High-χ, Si-Containing Block Copolymers and Process Strategies for Directing Their Self-Assembly

Christopher J. Ellison1*, C. Grant Wilson4,5, Dustin Janes1,2, Gregory Blachut5, Yasunobu Soymeya3, Paulina A. Rincon Delgadillo2, Geert Vandenberghhe2, Arjun Singh2, Jan Doise2, Natsuko Ito4, Ryuta Mizuochi5, Yusuke Asano5, and Austin P. Lane5

1 Department of Chemical Engineering and Materials Science, University of Minnesota-Twin Cities, Minneapolis, USA
2 Imec vzw, Kapeldreef 75, Heverlee, Belgium
3 Nissan Chemical Industries, Ltd. 635 Sasakura Fuchu-machi, Toyama, Japan
4 Department of Chemistry, University of Texas, Austin, USA
5 McKetta Department of Chemical Engineering, University of Texas, Austin, USA
*cellison@umn.edu

Si-containing block copolymer line and space patterns with 19.8 nm periodicity have been fabricated using lithographically defined guiding patterns. All processes were performed using leading edge production level nanofabrication tools on the 300 mm wafer scale. Under the conditions described here, top-down micrographs without dislocation defects can be readily obtained using automated inspection recipes and relatively low magnification. Future work will be directed toward continued resolution improvements, characterizing the through-film morphology, and demonstrating pattern transfer.

Keywords: Block Copolymers, Directed Self-assembly, Lithography, Etching

1. Introduction

Microelectronics manufacturers have a continuing desire to improve lithographic patterning resolution limits to advance geometric scaling, improve device performance, and, if possible, simultaneously decrease manufacturing costs. Immersion lithography tools using 193 nm wavelength light (i-193) are the current industry standard for high volume manufacturing, and are augmented in production by self-aligned multiple patterning strategies that successively halve the lithographic pitch, P. EUV and e-beam are possible next-generation lithography techniques which offer resolution advantages relative to i-193, but at steep tradeoffs to throughput and/or capital cost.

Directed self-assembly (DSA) of block copolymers (BCPs) is an alternative patterning methodology that utilizes a thin film of microphase-separated BCP domains as an etch-selective mask capable of forming sub-20 nm pitch line-and-space nanopatterns. These grating patterns are being intensely investigated by academic and industrial researchers because they represent the forefront of scalable, high-resolution nanopatterning and do not require the purchase of new, high capital cost tools. In practice the most persuasive and scalable demonstrations of DSA into line-and-space patterns have been performed using symmetric poly(styrene-block-methylmethacrylate) (PS-b-PMMA) possessing a microdomain periodicity, L0, of 28 nm [1,2]. While PS-b-PMMA is as close to a material standard as is possible in the wide-ranging DSA field, its relatively low Flory-Huggins interaction parameter, χ = 0.04, is a resolution-limiter. As L0 of PS-b-PMMA is decreased to about 24 nm and lower, its microdomains start to mix at the molecular level and form patterns with poor chemical definition and unsatisfactory etch selectivity [3].

Performing DSA of sub 20-nm L0 BCPs has required the development of new material platforms and processing methodologies. First, so-called “high-χ” block copolymers were synthesized such that relatively low-molecular weight materials were
still capable of microphase separation [4]. Our materials typically contain an etch-resistant heteroatom in one of the blocks (such as Si) to imbue the BCP with dry-etch selectivity [5]. Second, high-χ block copolymers often possess a surface energy mismatch that may preclude the lithographically-desirable perpendicular orientation of microdomains through the depth of the film upon thermal annealing. However, it is possible to deposit surface treatments at the bottom and top of the block copolymer film which energetically neutralize each interface such that the perpendicular orientation is obtained [4]. Finally, DSA flows need to be created which are capable of aligning these BCPs into nearly defect free-line and space patterns at the 300 mm wafer-scale using industry compatible tools. The aim of this manuscript is to update the community on our progress towards these ends, with an interest in providing a high-level description of our process-development strategies.

2. Materials

 Unless otherwise noted, the materials and methods are identical to that described in the previous work [6]. Crosslinkable poly(4-methoxystyrene) (XPMOST) and poly(2-vinyl pyridine) (XP2VP) were synthesized by free radical copolymerization of the respective monomers with 4-vinylbenzocyclobutene. Symmetric and monodisperse poly(trimethylsilylstyrene)-block-poly(4-methoxystyrene) (PTMSS-b-PMOST, $L_0 = 19.8$ nm) was synthesized by sequential anionic polymerization. Hydroxy terminated poly(styrene-co-tertbutylstyrene) (energetically neutral brush polymer) was synthesized by nitroxide-controlled free radical polymerization. Poly(maleic anhydride-co-styrene-co-3,5-dibutylstyrene) (energetically neutral top coat) was synthesized by free radical copolymerization. It was solubilized in methanol using trimethylamine [4].

3. Alignment strategies

 Three DSA alignment strategies are summarized in Fig. 1. The most common approaches described in the scientific literature are chemo-epitaxy (Fig. 1a) [7] and grapho-epitaxy (Fig. 1c). In chemo-epitaxy a topographically-smooth surface is imbued with a chemical nanopattern to align block copolymer microdomains into desired structures. Often the chemical nanopattern is fabricated by lithographically defining and trimming a crosslinked homopolymer mat possessing the same repeat structure of one of the blocks, which is preferentially wet by the corresponding BCP microdomain. In grapho-epitaxy, block copolymer is deposited into lithographically defined trenches whose sidewalls may be preferentially wet by one of the blocks. Both techniques can utilize sparse guiding patterns whose $P$ is an integer multiple of $L_0$. PS-b-PMMA can be aligned by a chemo-epitaxy strategy at 3X density multiplication, meaning $P = 3L_0$ [1].

In a strict sense, each of these techniques only provide driving force for self-assembly in only one coordinate axis. There is a lateral chemical pattern in the same plane as the substrate in the case of chemo-epitaxy, and a vertical structure perpendicular to the substrate in the case of grapho-epitaxy. It stands to reason that high-quality pattern fidelity may be maintained at even sparser pattern density (i.e. 4X – 6X density multiplication) if the guiding pattern possessed both lateral and vertical guiding features, thus reducing the pitch and dimension demands placed on the lithography and trim etch steps [8-10]. This hypothesis has led our exploration of the so-called “hybrid” film stack shown in Figure 1b. The process steps to obtain the “hybrid” film stack are closely related to the Liu-
Nealey chemo-epitaxy flow [7], but the starting guidestripe mat is considerably thicker. We previously compared the quality of microdomain alignment and size of defective areas at the top of PTMSS-\textit{b}-PMOST films directed by chemo-epitaxy to that by the “hybrid” strategy [6]. Improved microdomain alignment and reduction of defective areas were observed for the “hybrid” strategy. Here we targeted sample stack dimensions identical to our previous best-known “hybrid” strategy conditions.

4. Guidestripe crosslinking

XPMOST or XP2VP was spin-coated on the wafer and thermally crosslinked. Various rotational speeds, bake temperatures, bake times, and solvent rinse steps were investigated to obtain the desired thickness, in this case 19 nm. It is especially important to optically inspect the final mat for evidence of film thickness variations or dewetting. Some guidestripe mats are unstable on some inorganic surfaces and/or previously deposited organic layers [11].

5. Photolithography

Photolithography was performed atop the crosslinked mat using i-193 lithography. The optical characteristics and thickness of the film stack below the photoresist greatly influence the reflectivity of 193 nm UV light, and consequently alter the linewidth of photoresist obtained at a given exposure dose and mask critical dimension (CD). If reflectivity is very high, the process window of obtainable feature CDs may be very narrow. Especially when the guidestripe mat is very thin (< 10 nm), an antireflective coating such as silicon nitride may be deposited between the guidestripe mat and wafer to mitigate these effects [6, 11]. In our “hybrid strategy”, the guidestripe mat was thick enough to act as an antireflective coating and it could be deposited directly atop the wafer. Here we have targeted \( P = 79 \) nm to access 4X density multiplication.

6. Trim etch

A trim etch is used to shrink the lithographic feature CD, etch through the crosslinked guidestripe, and reveal at least some portion of the bare substrate. In our work so far we have utilized a single step, oxidizing, high-bias etch recipe. Afterwards, we inspected the pattern by top-down scanning electron microscopy (SEM) to determine feature CD and whether or not the bare substrate had been revealed. If the feature CD was too wide and/or the bare substrate was not revealed the etch process time was iteratively increased until these criteria were achieved. For some guidestripe composition, thickness, and \( P \), it can be especially challenging to

![Fig. 2. Representative top down SEM micrographs at 70,000X magnification of PTMSS-\textit{b}-PMOST films obtained from the “hybrid” patterning strategy depicted in Fig. 1. Brighter domains represent PTMSS. The label above each micrograph indicates the type of guidestripe used in DSA.](image-url)
find an etch process time capable of revealing the bare substrate without completely etching away the photoresist and oxidatively degrading the guidestripe’s top surface (i.e. over etching). In this work we targeted 1.5$L_0$ as the desired feature CD after etching; this dimension corresponds to roughly 29 nm in lateral width [6].

7. BCP film stack

Residual photoresist was removed by a basic developer rinse. The neutral brush was spin coated atop the patterned wafer and annealed. Ungrafted brush material was removed by rinsing with solvent, leaving behind an 8.6 nm grafted brush layer bound to the substrate. PTMSS-b-PMOST (33 nm) and top coat were deposited by sequential spin coating steps. Afterwards the film was thermally annealed at 205 °C to drive self-assembly. We employed a reducing etch to remove the top coat and partially etch into the BCP pattern, thus making it visible during top-down SEM inspection. Representative micrographs obtained for XPMOST and XP2VP guidestripes are shown in Fig. 2. Please note these are uncropped images acquired at 70,000X magnification using an automated inspection recipe.

The film surface morphology obtained for XPMOST guidestripe appears equivalent to our previous study. The microdomains are oriented in a direction parallel to the XPMOST guidestripe’s top surface (i.e. over etching). In this work we targeted 1.5$L_0$ as the desired feature CD after etching; this dimension corresponds to roughly 29 nm in lateral width [6].

The film surface morphology obtained for XP2VP and PMOST because they are both hydrogen bond acceptors. Future work will be devoted to studying the through film morphologies of these film stacks, aligning higher-resolution BCP materials, and demonstrating feasibility of pattern transfer for the novel “hybrid strategy” film stack.

Acknowledgements

The authors thank Geert Mannaert, Nadia Vandenbroeck, and Hari Pathangi for kind help with equipment and software.

References