Topcoat Approaches for Directed Self-Assembly of Strongly Segregating Block Copolymer Thin Films

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1. Introduction

Directed self-assembly of block copolymers (BCPs) on lithographically defined chemical templates is a promising route to obtain patterns with sub-lithographic resolution [1-4]. Extensive works have been reported by applying polystyrene-*block*-poly (methyl methacrylate) (PS-*b*-PMMA). However, since PS-*b*-PMMA is a weakly segregating system with small Flory-Huggins interaction parameter χ , the minimum dimension achievable is approximately 13 nm in half pitch [5]. BCPs composed of polymers with larger χ offers a solution to generating smaller patterns, but their use introduces another challenge in assembly because strongly segregating polymers often have significant differences in surface energy γ . Even a moderate γ difference results in segregation of domains with lower γ to the free surface, and disrupts the assembly on the chemical template.

One of the approaches to prevent the problem is to modify the boundary condition of BCP films to be thermodynamically favorable for the perpendicular orientation by placing additional layer on the top of BCP films [6,7]. In this study, we describe a generalizable strategy of the “topcoat approach” for DSA process. The Monte Carlo simulation enabled us to find out allowable properties of the topcoats. The strategy was experimentally demonstrated by directing the assembly of polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) films on chemically pre-patterned templates with neutral topcoats. We also successfully applied poly(methyl methacrylate)

(PMMA) as top-coat. The post-patterning on this topcoat layer allows us to selectively open the topcoat layer in the area of interest.

2. Methods

Chemical patterned templates with alternating stripes of PS and P2VP (full pitch $L_S = 53$ nm) were prepared by e-beam lithography of PS mat followed by backfilling of P2VP between the PS stripes, applying similar process described in Ref. 3. Lamella forming PS-*b*-P2VP (molecular weight Mw, PS 40.5 kg/mol, P2VP 40.5 kg/mol, lamella spacing $L_0 = 53$ nm H L_S) was spin-coated on the chemical templates. Cross-linked polymeric mats of PS, P2VP and random copolymer of PS and P2VP (PS-*r*-P2VP), and a PMMA film with Mw of 950 kg/mol were used as top-coats. The top-coat films were prepared on the separate substrates and transferred on the surface of PS-*b*-P2VP by either floating method or polymer off-set printing method [8]. After top-coating, samples were annealed at 190 °C for 24 hours.

3. Result and Discussions

3.1 Monte Carlo Simulation

Three dimensional morphology of a AB block copolymer film placed between a chemical template and a top-coat polymer C were investigated by Monte Carlo simulations applying a coarse-grained block copolymer model [9]. The model is defined by a set of parameters which can be mapped one-to-one with real systems, namely the Flory-Huggins parameters $\chi_{\alpha\beta}$ ($\alpha, \beta \in \{A, B, C\}$) associated with each pair of dissimilar polymers

and molecular weight of the components. The results are summarized in the phase diagram shown in Figure 1. The Flory-Huggins parameters between the blocks composing BCP and the topcoat, χ_{AC} and χ_{BC} , are rescaled by that of the AB diblock copolymer, χ_{AB} .

According to the simulation results, the equilibrium morphologies can be categorized into three groups; lamellae perpendicularly oriented through the BCP film (perpendicular), three dimensionally complex morphology with a wetting layer at the interface between topcoat (complex), and dissolved BCP into topcoat polymer (dissolved). As expected, the perpendicular morphologies are obtained around the line $\chi_{AC} = \chi_{BC}$, where the interfacial energies of topcoat polymer C against A and B blocks are the same. Thus, in this case, topcoat polymer C is non-preferential to A and B blocks, therefore the perpendicular orientation becomes most favorable. As topcoat C is getting preferential to one of the block, the morphology of BCP changes from perpendicular to complex. As shown in Figure 1b, the perpendicular domains were observed at $\chi_{AC}/\chi_{AB} = \chi_{BC}/\chi_{AB} = 0.6$. When χ_{AC}/χ_{AB} is increased, topcoat C becomes relatively favorable to B over A block and the B domain starts to selectively wet the topcoat C. It is noteworthy that the complex morphologies are not simple mixture of perpendicularly oriented lamellae from the bottom and parallel orientated lamellae by the top. Instead, the simulation predicts bicontinuous morphologies consist of the perforated layer of A block on the chemical pattern and B wetting layer at the interface between the topcoat.

Another phenomenon which should be noted is that the BCP can be mixed with topcoat polymer. The morphologies of dissolved BCP films were found in the space where either χ_{AC}/χ_{AB} or χ_{BC}/χ_{AB} is small. However, this dissolving issue can be resolved if we choose the topcoat layers with hard surfaces such as cross-linked polymers or polymers with higher glass transition temperatures, T_g , than thermal annealing temperature.

3.2 Cross-linked polymeric mat as topcoat

In order to experimentally demonstrate the topcoat process, we choose PS-*b*-P2VP film because the χ value is large enough to obtain sub 10 nm feature size. Furthermore, this BCP is useful for various applications because P2VP domain can be easily functionalized with other materials.

Figure 2 shows cross-sections of PS-*b*-P2VP thin films assembled on the chemical templates with crosslinked PS, P2VP and PS-*r*-P2VP mats and corresponding simulation results. In the case of PS or P2VP mat on the top of PS-*b*-P2VP films, the situations should correspond to $(\chi_{AC}/\chi_{AB}, \chi_{BC}/\chi_{AB}) = (1, 0)$ and $(0, 1)$ in the phase diagram shown in Figure 1a. In accordance with the phase diagram, we observed the complex morphology with clear wetting layer at the top surface with these topcoats. In contrast, when the PS-*r*-P2VP layer is placed as a topcoat, we obtain the perpendicularly oriented domains through the film as was expected from the phase diagram, e.g. $(\chi_{AC}/\chi_{AB}, \chi_{BC}/\chi_{AB}) = (0.5, 0.5)$ which is in the perpendicular window. It should be noted that phase diagram with crosslinked polymer topcoat is slightly different from that of the

Fig. 1. (a) Phase diagram of AB block copolymer films assembled between topcoat polymer C and chemical template. The morphologies of AB block copolymer were determined by the Monte Carlo simulation. (b)(c) Simulation snapshots showing the transition (b) from the perpendicular lamellae to complex morphology and (c) from the perpendicular to dissolved lamellae. Red, blue, and gray in snapshots represents A block, B block, and topcoat polymer C, respectively. Mw of AB diblock copolymer: 40kg/mol-*b*-40 kg/mol, topcoat polymer C: 950 kg/mol. Thickness of AB diblock copolymer: $1L_0$. Substrate: 1:1 chemical pattern. 3D images were created using open-source scientific visualization software ParaView, <http://www.paraview.org/>.

non-crosslinked polymer shown in Figure 1a. However, the slight differences were found only in the dissolved phase and the boundary of the perpendicular window.

3.3 PMMA film as topcoat

The phase diagram suggests that variety of polymers can be employed as a topcoat layer if χ_{AC}/χ_{AB} and χ_{BC}/χ_{AB} are in the perpendicular window. From this perspective, we choose PMMA as a topcoat layer for PS-*b*-P2VP. At annealing temperature of 190 °C, $\chi_{PS-PMMA}$ and $\chi_{PS-P2VP}$ are 0.036 and 0.103, respectively [4,10]. Therefore, a value of $\chi_{PS-PMMA}/\chi_{PS-P2VP}$ will be 0.350. A value of $\chi_{P2VP-PMMA}/\chi_{PS-P2VP}$ was estimated to be 0.563 from the solubility parameters of each polymer ($\delta_{PS} = 9.1$, $\delta_{PMMA} = 9.3$, and $\delta_{P2VP} = 9.9$) [11,12] using following equation.

$$\frac{\chi_{P2VP-PMMA}}{\chi_{PS-P2VP}} = \frac{(\delta_{P2VP} - \delta_{PMMA})^2}{(\delta_{PS} - \delta_{P2VP})^2}$$

Note that $(\chi_{PS-PMMA}/\chi_{PS-P2VP}, \chi_{P2VP-PMMA}/\chi_{PS-P2VP}) = (0.350, 0.563)$ is within the window of perpendicular phase in Figure 1a.

Morphology of PS-*b*-P2VP film between PMMA topcoat and underneath chemical template is shown in Figure 3a. The perpendicularly oriented PS-*b*-P2VP film with perfect registration on the chemical pattern was observed. Moreover, we did not observe mixing between PMMA topcoat and PS-*b*-P2VP film. This result reveals that PMMA topcoat was not mixed with both PS and P2VP blocks during annealing even though the annealing temperature was higher than T_g of three polymers. The mixing was supposed to be suppressed because all pairs of these polymers (PS-PMMA, P2VP-PMMA, and PS-P2VP) are sufficiently incompatible and the Mw of topcoat is also large (950 kg/mol).

Because the topcoat layer is an additional layer to control the orientation of a BCP film, it should be removable for further applications. From this point of view, the PMMA topcoat is technologically useful since the layer can be selectively removed by e-beam lithography. After we achieved the DSA of PS-*b*-P2VP films with thermal annealing, we exposed e-beam on the rectangular area of PMMA topcoat/PS-*b*-P2VP bi-layered film. The exposed area of topcoat PMMA was selectively removed by the development with mixture of MIBK and IPA. From this topcoat-opened area, directed assembled PS-*b*-P2VP films were clearly observed (Figure 3b). The patternable property of topcoat layer allows us

not only to remove the topcoat layer from a BCP film but also to define the target area to utilize directed assembled structures of a BCP film.

3.4 Sub-10nm features

Above results demonstrate convincingly that the topcoat PMMA is working for PS-*b*-P2VP film. In order to reduce the feature size down to sub-10

Fig. 2. Cross-sectional SEM and corresponding 3D Monte Carlo simulation images of PS-*b*-P2VP thin films assemble on chemical templates with preferential and non-preferential cross-linked polymeric top coat mats.

Fig.3. (a) Cross-section and (b) top-down SEM images of PS-*b*-P2VP films assembled between PMMA topcoat and chemical template.

nm scale, we replaced the PS-*b*-P2VP with smaller Mw P2VP-*b*-PS-*b*-P2VP, whose bulk morphology is also lamellae (Mw; 7.9k-*b*-17.0k-*b*-7.9k).

Fig. 4. (a)(b) Cross-sectional SEM images of P2VP-*b*-PS-*b*-P2VP films on the neutral brushes (a) under free surface and (b) under PMMA topcoat. (c) Top-down SEM image of P2VP-*b*-PS-*b*-P2VP films after removal of PMMA topcoat.

Figure 4a and 4b show the cross-sections of the triblock copolymer films with and without PMMA topcoat on the substrates modified by the neutral PS-*r*-P2VP brushes. Because the block with lower surface energy (PS) is in the middle of polymer chain, the parallel orientation from the free surface may be suppressed somehow by the entropic penalty. However, as shown in Figure 4a, we could not avoid the parallel orientation on the neutral substrate without topcoat. Consequently, the parallel orientation from the free surface persists through the film to the non-preferential substrate. On the other hand, when the triblock copolymer film was annealed under PMMA topcoat, the perpendicularly oriented lamellae domain was

successfully observed as shown in Figure 4b. After removal of PMMA topcoat with e-beam exposure and wet development, we could observe the fingerprint pattern of perpendicularly oriented lamella (Figure 4c). Although the neutral non-patterned substrate was applied in this study, the present results strongly suggest that DSA with density multiplication of sub-10nm features can be achieved by replacing the substrate with the chemical template.

4. Conclusion

We have described the topcoat approach to enable the DSA of BCP films with blocks exhibiting differences in surface energy. By coating a topcoat layer on the BCP film, thermodynamically favorable boundary condition at the top surface of the film could be engineered for DSA with desired orientation. It is important to note that sub-10 nm feature with lithographically useful orientation was realized by high χ BCP film with topcoat process applying simple thermal annealing process. Although the approach was demonstrated in specific cases in this study, we expect our approach can be extended to the other cases such as cylinder-forming BCP and DSA with higher density multiplication factors.

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