Ultra-Fast Block Copolymers for Sub-5 nm Lithographic Patterning

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DSA lithography is a chemical assisted patterning approach, which has attracted a great deal of interest due to its potential high resolution and low cost. Researchers around the world discovered some sub-5 nm high resolution DSA materials, and all these materials required high annealing temperature or long annealing time. In this study, we design and synthesize some PS-typed and PMMA-typed fluoro-containing BCPs. The finest half pitch of these BCPs is less than 5 nm. And the thermal annealing time of PS-typed BCPs is optimized to 1 min, which has been the highest assembly speed for sub-5 nm nanopatterning. The self-assembly speed of PMMA-typed BCPs is much slower than the PS-typed. We further exhibit that ordered nanopatterns are assembled to appear straight 10 nm lines in the silicon template.

Keywords: Block copolymer, Directed self-assembly, Sub-5 nm, Ultra-fast annealing

1. Introduction

It is well known that the semiconductor industry has been driven by Moore’s Law for 50 years. And the lithographic materials played a quite important role in it. Recently, 13.5 nm EUVL has been deeply developed and getting more and more mature, which is widely considered as the next generation lithographic patterning technology for 7 nm and 5 nm nodes [1,2]. However, due to the high cost and low throughput of EUVL, the industry also searching another alternative patterning technique. In this regard, the directed self-assembly (DSA) of block copolymers has attracted a great deal of interest due to its potential applications in sub-10 nm even sub-5 nm node lithographic patterning technology [3-5].

The conventional DSA materials poly(styrene-block-methyl methacrylate) (PS-b-PMMA) have been extensively studied [6,7], however, its resolution is up to 18 nm, which limits its application in the sub-5 nm patterning. And there are limited number of copolymers that could form single nanometer full pitch dimensions due to the intrinsically large interaction parameters required for the self-assembly of low molecular weight BCPs [5]. Recently people discovered several high χ BCPs (Flory-Huggins interaction parameter) for sub-5 nm patterning [8-13]. However, their thermal annealing time is too long, which is not suitable in the semiconductor manufacturing process.

Based on our previous research of modified PS-b-PMMA BCP system, we further optimized our BCP system to achieve higher resolution and faster self-assembly [14]. In this study, we designed and synthesized novel fluoro-containing BCPs which show ultra-fast assembly speed to achieve sub-5 nm micro phase-separated structures (Scheme 1). Different pitches and morphology are obtained by precise control of the two blocks. We observed that the PS-typed BCPs become to have long range order after 1 min thermal annealing. However, the annealing time of PMMA-typed fluoro-containing BCPs is much longer, such as 1 hour at 180 °C. It is worth noting that the finest half pitch of these BCPs is less than 5 nm, which meets the requirements of semiconductor patterning materials with small features. We further exhibit that ordered nanopatterns are assembled to appear straight 10 nm lines in the silicon template.
2. Experimental

2.1. Synthesis and characterization

In this study, a series of block copolymers with low PDI (< 1.15) were synthesized. The PS-typed fluoro-containing BCPs and PMMA-typed fluoro-containing BCPs were synthesized by living anionic polymerization and atom transfer radical polymerization, respectively. All the monomers, initiators were purchased from Energy Chemical and J&K and were distilled from CaH₂ under vacuum to remove the moisture and impurities. Lithium chloride was purchased from Alfa Aesar. All the solvents (THF, hexane, methanol) were obtained from Titan. All the other reagents and solvents were used as received unless otherwise noted.

Each PS-typed fluoro-containing block copolymer was synthesized according to the following procedure. The flask was dried under vacuum and purged with argon for 3 times. 25 ~ 35 mL of THF and 1~5 mL of styrene were transferred to a flask loaded with dry LiCl (5 eq of the initiator). The flask was cooled to −80 ~ −85 °C, and 0.5 mL of sec-butyllithium (1 M in hexane) was injected. After 30 min of polymerization, styryl anions were capped with 0.1 mL of DPE. Then fluoro-containing methacrylate monomer was added into the system and polymerized, then terminated with degassed methanol. After the polymerization, all the polymer was purified by dissolution and precipitation following with the gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) measurement.

¹H-NMR spectra were acquired on a 400 MHz AVANCE III instrument using CDCl₃ as solvent and TMS as internal standard. From the ¹H-NMR spectra we can identify the characteristic peak of each component and calculate the ratio of two blocks. GPC measurements were used to calculate the molecular weight and PDI (Polydispersity index). Narrowly distributed polystyrene samples were used as calibration standards. All the block copolymers show a narrow distribution up to 1.15 during this synthesis process. Small-angle X-ray scattering (SAXS) patterns were collected on a Nanostar SAXS (Bruker AXS GmbH, Germany), with pinhole collimation for point focus geometry. Field emission scanning electron microscope (FESEM) images were observed using a Zeiss Ultra 55 with In-lens detector at 3 kV. Reactive Ion Etch (RIE) was performed on Trion Sirus T2 RIE system.

2.2. Thermal annealing process

The sample preparation and thermal annealing process are shown in Figure 1. As for the sample preparation for TEM & SAXS measurement, 5 wt% BCP solution (in toluene) was drop-cast on the silicon wafer and then dried in vacuum oven at room temperature for 2 h. To make sure the exact time of the thermal annealing process is 1 min, we chose the icy plate to chill the samples after annealing at 80 °C. After 1 min thermal annealing, we got the lamella or hexagonal structures with sub-5 nm half-pitch. Phase separation morphologies and micro domain spacings (D) of the block copolymers were characterized by SAXS and TEM.

2.3. Silicon template preparation

The silicon templates were prepared by e-beam lithography (EBL). Both positive resist and negative resist are used in this study. The positive resist PMMA is spin-coated on the silicon wafer at 3000 rpm for 40 s, and then baked at 180 °C for 30 s. The accelerating voltage is 20 kV, with 7.5 μm aperture and the exposure dose varies from 120 to 200 μC/cm². As for the following plasma etch of silicon, two processes are used. The first is 18 scem CHF₃ and 35 scem SF₆ plasma at 30 mTorr for 60 s. And the second process is 2 scem CHF₃ and 50 scem SF₆ plasma...
at 150 mTorr for 60 s. As for the negative resist HSQ, which is spin-coated on the silicon with 6000 rpm for 1 min, and then baked at 180 °C for 2 min. The exposure dose varies from 60 to 80 μC/cm².

3. Results and discussion

3.1. SAXS results of PS-typed BCP

By changing the molar ratio and the molecular weight in the block copolymers, different phase separation pitches and morphologies were obtained. These block copolymers show the potential as DSA material with high intrinsic resolution for sub-5 nm lithographic patterning technology.

The domain spacing \( (L_0 = 2\pi/q^*) \) of BCPs is calculated by SAXS results, peaks with \( q/q^* \) of 1, 2, 3, 4 indicating the forming of lamella (Lam) morphology. As for the PS-typed fluoro-containing BCPs, we observed fast assembling of three BCPs. As preliminary result, lamella morphology with different domain spacing from 10.2 nm to 17.3 nm was obtained after 5 min at 80 °C and 1 min at 120 °C, respectively. For the low \( T_g \) BCP, ordered lamella separation appeared even after 1 min at 50 °C (Fig. 2).

3.2. SAXS results of PMMA-typed BCP

The more hydrophilic PMMA block was employed instead of PS-typed block in the BCPs. According to the SAXS results in Fig. 3, the PMMA-typed BCP did not clearly phase separated for 1 min at 120 °C, and much ordered structure was obtained at 180 °C. The domain spacing of this PMMA-typed BCP is 14.1 nm with lamella morphology after 1 hour annealing at 180 °C. Compared with the PS-typed BCPs, PMMA-typed BCPs need much longer annealing time at higher temperature. Also some silicon-containing fluoro BCPs were also synthesized and studied, which showed slow annealing process similar to PMMA-typed BCPs (Fig. 3).

3.3. Single \( T_g \) of BCPs

The glass transition temperature \( (T_g) \) was measured by DSC (Fig. 4). Only one \( T_g \) was observed: 83 °C, 74 °C and 66 °C for PS-1, PS-2 and PS-3, respectively.
3.4. SEM results in silicon template

We spin-coated and annealed our DSA materials in the silicon templates (Fig. 5). Figure 5a illustrates the directed self-assembly of hexagonal morphology in the template trench. Actually, we didn’t observe the vertically aligned lamellar morphology after thermal annealing in the silicon template. It was found that the BCP with lamella morphology was parallel to the bottom surface instead of the trench wall. On the other hand, the hexagonal morphology was observed in the trench. After spin-coated on the template wafer and then dried in vacuum for 2 hours, the BCP thin film was annealed and self-assembled in Figure 4b. In order to improve the contrast of image, samples for SEM measurement were post CF₄ plasma etch for 45 s at 75 mTorr, and RF power is 10 W. As displayed in the SEM image (Fig. 5), the hexagonal line of 10nm along with the trench wall was observed after fast thermal annealing.

4. Conclusion

In this study, we designed and synthesized a series of PS-typed and PMMA-typed BCPs. Similar to the high-resolution materials reported, we discovered that by adequate monomer design and the precise control of both molecular weight and molar ratio of two blocks, we can obtain BCP with high resolution to 5 nm. Besides the high resolution, the PS-containing BCPs showed fast assembling speed, e.g. 1-5 min even at mild temperature. More details will be reported later. After DSA process in Si template, straight lines of 10 nm along with the trench wall were obtained after thermal annealing.

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References