Selective Area Morphology Control of Self-Assembled Patterns using Silsesquioxane-containing Block Copolymers

Suguru Ushiro, Haruka Mikami, Mizuki Sato, Chiharu Hirano, Yoshinori Suzuki, Rina Maeda, Yoshihito Ishida, Teruaki Hayakawa, Kohei Aida*, Yasuhiko Tada* and Hiroshi Yoshida*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,

2-12-1-S8-36 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

**Materials Research Laboratory, Hitachi Ltd., 7-1-1 Omika, Hitachi, Ibaraki 319-1292, Japan
hayakawa.t.ac@m.titech.ac.jp*

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1. Introduction

Self-assembling block copolymers have attracted a considerable research interest because of their ability to create periodic nanostructures in the thin films. Patterning the self-assembled nanostructures allows the possibility to produce a wide variety of templates targeting for many potential applications such as plasmonic waveguides, magnetic logic gates, magnetic data storage and microelectronic devices [1-7]. Recent studies have demonstrated that directed self-assembly such as graphoepitaxy (lithographically predefined templates with topographic relief) [8, 9] or chemical heteroepitaxy (chemically prepatterned substrates) [10] can have long-range ordering, good feature registration, and accurate placement with a very low number of defects for patterning of the block copolymer nanostructures in the thin films. However, these patterning methods are required to prepare the lithographic prepatterned templates as a substrate through multistep and/or time-consuming lithographic techniques such as photolithography or electron-beam lithography. One proposed pathway without using the prepatterned substrates to less time-consuming and simpler patterning objectives involves utilizing multifunctional block copolymer resist materials.

We have recently reported a new series of silicon-containing block copolymers based on

polyhedral oligomeric silsesquioxane (POSS)-containing poly(methacrylate) (PMAPOSS) [11-15]. PMAPOSS-based block copolymers can self assemble with small periodic features with a full pitch around 10 nm and the resulting phase morphologies can be reversibly controlled with a long-range order by solvent and/or thermal annealing. Furthermore, PMAPOSS domains have significantly excellent etch resistance to oxygen reactive ion etching because of producing the oxidized crosslinking layer of the PMAPOSS domains. These features can allow a simpler patterning process for precise location of the self-assembled block copolymer nanostructures.

In this study, we demonstrated the patterning of PMAPOSS-based block copolymer self-assembled nanostructures in selective area of the thin films by combining solvent or thermal annealing with UV/Ozone or oxygen plasma treatment. The ordered arrays of dots and lines in the thin films were firstly prepared by solvent annealing through microphase-separation, respectively. Second, in order to lock the nanostructures in selective area, a half size of the resulting thin films was exposed by Ultra Violet (UV)/Ozone or oxygen plasma with a mask of silicon wafer, which induces a crosslinking network of PMAPOSS polymer chains through oxidation. Finally, after removal of the mask, solvent or thermal annealing was carried

out again to change the morphology. This second annealing induces the order-order transition of the nanostructures between dots and lines in the un-exposed area, while no transition occurs in the exposed area. With this simple procedure, the patterns composed of different kinds of microphase-separated nanostructures in the selective area can be obtained. Herein, we report the control and lock of the morphology in the PMAPOSS-based block copolymer nanostructures in the thin films to create the patterns. We also show the atomic force microscopic (AFM) images for the order-order transition of the microphase-separated nanostructure during thermal annealing, which monitored *in situ* to clarify how the transition of self-assembled domains occurs.

2. Experimental Section

2.1. Materials

Synthesis of poly(methyl methacrylate)-*b*-PMAEtPOSS (PMMA-*b*-PMAEtPOSS)

Diblock copolymer of PMMA-*b*-PMAEtPOSS was synthesized as follows: 40 mL of distilled THF was transferred to a shrenk flask containing 100 mg of dry Lithium Chloride (LiCl) (2.4 mmol), and the reactor was cooled to -78 °C. Five minutes later, *sec*-Butyllithium (*sec*-BuLi) was added until color changed to light yellow. The flask was removed from the cooling bath and allowed to reach room temperature upon which the solution becomes colorless. The flask was cooled back to -78 °C, and *sec*-BuLi solution in hexane/cyclohexane (0.12 mmol) was added. Then, 1,1-Dyphenylethylene (DPE) (0.14 mmol) was added to the flask, resulting in a deep red color. After 30 min, 0.66 mL of methyl methacrylate (6.0 mmol) was transferred to the polymerization flask via cannula with vigorous stirring. The deep red color changes to light yellow. In a second flask, 1.40 g of POSS methacrylate, which ethyl groups are substituted to the silicon atoms of POSS, (MAEtPOSS) (1.9 mmol) was dissolved in THF (3.0 mL). After 3 h, the MAEtPOSS solution was transferred to the polymerization flask via cannula. After 12 h at -78 °C, an excess of methanol (MeOH) was added to the flask in order to prepare the proton-terminated diblock copolymer. The polymer was then precipitated into MeOH, filtered, and dried under vacuum at room temperature for 24 h (Fig.1). The polymers described as below were used in this study. PMMA₃₁-*b*-PMAPOSS₂₀: molecular weight (M_n) = 18,100 g mol⁻¹, polydispersity index (M_w/M_n) =

1.05, volume fraction of PMAEtPOSS (ϕ_{PMAPOSS}) = 0.81, morphology (bulk): PMMA sphere with a domain spacing of 14.7 nm.

2.2. Film Preparation

Silicon wafers were cleaned by treating with a piranha solution (H₂SO₄/ H₂O₂ = 70/30 (v/v)) at

Fig. 1. Synthesis of PMMA-*b*-PMAEtPOSS.

100 °C for 1 h and subsequent rinsing with deionized water. Thin films of PMMA-*b*-PMAEtPOSS were prepared from the dilute solutions in chloroform by spin casting onto silicon wafers. The thickness of layer was 73 nm measured by ellipsometry.

2.3. Solvent annealing

As spun thin films were exposed to carbon disulfide (CS₂) vapor or CS₂/acetone = 50/50 (v/v) mixture solvent vapor and held for 2 h. The swollen film thickness was controlled indirectly with nitrogen counter-flow in a sealed chamber and swelling ratio (SR) was controlled 150%. The solvent was removed instantaneously by opening the chamber

2.4. UV/Ozone or oxygen plasma treatment

A half size of the PMMA-*b*-PMAPOSS thin film with dots array was exposed by UV/Ozone (0.6 mW/cm², 10 min) or oxygen plasma (20 W, 1 Pa, 20 sec) to lock the nanostructure. Subsequently, the resulting thin film was annealed in CS₂/acetone = 50/50 (v/v) mixture solvent vapor for 2 h or heating at 180 °C for the re-assembly. The order-order transition behavior was monitored by AFM *in situ* from room temperature to 180 °C (Fig.2).

2.5. Measurements

Surface Morphologies of the block copolymer thin films were measured by using a Seiko model SPA 400 AFM and a Hitachi S-4800 SEM.

Order-order transition was investigated by using a Seiko model E-sweep.

Fig.2. Schematic illustration of patterning procedure for PMMA-*b*-PMAEtPOSS nanostructured thin films in selective area by combining UV/Ozone or oxygen plasma treatment and subsequent solvent or thermal annealing.

3. Results and Discussion

3.1. Synthesis, characterization, and thin film morphology of PMMA-*b*-PMAEtPOSS

The desired PMMA₃₁-*b*-PMAPOSS₂₀ was prepared by living anionic polymerization. The chemical structure and the composition were characterized by ¹H, ¹³C, ²⁹Si NMR and Infrared spectroscopy. The pattern formation and the *d*-spacing of PMMA₃₁-*b*-PMAPOSS₂₀ were investigated by SAXS and AFM measurements. Note that the molecular weight (*M_n*) and volume fraction of PMAPOSS (ϕ_{PMAPOSS}) are 18,100 and 0.81, respectively, and the bulk morphology is the PMMA sphere with *d* spacing of 14.7 nm measured by small angle X-ray scattering (SAXS). The thin film was prepared by spin casting from the polymer solution in chloroform onto a silicon wafer and subsequently annealed in CS₂ or CS₂/acetone mixture solvent vapor for 2 h. They provided to form dots and lines in the thin films derived from sphere and parallel oriented cylinder morphologies, respectively (Fig.3). This is because CS₂ is slightly preferential for PMAEtPOSS more than PMMA and also acetone is preferential for PMMA more than PMAEtPOSS. Therefore, for

Fig.3. SEM images of self-assembled PMMA-*b*-PMAEtPOSS nanostructures of (a) dots and (b) lines in thin films.

the thin film annealed in CS₂/acetone mixture solvent, apparent volume fraction of PMMA increases and line structure can be formed under thermodynamically metastable state.

3.2. Order-order transition from cylinders to spheres

The thin film with line nanostructures prepared by solvent annealing in CS₂/acetone = 50/50 (v/v) mixture solvent vapor was thermally annealed from room temperature to 180 °C using a heat stage of AFM under vacuum. Transition from line to dot structure was observed between temperatures at 120 °C and 140 °C. In particular, drastic transition occurred at 132 °C whereas almost line structure disappeared and many dots were formed as shown in Fig.4. This temperature is 56 °C higher than *T_g* of PMAEtPOSS and 28 °C higher than *T_g* of PMMA. As the result of thermal annealing, the volume fraction of the corresponding PMMA microdomains in the solvent annealed thin film may decrease with reassembly of the polymer chains.

Fig.4. AFM images of PMMA-*b*-PMAEtPOSS thin films during thermal annealing, temperature at (a) 90 °C (lines), (b) 132 °C (from lines to dots), and (c) 140 °C (dots), measured *in situ*.

3.3. Lock of morphology in thin films by UV/Ozone or oxygen plasma treatment

Based on the above self-assembling behaviors of PMMA-*b*-PMAEtPOSS, the nanostructure of dots in a half area of the thin film was firstly attempted to lock with a mask by UV/Ozone and oxygen plasma, respectively. Both of the treatment successfully fixed the nanostructures. This could be due to the crosslinking of PMAPOSS chains with oxidation.

3.4. Reassembly of PMMA-*b*-PMAEtPOSS in unexposed area

Morphology change of the resulting locked nanostructures of dots and lines was carried out by solvent annealing and/or thermal annealing. The unlocked dots in the unexposed area were converted to the nanostructure of lines by solvent

annealing in CS₂/acetone = 50/50 (v/v) mixture solvent vapor. The unlocked nanostructure of lines also changed completely into the dots by thermal annealing at 180 °C. In contrast, the nanostructures in the exposed area did not show any morphology changes (Fig.5). This indicates that both of exposure treatments of UV/Ozone and oxygen plasma with a mask can be used the locking of PMMA-*b*-PMAEtPOSS nanostructures in the selective area via crosslinking of PMAPOSS polymer chains in the thin films. Note that relatively clear boundary between nanostructures of dots and lines was observed in the thin films exposed by oxygen plasma. This could be due to a calibration of backscattered dose of UV around boundary area. On the other hands, location of boundary cannot be controlled accurately because of diffusion of O₂ plasma.

Fig.5. SEM image of PMMA-*b*-PMAEtPOSS thin films after exposure of oxygen plasma with a mask of silicon wafer in selective area and solvent annealing at 180 °C.

4. Conclusion

We have shown the synthesis, characterization, and patterning ability with the control of morphology change of PMMA-*b*-PMAEtPOSS. The nanostructures of dots and lines were obtained by choosing the solvents of CS₂ and CS₂/acetone in the solvent annealing, respectively, and they were able to change between them reversibly. Thermal annealing for the nanostructure of lines was effectively induced to morphologically change into the dots. Both of the nanostructures in the thin films were able to lock by exposure of UV/Ozone or oxygen plasma treatment. By further solvent or thermal annealing, the unlocked nanostructures changed, and the patterns with coexisting nanostructures of dots and lines were successfully obtained. This simple patterning process can be expected to apply the creation of more complicated

patterned templates based on block copolymer nanostructures with cost-effectiveness, scalability, and compatibility with other well-established processing techniques.

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