Development of Directed Self-Assembly Materials for Sub 10 nm Patterning

Hiroyuki Komatsu, Masafumi Hori, Shinya Minegishi, Takehiko Naruoka, and Tomoki Nagai

Fine Electronic Research Laboratories  
Semiconductor Materials Laboratory  
JSR Corporation  
100, Kawajiri-cho, Yokkaichi Mie 510-8552 Japan

Directed self-assembly (DSA) technique has been focused as the novel semiconductor manufacturing process replacing photo-lithography process for semiconductor applications. We synthesize block copolymers (BCP) containing silicon unit, which show cylinder and lamellae structure from micro-phase separation by only heat annealing (220 °C/ 60 sec). Moreover, we could get hexagonal cylinder, maybe lamellae structure along the guide pattern for pattern division by grapho-epitaxy. The examined BCPs are expected to be promising materials for sub 10 nmP patterning.

Keywords: Directed self-assembly, anionic polymerization, block copolymer, high-χ

1. Introduction

For the latest decade, directed self-assembly (DSA) technique has been focused as the novel semiconductor manufacturing process replacing photo-lithography process for semiconductor applications, which can be regularly arranged micro domain such as cylinder and lamella on the length scales from a few to hundreds of nanometers [1].

For example, block copolymer of styrene and methyl methacrylate (PS-block-PDMA) can form a self-assembly with aimed formation and/or length scale by changing key factors such as degree of polymerization, and fraction volume, which can use template to micro-fabricate on the silicon wafer by selectively removing only methyl methacrylate in polymer domain, based on wet and dry etching [2]. However, PS-block-PDMA is difficult to form line and space (LS) and contact hole (CH) below 25 nm pitch by block copolymer lithography on grounds of low Flory-Huggins interaction parameter (χ) [3], if only it could arrange enough lower molecular weight of polymer.

Therefore, many researchers are investigated the introduction of hydrophilicity and silicon group for finding monomers with higher Flory-Huggins interaction parameter (χ). For example, it reports the block copolymer lithography candidates such as poly(styrene-block-ethylene oxide) (PS-block-PEO) [4], poly(styrene-block-2-vinyl pyridine) (PS-block-2VP) [5], poly(styrene-block-dimethylsiloxane) (PS-block-DMS) [6], and poly(styrene-block-silsesqioqusane) (PS-block-POSSMA) [7].

Block copolymers and graft copolymers with siloxane or silsesqioqusane in the main or side chain is mainly influenced micro-phase separation by weight percent of silicone to all compound, fraction volume of silicon unit, other kinds of segments. Moreover, the silicon monomer is also priority for litho-selectivity on the ground of higher anti-etching than that of styrene and alkyl (meth)acrylate monomer for O2 etching gas. Colburn et. al. reports to have anti-etching compared to polystyrene under standard O2 RIE, when the silicon component in applicable block unit is more than about 12% [8]. On the other hand, it is not often suitable for lithography, since it is difficult for organic-organic high-chai block copolymers to get selective etching by non-polar and polar organic segment.

Herein, we synthesized block copolymers consisted of organic segment and inorganic segment with appropriate silicone amounts (>12%), which could get cylinder and lamella structure print derived from micro-phase separation. Moreover, we report 10 nm patterning technique by block copolymer lithography.
2. Experiment and Measurement

2.1 Synthesis of block copolymers

Block copolymers (BCP) of monomer 1 (M1) and monomer 2 (M2) were synthesized by anionic polymerization at -78 °C in tetrahydrofuran (THF) with sec-BuLi initiator system. The polymer solution is precipitated in methanol/water=9/1, and extracted in methyl i-butyl ketone/1wt% oxalic acidic aqueous solution. The resulting polymer was vacuumed oven at 60 °C. Size exclusion chromatography (SEC) analysis was performed on Tosoh ECO SEC HLC-8320GPC equipped with a refractive index detector, and polystyrene gel tandem columns (Tosoh TSK gels G4000HXL, G3000HXL, G2000HXL*2) eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. at 40 °C. Polystyrene standards were used for calibration.

2.2 Micro-phase separation characterization of BCP

BCP is also patterned from following conditions. [Substrate: 12 inch silicon wafer, Tool: TEL ACT12, Neutral layer: NFC DS037Y (FT: 5nm, from JSR corporation), DSA materials: 3a-3e], Film thickness=22 nm, Annealing: 220 °C/60 sec., Development: No developer/no rinse. The patterning image was observed by scanning electron microscope (SEM) HITACHI CG4000. The periodic analysis is carried out by IMEC calculation tool, based on SEM image (300K).

2.3 Pattern division with BCP for LS and CH by grapho-epitaxy

Guide resist is patterned from following conditions. [Substrate: 12 inch silicon wafer, Tool: ASML NXT: 1950i, Substrate: NFC DS037Y (FT: 5 nm, from JSR corporation), ISX420 (FT: 33 nm, from JSR corporation), HM8102 (FT: 135 nm, from JSR corporation), PR: Self-freezing type guide resist. Block copolymer is also patterned from following conditions. [Tool: TEL ACT12, DSA material: 3a-3e, Film thickness=22 nm, Annealing: 220 °C/60 sec., Development: No developer/no rinse]. The patterning image was observed by SEM, HITACHI CG4000. The periodic analysis is carried out by IMEC calculation tool, based on SEM image (300K).

3. Results and Discussion

3.1 Synthesis of BCP

Block copolymers (BCP) of monomer 1 (M1) and monomer 2 (M2) were also synthesized by anionic polymerization (Scheme 1). The GPC profiles of the BCPs are shown in Figure 1. The profiles after second process increase ‘Mn’ maintaining a narrow polydispersity, compared first process to second process (Figure 1). The fraction volume of each segment was also accorded with theoretical monomer feed. Therefore, the post-polymerization experiment reveals the living nature of the polymerization. Then, the living block nature of the polymerization of M1 and M2 was confirmed by the polymerization under various concentration of the initiator. Regardless of the concentration of initiator, we could be obtained BCPs with narrow polydispersity (Mw/Mn< 1.05) [Figure 2].

Figure 1. SEC profiles of homopolymer [(a), (b), (c)]

Figure 2. SEC profiles of block copolymer (3a), (3d), and (3e)
Table 1. Block copolymer of $M_1$ and $M_2$ by anionic polymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed ratio $M_1 / M_2$ (mol%)</th>
<th>Fraction volume ratio</th>
<th>$M_n$ (3a)’s $M_n$</th>
<th>$M_w/M_n$</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>60 / 40</td>
<td>27 / 73</td>
<td>1.00</td>
<td>1.03</td>
<td>73</td>
</tr>
<tr>
<td>3b</td>
<td>80 / 20</td>
<td>50 / 50</td>
<td>0.95</td>
<td>1.03</td>
<td>74</td>
</tr>
<tr>
<td>3c</td>
<td>90 / 10</td>
<td>69 / 31</td>
<td>0.95</td>
<td>1.02</td>
<td>76</td>
</tr>
<tr>
<td>3d</td>
<td>60 / 40</td>
<td>29 / 71</td>
<td>0.89</td>
<td>1.03</td>
<td>76</td>
</tr>
<tr>
<td>3e</td>
<td>60 / 40</td>
<td>29 / 71</td>
<td>0.78</td>
<td>1.03</td>
<td>80</td>
</tr>
</tbody>
</table>

1) Estimated by profiles of GPC with first process and second process sample (THF, polystyrene standards),
2) Calculated by following equation [($M_n$ (3a)’s $M_n$), by $M_n$ of GPC],
3) Determined by GPC.
4) Yield after precipitated and extracted by removing metal.

3.2. Micro-phase separation characterization of BCP

It is important to estimate fraction volume of each other segments for observing micro-phase separation behavior. Fraction volume of di-block copolymer consisted of two segment was estimated by GPC profile of first process and/or second process and $^1$H NMR spectroscopy of BCP. We synthesized BCPs with differential fraction volume ($3a$, $3b$, and $3c$) and with differential molecular weight ($3d$ and $3e$) [Table 1]. They were expected to show lamella and cylinder structure by each fraction volume ratio. At first, we examined pattern formation by SEM for each micro-phase separation characterization under thin film thickness (ca. 22 nm) and only heat annealing (220 °C/60 sec.). The synthesized BCPs showed micro-phase separation on only neutral layer without top coat neutral layer and vapor annealing. We are extensively observed finger print or hexagonal contact hole pattern derived from maybe lamella, perpendicular cylinder, and parallel cylinder structure by SEM. At second, they are shown ($3a$) 18 nmP perpendicular cylinder, ($3b$) 20 nmP maybe lamella, and ($3c$) 20 nmP parallel cylinder, as the result of morphological identification and periodic analysis (Table 2).

Table 2. Morphology identification of BCPs ($3a$, $3b$, and $3c$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$3a$</th>
<th>$3b$</th>
<th>$3c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction</td>
<td>M1 Block / M2 Block = 27 / 73</td>
<td>M1 Block / M2 Block = 50 / 50</td>
<td>M1 Block / M2 Block = 69 / 31</td>
</tr>
<tr>
<td>Estimated morphology</td>
<td>M1-core Perpendicular Cylinder</td>
<td>Perpendicular Lamellar</td>
<td>M2-core parallel cylinder</td>
</tr>
<tr>
<td>Fingerprint image (300K)</td>
<td>17.9nmP</td>
<td>20.2nmP</td>
<td>19.5nmP</td>
</tr>
<tr>
<td>Periodic analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Next, we examined BCPs (3d and 3e) with lower molecular weight compared to 3a. They revealed M₁ core-cylinder below 10 nm half pitch (3a): 9 nmhP, (3d): 8 nmhP, (3e): 7 nmhP, as the result of periodic analysis (Table 3). The pitch scale of cylinder pattern depends on molecular weight of BCPs (3a, 3d, and 3e) as well as that of PS-b-PMMA. The limitation of resolution will be also examined by O₂ etching gas from now on. They may be promising high-χ material candidate for BCP lithography.

Table 3. Morphology identification of BCPs (3a, 3d, and 3e) with different molecular weight

<table>
<thead>
<tr>
<th>Sample</th>
<th>3a</th>
<th>3d</th>
<th>3e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fingerprint image (300K)</td>
<td>17.9nmP</td>
<td>16.1nmP</td>
<td>13.9nmP</td>
</tr>
</tbody>
</table>

3.3. Pattern division with BCPs for LS and CH by grapho-epitaxy

The grapho-epitaxy used guide pattern is effective application for the orientation control of lamella and hole domains [9]. Therefore, we examined pitch division with different morphology BCPs along the guide pattern. It is shown SEM graphics after micro-phase separation (Table 4). We observed LS or hexagonal CH pattern structure below 10 nmhP along the guide pattern.

Table 4. Pattern division with BCPs by grapho-epitaxy method

<table>
<thead>
<tr>
<th>Sample</th>
<th>3a M₁-core perpendicular cylinder</th>
<th>3b Perpendicular Lamellar</th>
<th>3c M₂-core parallel cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP patterning</td>
<td>18nmP CH</td>
<td>20nmP LS</td>
<td>19nmP LS</td>
</tr>
<tr>
<td>Annealing: 220°C/60s</td>
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</tbody>
</table>

4. Conclusion

We observed the formation of fingerprint and hexagonal cylinder pattern below 10 nmhP for our BCPs with narrow polydispersity (PDI< 1.05) on only heat annealing (220 °C/60sec.). For pattern division by grapho-epitaxy, we could get recreation of hexagonal cylinder, maybe perpendicular lamella, and parallel cylinder structure along the guide pattern by each BCPs at primary evaluation. The synthesized BCPs (3a-3e) will be promising material candidate for BCP lithography. As next stage, we will progress to transfer the pattern on the silicon wafer by dry etching of novel BCPs.

These studies will be reported as original article in the other opportunity.

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References


