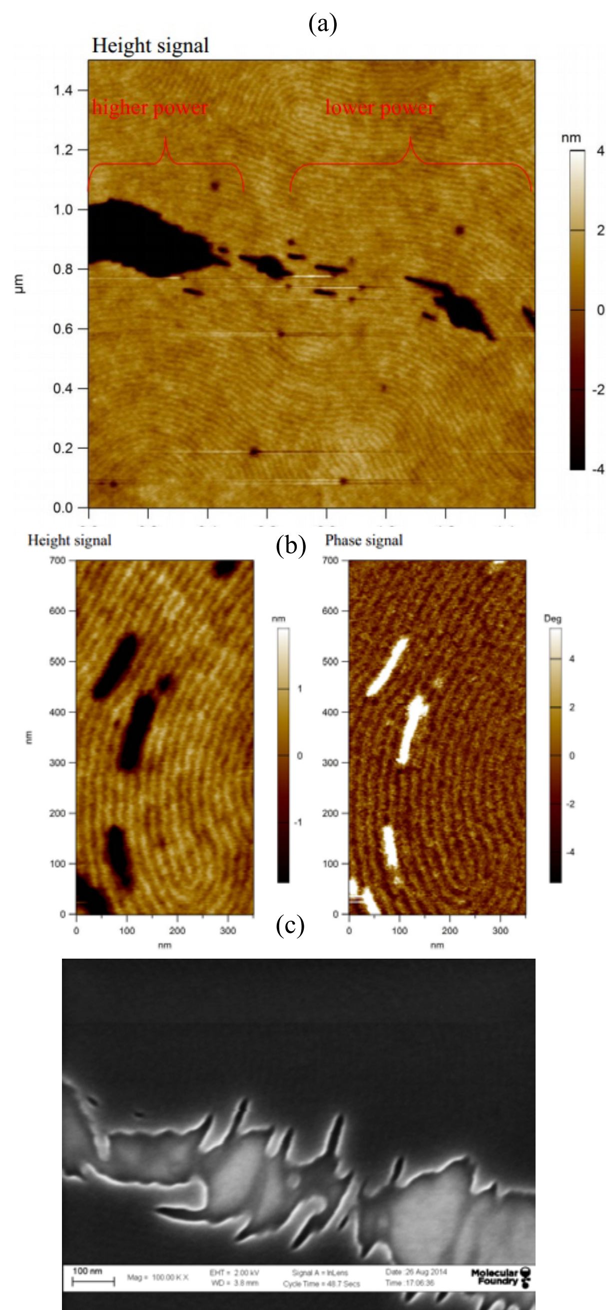

Figure 3. Ablation of P2VP-*b*-PS-*b*-P2VP without Pt. (a) AFM height and phase images. (b) Zoomed in AFM height and phase images suggesting the removal of one block in sporadically. (c) SEM image shows the ablation favors removal along the fingerprint pattern.

3.2 Selective ablation in PS-b-PHOST

Figure 2 illustrates the selective ablation process on PS-*b*-PHOST. The PHOST block is

removed in the 46 nm pitch system using powers of 7.5 mW, dwell times of 2 seconds, and pixel size of 333 nm. Selective ablation could be achieved in 40 nm samples , smaller pitches could not be selectively ablated. AFM phase imaging showed contrast within one block suggesting incomplete phase separation at smaller pitches. In addition, we found that in ablations studies of the underlayer, a cross-linked mixture of PS, poly(glycidyl methacrylate), and poly(acetoxy styrene),[21] did not ablate, at under similar conditions. However similar powers as those used to remove the PHOST block from the BCP. For pattern transfer, this would indicate that a descum would be necessary.

3.3 Ablation in PS-b-PVP

We investigated ablation in the PS-*b*-PVP system which was expected to occur via a different mechanism than PS-b-PHOST since there are no aromatic-OH groups present. Previous authors found PS had a lower ablation threshold than PVP. [14, 15] Figure 3 shows AFM images of P2VP-*b*-PS-*b*-P2VP with a 20 nm pitch. Relatively high powers were needed to see any ablation (above 21 mW). The ablation was found to proceed with a preference to ablate along the block copolymer fingerprint pattern. As the dose was reduced at constant power, single blocks appeared to be removed but in an inconsistent fashion. Hence optimum conditions were not found for selective removal for the non-metal doped system.

4. Conclusions

Selective laser ablation was investigated as a means to selectively remove one block from two types of block-copolymer systems. Using a 532 nm CW laser, we confirmed the mechanism that gave rise to the selective ablation in e-beam patterned resists was consistent with studies in the PHOST system using protected and deprotected PHOST. We showed that the selective removal of PHOST could be achieved in PS-*b*-PHOST and verified the removal down to 20 nm half-pitch. We then investigated P2VP-*b*-PS-*b*-P2VP. There was a preference to ablate in the direction of the pattern but conditions with high selecitivity were not identified. Overall, laser ablation appears to be a viable path for patterning block copolymers where optical selectivity is available.

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