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Journal

Journal of Vacuum Science & Technology B Nanotechnology and Microelectronics Materials Processing Measurement and Phenomena, 44(1)

ISSN

2166-2746

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Publication Date

2026

DOI

10.1116/6.0005088

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Si content in methacrylamide-containing A-*b*-(B-*r*-C) block copolymers and its impact on reactive ion etching properties

Running title: Etch behavior of Si-containing block copolymers

Running Authors: Eom et al.

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Block copolymers (BCPs) of an A-*block*-(B-*random*-C) architecture have been explored as materials for nanolithography because the composition and chemistry of the random block enables modification of thermodynamic and wetting properties to meet manufacturing criteria. Here, A-*b*-(B-*r*-C) BCPs created by an amidation reaction of polystyrene-*block*-poly(pentafluorophenyl methacrylate) (PS-*b*-PPFMA) with controlled amounts of Si add insight to previous conclusions about the dual contributions of BCP chemistry and reactive ion etch (RIE) gas chemistry on etch properties. We focus on two RIE etch characteristics: organosilicon etch resistance in H₂/N₂ plasma etching and enhanced removal of non-styrenic structures in an Ar/O₂ etch. Consistent with previous studies, higher amounts of Si result in greater etch resistance under H₂/N₂ RIE, where at least ~10 wt % Si is necessary to exhibit sufficient etch resistance. By contrast, Ar/O₂ etching resulted in etch rates independent of Si content. We observe previously unreported surface roughening aligned with morphological domains during the H₂/N₂ etch of modified

PS-*b*-PPFMA BCPs. Limited in the amount of allowable Si to attain equal surface energy between blocks, these BCPs are further disqualified in forming a Si-containing mask. However, in an Ar/O₂ etch the same BCPs exhibit suitable etch contrast and smooth domain structures, forming a uniform PS mask. Ultimately, this study uses the chemical flexibility of these materials to demonstrate the mechanisms of interactions between BCP and etch chemistry that must be considered to design effective materials for pattern transfer applications.

I. INTRODUCTION

Directed self-assembly (DSA) of block copolymers (BCPs) is a robust patterning strategy to create nanoscale patterns for high-resolution and low energy cost lithography.¹ As a complementary approach to fabricating such features, DSA has seen particular utility in the density multiplication^{2,3} and pattern rectification^{4,5} of underlying chemical patterns, including patterns created with extreme ultraviolet (EUV) lithography.^{6,7} The use of *A-block-(B-random-C)* BCPs has significantly increased the range of materials that can be used in DSA.^{8,9} While the *A-b-(B-r-C)* BCP platform can enable the decoupling of the surface energy difference between the A and B-*r*-C blocks from other thermodynamic contributions that normally co-vary with surface energy, it also facilitates the incorporation of a diverse array of functional groups to impart additional design parameters into these materials. For instance, an etch-resistant block could be very useful in providing etch contrast between the blocks of BCP, thereby enabling the assembled and etched BCP to serve as a mask for pattern transfer into the underlying semiconductor substrate. Because maximizing the remaining material is desirable for robust pattern transfer, it is essential to achieve high etch contrast between the two blocks.

This report used the *A-b-(B-r-C)* BCP architecture as a model system to study the chemical contributions of both the BCP and etch gas chemistry on the resulting etch mask morphology.¹⁰ An amidation reaction of polystyrene-*block*-poly(pentafluorophenyl methacrylate) (PS-*b*-PPFMA) with specific combinations of 4-methoxybenzylamine (4OMeBz), 2-picolylamine (2Pyr), and (trimethylsilyl)methylamine (TMS) was employed to generate *A-b-(B-r-C)* BCPs with a range of components and molar ratios of monomeric units within the B-*r*-C block. Key to the chemical design of the BCP for etch characteristics is the selection of TMS for the B monomers, which include organosilicon

groups within the BCP. In addition to enhancing the Flory-Huggins interaction parameter (χ) of these materials, recent work has shown that Si-containing styrenic polymers can form etch-resistant organosilicon polymers (OSPs) at the early stages of etching in an H₂/N₂ reactive ion etch (RIE), thereby enhancing their etch resistance.^{11,12} The etch rate of the B-*r*-C block designed here was studied with two different RIE chemistries: Ar/O₂, which effectively removes organic films, including various photoresist and polymeric materials, and is well known to etch aromatic groups slower than aliphatic moieties,¹³ and H₂/N₂, which has been extensively studied for the formation of Si etch barriers.^{14,15} Building on the knowledge of the etch characteristics of the B-*r*-C block, we further investigated the morphology evolution of the A-*b*-(B-*r*-C) fingerprint patterns in both H₂/N₂ and Ar/O₂ RIE, a critical step in converting BCP patterns into an etch mask. Collectively considered, these A-*b*-(B-*r*-C) BCPs serve as meaningful materials to assess the Si content necessary to effectively form a Si-containing etch mask, whether this composition is compatible with restrictions to balance surface energy between blocks, and ultimately how to determine the most desirable approach to forming a uniform mask from these Si-containing BCPs for applications in pattern transfer.

II. EXPERIMENTAL

A. *Materials and Characterization*

PS-*b*-PPFMA and PPFMA homopolymer used for etch tests were synthesized and functionalized as previously described.¹⁶ Hydroxyl-terminated poly(styrene-*random*-methyl methacrylate) (P(S-*r*-MMA)) containing 15 mol% PS, as well as PS-*b*-PMMA, were purchased from Polymer Source Inc. 4-Methoxybenzylamine (4OMeBz) was

obtained from Combi-Blocks and used as received. 2-Picolylamine (2Pyr), (trimethylsilyl)methylamine (TMS), and triethylamine were supplied by Sigma-Aldrich and used as received.

Scanning electron microscopy (SEM) images were collected on a Zeiss Merlin instrument with a 1–2 keV accelerating voltage at a working distance of 3–4 mm with an Inlens secondary electron detector. Image brightness and contrast were adjusted in ImageJ. Atomic force microscopy (AFM) was performed on an Asylum Research Oxford Instruments Cypher ES AFM in AC tapping mode. A J.A. Woollam Alpha SE ellipsometer was employed to measure film thicknesses, and data were fit to a Si-SiO_x-Cauchy model with a preset native oxide SiO_x layer of 1.5 nm.

B. Substrate Preparation

The hydroxyl-terminated P(*S-r*-MMA) brush was prepared as a 1 wt % solution in toluene and spin-coated at 1500 rpm on silicon wafers cleaned by oxygen plasma. After grafting the brush by annealing the wafer at 230 °C for 30 min in a nitrogen atmosphere glovebox, substrates were then sonicated 3 times for 5 min each in toluene and subsequently soft baked at 50 °C for at least 15 min before further use. Typical final thicknesses of brushes and mats prepared in this manner were 13 nm.

C. Preparation of Thin Films

Functionalized PPFMA samples were spin-coated from 3–5 wt % solutions in methyl ethyl ketone (MEK), or toluene for PS, onto silicon wafers cleaned with oxygen plasma such that the thickness of polymer films was >100 nm. Thermal history was erased on the samples by annealing them in a nitrogen atmosphere glovebox at 195 °C for 1 h. Fingerprint samples of equal surface energy compositions of functionalized PS-*b*-

PPFMA were prepared in 1.5 wt % solutions in MEK and spin-coated onto P(S-*r*-MMA) brush grafted silicon wafers at 2500 rpm. After annealing at 195 °C for 30 min in a nitrogen atmosphere glovebox, the film thickness of these samples averaged ~47.5 nm.

D. Etching

Reactive ion etching was performed on a Plasma-Therm inductively coupled plasma etcher. An H₂/N₂ plasma etch was performed on thin films of homopolymers and random copolymers for etch tests, as well as on the BCPs, using the following settings: pressure = 20 mTorr, RF power = 200 W, H₂ flow rate = 45 sccm, N₂ flow rate = 15 sccm. An Ar/O₂ plasma etch utilized the following settings: pressure = 10 mTorr, RF power = 65 W, Ar flow rate = 50 sccm, O₂ flow rate = 5 sccm. Etch rates were determined by calculating the slopes of plots of etch time against etch depth. Etch rates of TMS-containing polymers in the H₂/N₂ etch conditions were calculated using etch times after 10 s to compensate for the initial period of the etch process necessary to form the etch resistant barrier in Si-containing polymers.

E. Calculations

The Si content of the functionalized PPFMA copolymers (w_{Si} in wt %) was calculated with

$$w_{Si} = \frac{F_{TMS} \times MW_{Si}}{(F_{TMS} \times MW_{TMS}) + (F_{Rc} \times MW_{Rc})} \quad (1)$$

where F_{TMS} and F_{Rc} are the molar fraction of TMS and the polar group (2Pyr or 4OMeBz) in the copolymer, respectively, MW_{Si} , MW_{TMS} , and MW_{Rc} are the molecular weights of elemental Si, the TMS-functionalized PPFMA repeat unit, and the polar group-functionalized PPFMA repeat unit, respectively.

The Si atomic density (n_{Si}) was determined with:

$$n_{Si} = \frac{N_A \times w_{Si} \times ((F_{TMS} \times \rho_{TMS}) + (F_{Rc} \times \rho_{Rc}))}{MW_{Si}} \quad (2)$$

where N_A is Avogadro's number, and ρ_{TMS} and ρ_{Rc} represent the densities of TMS- and polar group-functionalized PPFMA, respectively, which were determined using Parachor parameters.¹⁷ The number of Si atoms per unit area was estimated by multiplying n_{Si} by the amount of polymer film etched at the inflection point of its etch plot, therefore by the time the etch resistant layer forms. The etch times associated with this point used in the calculation are 5 s for PPFMA(TMS) and PPFMA(TMS-4OMeBz[High-Si]), 10 s for PPFMA(TMS-4OMeBz[Mid-Si]), and 20 s for PPFMA(TMS-4OMeBz[Low-Si]).

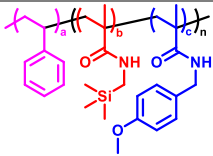
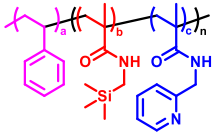
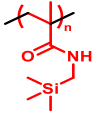
III. RESULTS AND DISCUSSION

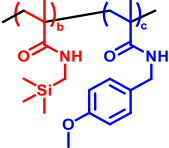
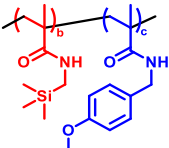
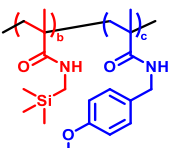
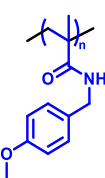
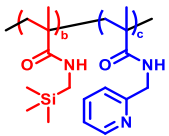
A. *BCP and Etch Chemistry*

Table 1 summarizes the A-*b*-(B-*r*-C) copolymers and the corresponding B-*r*-C copolymers used in this study. A-*b*-(B-*r*-C) copolymers with equal surface energy between blocks were prepared by functionalizing PS-*b*-PPFMA BCPs, as previously reported.¹⁶ The PPFMA block was functionalized with a mixture of two amines (B and C) to form highly polar methacrylamide side chain groups, therefore enabling the modified block to have a surface energy equal to that of PS. The B component was TMS, which can form etch resistant inorganic SiO₂ or OSPs during the initial stage of RIE, to study its impact on the etch behavior of the BCPs. The SiO₂ or OSP layer was shown to act as an etch barrier in styrenic polymers, which far exceeds the etch resistance of conventional carbon-based polymers.^{11,12,18} Notably, achieving equal surface energy in Si-containing BCPs was particularly challenging due to the intrinsically low surface energy of Si-containing groups.¹⁹ Because the highly nonpolar organosilicon moieties in

TMS substantially reduce the surface energy of the B-*r*-C block,^{19,20} the C component was chosen as either 4OMeBz or 2Pyr, both more polar than TMS and PS, to balance the surface energy between the blocks. In addition, their aromatic rings contributed further etch resistance compared to aliphatic components, consistent with the higher etch durability of aromatic polymers.^{13,21} To examine the etch properties of the B-*r*-C block, the PPFMA homopolymer was functionalized with the same B/C pairs, and its thickness change during RIE was monitored.

TABLE I. Summary of materials used in this study. Functionalized PS-*b*-PPFMA BCPs (top two rows) were employed for self-assembled thin film studies, while functionalized PPFMA homopolymers (remaining rows) were used in etch rate studies. PPFMA functionalization resulted in copolymers containing TMS and a polar group (4OMeBz or 2Pyr) in the compositions indicated. Si wt % and Si atom density are calculated for the functionalized PPFMA copolymer component using Eqs. (1) and (2), respectively.

Sample Name	Structure	Parent polymer	Composition TMS (mol%)	Si content (wt %)	Si density (atoms/nm ³)
PS- <i>b</i> -PPFMA (TMS-4OMeBz)		PS- <i>b</i> -PPFMA	20.1	2.84	0.68
PS- <i>b</i> -PPFMA (TMS-2Pyr)		PS- <i>b</i> -PPFMA	27.3	4.38	1.05
PPFMA(TMS)		PPFMA	100	16.4	3.76

PPFMA(TMS-4OMeBz[High-Si])		PPFMA	82.6	13.1	3.03
PPFMA(TMS-4OMeBz[Mid-Si])		PPFMA	61.0	9.28	2.18
PPFMA(TMS-4OMeBz[Low-Si])		PPFMA	22.9	3.25	0.78
PPFMA(4OMeBz)		PPFMA	0	0	0
PPFMA (TMS-2Pyr)		PPFMA	30.2	4.85	1.16

B. Relation Between B-r-C Chemistry and Etch Rates

The dependence of etch rate on chemical moieties was studied using functionalized PPFMA homopolymers, along with PS and PMMA. Two different RIE chemistries were investigated: (i) a 3:1 H₂/N₂ plasma, which is effective for forming an OSP etch barrier from Si-containing polymers, and (ii) a 10:1 Ar/O₂ plasma, which is an effective RIE for removing organic material while providing additional gentle ion bombardment, resulting in high-quality PS etch masks when employed on PS-*b*-PMMA, a well-studied DSA material.

A few notable comparisons can be made regarding the etch behavior, both in this specific BCP system and broadly. Our study of etch rates of PPFMA functionalized with a mixture of amines enables us to quantify the effects of Si content on etch rate (Figure 1a) for Si-containing methacrylamide polymers. The characteristic of the etch rates of these polymers is the difference in rates associated with early and late etch times, where all polymers studied here exhibited similar early etch rates in H₂/N₂ before diverging at longer etch times. This is consistent with conclusions drawn by Azarnouche *et al.* as well, where a period of etch was necessary to first form the etch resistant barrier from the Si functional groups before differences in etch rates were observable. After this initial stage, the etch rate of polymers decreased with increasing Si wt %, also consistent with Azarnouche *et al.*¹¹

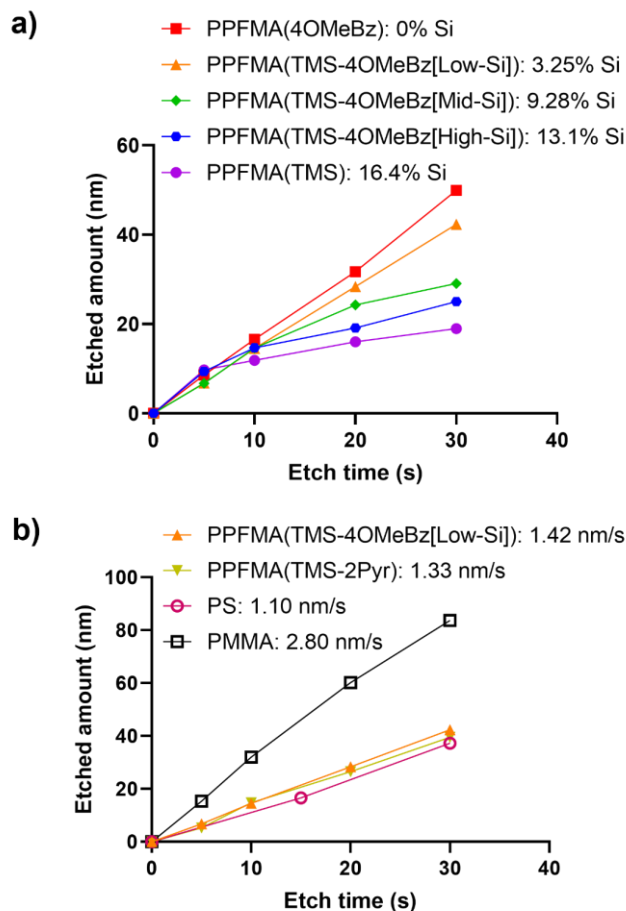


FIG. 1. Plots of etch time versus etch depth in a H_2/N_2 etch process of >100 nm thick films of (a) TMS-4OMeBz functionalized PPFMA copolymers (including the wt % of Si in each polymer) and (b) homopolymers (PS and PMMA) and functionalized PPFMA random copolymers at approximately equal surface energy composition (with the corresponding etch rates indicated).

These studies qualitatively show that etch resistance is only significant when the Si content exceeds ~ 10 wt %, as apparent by the amount of Si necessary to exhibit effective differences in early versus late etch rate behavior. Furthermore, given the etch data available over a wide array of Si content, we can estimate the number of Si atoms per unit area necessary to remain in forming the protective layer, as outlined in the

Experimental section. Assuming no loss of Si in the etch process, the protective layer threshold for copolymers at or above ~10 wt % Si based on calculations of three samples, PPFMA(TMS), PPFMA(TMS-4OMeBz[High-Si]), and PPFMA(TMS-4OMeBz[Mid-Si]), is 33.2, 28.4, and 31.8 Si atoms/nm², respectively. This suggests that the Si content needed to effectively form the etch resistant barrier is relatively consistent across these samples and averages around 31.1 Si atoms/nm². In contrast, estimates for PPFMA(TMS-4OMeBz[Low-Si]), which contained 3.25 wt % Si, show that at the etch times necessary to form an etch-resistant barrier, this amount is 22.1 Si atoms/nm², less than that necessary to form the protective layer. These systematic determinations therefore reinforce previous conclusions of the threshold value of ~10 wt % Si content for forming an effective protective layer.¹⁸

This outcome is critical when considering the concentration of Si groups in these A-*b*-(B-*r*-C) BCPs and whether the equal surface energy composition of the random block would be sufficient to have useful etch resistance in this RIE condition. This comparison is presented in Figure 1b, where the etch rates of PS, PMMA, and the B-*r*-C random copolymers of equal surface energy composition to PS are overlaid. The compositions of these random copolymers are <10 wt % out of necessity to achieve equal surface energy to PS, thereby precluding them from exhibiting effective etch resistance. But also notable is the apparent lack of etch contrast between blocks in A-*b*-(B-*r*-C) BCPs of PS with these two B-*r*-C candidates, in contrast to Azarnouche *et al.*, in which styrenic polymers with similar Si content showed substantially higher etch resistance than PS in H₂/N₂ RIE. We attribute this to differences in the structure of the polymer side chain by which the organosilicon groups are attached to the hydrocarbon main chain,

where the styrenic system studied by Azarnouche *et al.* benefits from the inherent etch resistance of aromatic groups in addition to the contribution from the Si moieties. The methacrylamide of the polymers in this work does not offer the same reinforcing effect to the etch resistance of the attached Si. This observation highlights an important design consideration for A-*b*-(B-*r*-C) copolymers: achieving high etch resistance in either block requires careful selection of both elemental pendant moieties and the side chain structure. We therefore conclude that an H₂/N₂ plasma process would not be suitable for these materials as it relates to minimum Si content, etch contrast of these BCPs, and side chain chemistry.

This contrasts to the different behavior of these same polymers in an Ar/O₂ etch (Figure 2a), where the etch rates of these polymers were independent of Si content. Though one could expect a contribution of the organosilicon groups to the etch behavior of these copolymers, the low O₂ flow rate relative to Ar could be insufficient to oxidize the organosilicon groups to form a protective SiO_x barrier. Moreover, the high Ar flow could effectively enhance physical etching and ion bombardment,^{13,22,23} which could remove any partially formed Si-containing barriers, thereby diminishing the contribution of organosilicon groups to the overall etch resistance. Employing this etch chemistry is an important comparison, as it is an assessment of how these Si-containing BCPs would behave during etching independent of any mechanisms of forming Si-O groups towards the etch resistant protective barrier seen in oxidizing RIE chemistries.

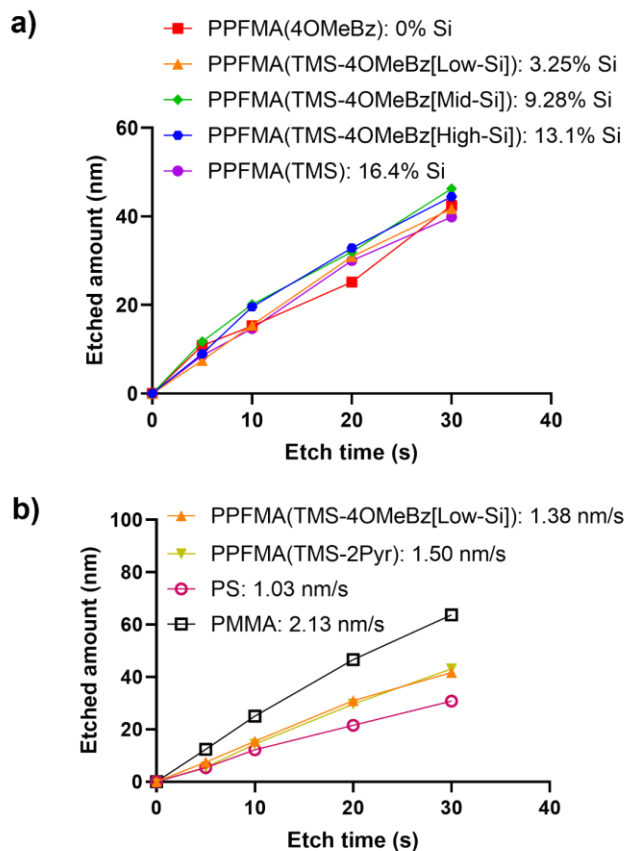


FIG. 2. Plots of etch time versus etch depth in an Ar/O₂ etch process of >100 nm thick films of (a) TMS-4OMeBz functionalized PPFMA copolymers (including the wt % of Si in each polymer) and (b) homopolymers (PS and PMMA) and functionalized PPFMA polymers at approximately equal surface energy composition (with corresponding etch rates indicated).

Figure 2b illustrates the comparative etch rates in an Ar/O₂ RIE of the functionalized PPFMA random copolymers with compositions of the B-*r*-C block close to those of equal surface energy to the PS block. Both random copolymers exhibited intermediate etch rates between PS and PMMA, consistent with expectations based on their mixed aliphatic-aromatic composition, as well as the low impact of Si on etch resistance demonstrated in Figure 2a. It is worth noting that the etch contrast between PS

and PMMA under H_2/N_2 (2.55:1) is higher than that under Ar/O_2 (2.07:1). Although Ar/O_2 is widely used as the standard chemistry for PS-*b*-PMMA pattern transfer, this result highlights that its etch contrast can vary significantly with plasma conditions. Ultimately, given the wealth of tools available to modulate the etch contrast between PS and PMMA, we envision that similar considerations can be applied to evaluate the factors that result in etch characteristics of a random copolymer block relative to a PS block, such as we have demonstrated here with these two etch chemistries.

C. Morphological Evolution of Fingerprint Patterns under RIE

The same etch conditions were applied to the two A-*b*-(B-*r*-C) BCPs exhibiting equal surface energy between the blocks, and the resulting film topography of each sample was characterized by AFM. Under 3:1 H_2/N_2 etch conditions, as shown in Figure 3, the changes in structure associated with etch time was notable: early etch times showed discrete lamellar structures, but longer etch times began exhibiting surface roughening into granular structures that aligned with the BCP domains.²² The formation of these surface roughening granules also evolves with etch time. To assess what component of the A-*b*-(B-*r*-C) BCP contributed to this observation, the random copolymer and homopolymer samples composed of functionalized PPFMA used in the etch tests were also imaged by AFM. Though imaging of these polymer thin films was made challenging due to the relative flatness of the samples and sometimes resulted in imaging artifacts being more prominent and visible, the collection of the data did not preclude the ability to draw some observations.

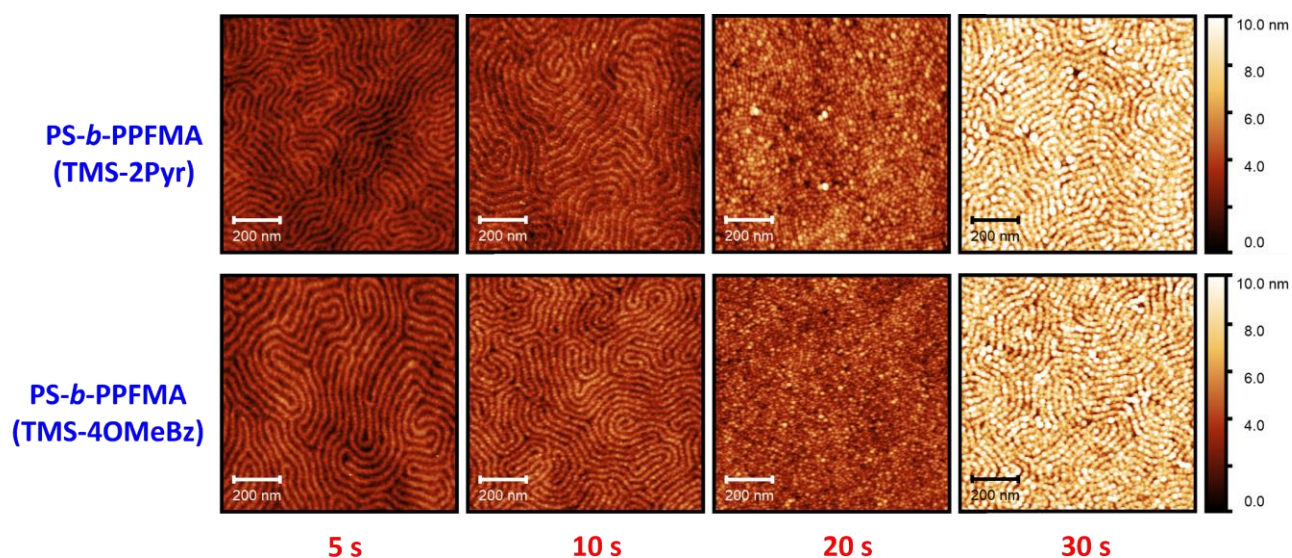


FIG. 3. AFM images (1 μm window) of functionalized PS-*b*-PPFMA with the indicated amine pairs, subjected to different H_2/N_2 etch times.

A comparison between a representative pair, TMS and 4OMeBz, and the fully functionalized PPFMA polymers of these amines suggested that long etch times of the polar amine-functionalized polymers led to roughening of the surface into a granular structure (Figure S1, supplementary material). This granular roughness was apparent, consistent with observations found in fingerprint samples, while the TMS-functionalized polymers did not exhibit such behavior. This observation is supported by comparisons between TMS-4OMeBz mixed functionalization images at longer etch times (Figure S2, supplementary material), where the greater 4OMeBz composition random copolymers exhibited more granules, and identical results in both amine pairs at the same (equal surface energy) composition (Figure S3, supplementary material). Finally, a significant comparison can be drawn with the characteristics of thin films of PS-*b*-PMMA subjected to the H_2/N_2 etch (Figure S4, supplementary material), where the granules seem to similarly appear over the course of an etch process. This demonstration gives valuable

insight by isolating the chemistry of the side chain from its pendant group. Consistent with previous studies that etch organosilicon-containing BCPs with an H_2/N_2 etch,¹² the TMS-functionalized PPFMA does not exhibit surface roughening granules throughout the etch process. For the functionalized PPFMA polymers that do not contain Si groups, these methacrylamides do not exhibit the same smooth surface characteristics as seen with the styrenic derivatives, pointing to the role that the aromatic side chain also plays in the quality of etched domains in BCPs. Given extensive studies previously on contributions to surface roughening, such as cross-linking, chain scissioning, and ion landing energy,²² it would be possible to elucidate the specific chemical mechanisms by which these features arise from the functional groups in this work. Altogether, the data shows that even for a BCP system where etch rate data suggests very suitable use based on the high etch contrast between blocks, a consideration of the integrity of domains throughout an etch process is essential, which itself is a product of the entire chemistry of the BCP side chains and how they may promote surface roughening mechanisms.

By contrast, under a 10:1 Ar/O₂ etch process (Figure 4), the lamellar structure of these identical materials are preserved through the entire etching time, with only a slight hint of the surface roughening granules exhibited in the H_2/N_2 starting to form at 30 s etch time. Moreover, though the etch resistant chemistries of these BCPs are not as stark as in PS-*b*-PMMA optimized in this plasma process, the etch selectivity of these BCPs is apparent, as demonstrated by the evolution of the profiles of these materials over the duration of the etch process (Figure 5). This serves as proof of concept of how the unique chemical characteristics of this BCP can be considered towards designing a suitable etch process. In this case, with the combined contributions of the Ar bombardment etching

away the B-*r*-C block at low amounts of Si and the O₂ gas selectively etching aliphatic groups faster than aromatic groups, the Ar/O₂ plasma provides a means of etching this A-*b*-(B-*r*-C) BCP to create a PS mask. By circumventing the formation of etch resistance in the RIE of organosilicon groups, this etch process may also exclude the mechanisms of the granules observed in the H₂/N₂ process, though a separate study would be necessary to determine this.

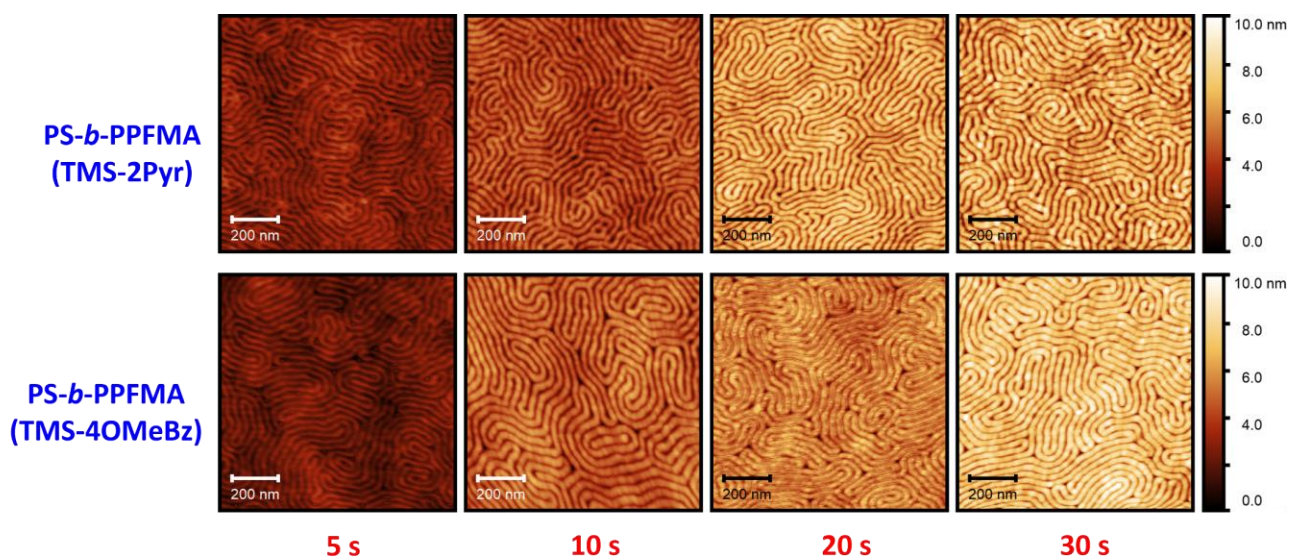


FIG. 4. AFM images (1 μm window) of functionalized PS-*b*-PPFMA with the indicated amine pairs, subjected to different Ar/O₂ etch times.

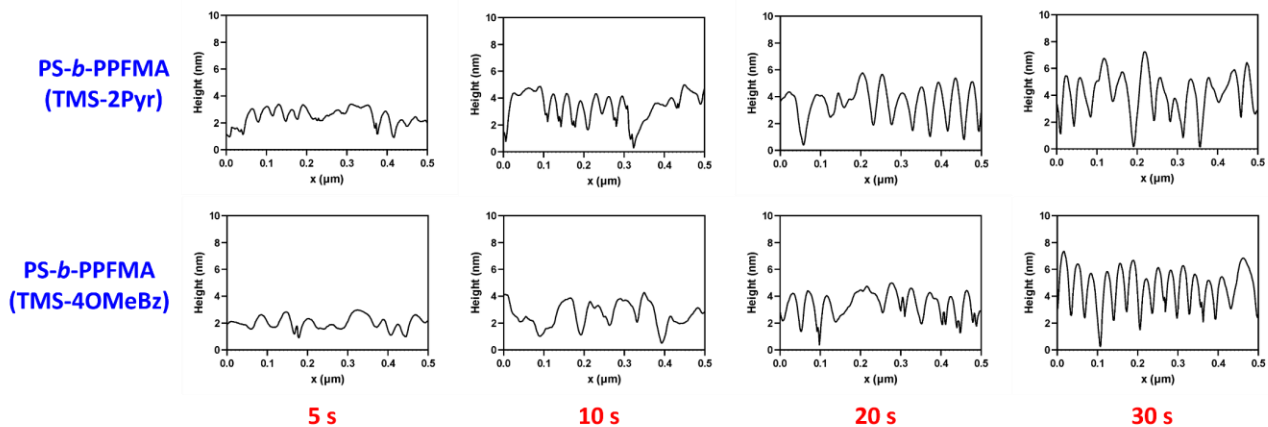


FIG. 5. AFM profiles of functionalized PS-*b*-PPFMA with the indicated amine pairs, subjected to different Ar/O₂ etch times. The AFM images from which these profiles are drawn is indicated in Figure S5 (supplementary material).

In this scenario, the mechanism of etch resistance of organosilicon is not directly leveraged, given the low Si content in the BCP and oxygen concentration in the RIE gas. However, there is considerable value in the incorporation of the hydrophobic Si groups in greatly increasing the χ of these BCPs. Previous work with Si-containing BCPs has demonstrated its ability to attain large values of χ ,¹² including estimates for the high χ of the A-*b*-(B-*r*-C) BCPs employed in this study.¹⁶ Considering the high χ imparted by Si is crucial beyond BCP etch behaviors because it relates to the quality of pattern transfer, particularly in line roughness. The effect that χ has on reducing domain fluctuations and providing greater structural uniformity in BCP films could thereby significantly contribute to the line roughness in determining pattern transfer quality.²⁴ Therefore, in addition to the ability to achieve high χ BCPs amenable for thermal annealing via equal surface energy between the blocks, for high quality pattern transfer it is necessary to consider the through-film BCP structure provided by the given etch process.

IV. SUMMARY AND CONCLUSIONS

This report provides new insight on the RIE etch characteristics of A-*b*-(B-*r*-C) BCPs organosilicon moieties, especially in studies of the evolution of thin film morphologies during an etch process. Etch studies on random copolymers containing different amounts of Si show that etch rate is inversely proportional to the wt % of Si in an H₂/N₂ etch, where significant etch resistance is only exhibited above ~10 wt %, and the chemistry of the polymer side chain has a considerable impact on the etch rates with any amount of Si. This etch rate is independent of Si content in the Ar/O₂ etch used here, in which Ar ion bombardment circumvents the mechanism of forming the etch resistant SiO_x barrier and O₂ imparts etch characteristics based on differences in aliphatic versus aromatic functional groups. Given that only a limited amount of Si can be incorporated in these A-*b*-(B-*r*-C) BCPs to achieve equal surface energy blocks as well as the surface roughening granules apparent in structures etched by H₂/N₂, directly employing the etch resistance of organosilicon groups in a plasma condition is not a feasible option for using these materials to create the necessary Si barrier for mask formation. However, the Ar/O₂ plasma is suitable for these BCPs, relying instead on differences in aliphatic and aromatic side chain chemistry to provide etch contrast, with PS able to form an effective mask. These materials could serve as meaningful models for studying the ultimate effects of BCP chemistry and etch mechanisms on line roughness and pattern transfer, where the high χ of these materials may play a significant role. Future work could consider how this benefit could be paired with chemical properties that would lend organosilicon the potential for high etch resistance. This could be achieved with different synthetic

approaches, such as increasing Si content with organosilicon groups that contain more Si groups per repeat unit or using different forms of Si-containing moieties (e.g., Si-O groups).

SUPPLEMENTARY MATERIAL

SUPPLEMENTAL FIGURES S1-S5

ACKNOWLEDGMENTS

This work was supported as part of the Center for High Precision Patterning Science (CHiPPS), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at Lawrence Berkeley National Laboratory. This work made use of the shared facilities at the University of Chicago Materials Research Science and Engineering Center, supported by the National Science Foundation under award number DMR-2011854. It also made use of the Pritzker Nanofabrication Facility of the Pritzker School of Molecular Engineering at the University of Chicago, which receives support from Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), a node of the National Science Foundation's National Nanotechnology Coordinated Infrastructure.

AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.

Author Contributions

C. J. Eom and K. Lee contributed equally to this work.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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