Hemicellulose Block Copolymers for Advanced Lithography Process

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Directed self-assembly (DSA) lithography is one of the promising next-generation lithography technologies. However, there are two main limitations to the use of DSA. One is the narrowness of the pattern size window and the other is the fabrication of the underlayer. To address the former limitation, wide-range DSA has been applied to expand the applicable patterning size while the latter has been achieved by utilizing the newly developed reactive hemicellulose hardening (R2H) technique. In R2H, the hemicellulose unit is selectively hardened by a chemical reaction. In this study, hemicellulose block copolymers for wide-range DSA lithography and its fabrication technology were newly developed. A hemicellulose high-chi block copolymer (OPAL-BCP) and its underlayer were fabricated using R2H. After reactive ion etching of the underlayer with R2H, a pattern depth of over 300 nm and etching selectivity of 24 were obtained.

Keywords: Directed self-assembly, Block copolymer, High-chi BCP, Wide-range, Hemicellulose, Reactive hemicellulose hardening, R2H, High etching resistance

1. Introduction

Directed self-assembly (DSA) lithography [1] is among the promising next-generation lithography technologies. To address the narrowness of the pattern size window, wide-range DSA has been applied to expand the applicable patterning size [2,3]. Block copolymers with a hydrophobic part and a hydrophilic part are used. Depending on the ratio of the hydrophobic part to the hydrophilic part, various patterns, such as the L/S or hole patterns, can be created (Fig. 1) [4]. PS-PMMA is the typical DSA material [5-9]. For smaller-size patterning, high-chi block copolymers are required [10-17].

In order to enable the wide application of DSA (Fig. 2), two main limitations need to be addressed: narrowness of the pattern size window and fabrication of the underlayer. The former has been addressed by employing wide-range DSA to expand the applicable patterning size [2]. A wide range implies a range of micro-phase separation wider than that in conventional DSA materials such as PS-PMMA and high-chi materials. Hemicellulose [18] is a component of plant cell walls from hard woods and has high hydrophilicity [3]. Therefore, hemicellulose block copolymers have a high aggregation property and are high-chi materials. Fabrication of the underlayer was achieved by the newly developed hardmask technology. This paper describes the high fabrication property of hemicellulose block copolymers.
copolymers using the new hardmask technology.

2. Concept of hemicellulose block copolymers (OPAL-BCP) for wide-range DSA and reactive hemicellulose hardening (R2H)

2.1. Hemicellulose block copolymer for wide-range DSA

Hemicellulose has many hydroxy groups in one molecule (Fig. 3). This implies that hemicellulose block copolymers are promising as high-chi block copolymers, in terms of their smaller size separation as well as larger size separation with less placement errors, short annealing time, and low defect density based on its strong phase-separation ability. Figure 4 shows the structure of a hemicellulose block copolymer (OPAL-BCP). The structure has four parts: a length adjustment part and hydrophobic strong condensation part in the hydrophobic part, and a length adjustment part and hemicellulose strong condensation part in the hydrophilic part.

Wide-range DSA with hemicellulose block copolymers can be achieved using the structure of the hemicellulose itself and the structure model.

2.2. Fabrication improvement using reactive hemicellulose hardening (R2H)

To improve the fabrication property of the underlayer, the reactive hemicellulose hardening (R2H) technique was developed. Via R2H, the hemicellulose unit is selectively hardened by a chemical reaction. The unique structures of hemicellulose are bonded to one another by chemical species (Fig. 6), and high etching resistance can be achieved. Hemicellulose spin-on-carbon (SOC) material with R2H, when used as the hardmask, yielded high-aspect-ratio patterns [19,20]. The dry etching selectivity was 25.

As a fundamental study, the etching properties
of a conventional polymer and hemicellulose were evaluated. Figure 7 shows the etching properties of the conventional polymer and hemicellulose, with and without R2H. Figure 7(a) shows the results using oxygen gas and Fig. 7(b) shows the results using CHF3 gas. For hemicellulose, the effect of R2H is larger than that for the conventional polymer, especially for CHF3. Thus, it was confirmed that hemicellulose with R2H is stronger than the conventional polymer. Therefore, hemicellulose with R2H can be used as a hardmask. To achieve better fabrication of the underlayer, R2H was applied to the hemicellulose block copolymer.

3. Results and discussion

3.1. Preparation of OPAL-BCP and process flow on 300 mm wafer

All OPAL-BCP samples were synthesized from hemicellulose extracted from hard wood. The synthesized polymers were characterized by nuclear magnetic resonance (NMR) on JEOL JNM-ECS-400 and gel permeation chromatography (GPC) on Waters Agilent1100 (column: Shodex GPC KF-806L, KF-803L, KF-801). The hemicellulose block copolymers were dissolved in PGMEA and metal contamination was removed. Figure 8 shows the process flow for evaluating OPAL-BCP. Spin coating was performed using SOKUDO DUO made by SCREEN. On a 300 mm wafer with the underlayer, the brush material was coated. Subsequently, OPAL-BCP was spin-coated and annealed (230 °C, 3-5 min), following which R2H was applied to convert the hemicellulose part of OPAL-BCP into the hardmask. Reactive ion etching (RIE) of the OPAL-BCP and underlayer were subsequently carried out.

3.2. Effect of R2H

To confirm the effect of R2H, the underlayer was fabricated using OPAL-LC01 (CD 42 nm cylinder).

Figure 9 compares the SEM images of the reactive-ion-etched OPAL-BCP and Si underlayer. The images confirm that multiple cylinders on the...
post guides [21] were successfully transferred into the underlayer.

Figure 10 was used to evaluate the effect of R2H. The depth of the hole pattern in the underlayer was only 30 nm without R2H, but 340 nm with R2H. Thus, R2H improved the depth by 11 times.

3.3. Results using OPAL-BCP on the 300 mm wafer
Table 1 shows the CD-SEM images of OPAL-LC01 at the center, middle, and edge areas on the 300 mm wafer for each process (phase separation, after treatment, underlayer RIE). The images confirm that the micro-phase separation pattern was transferred into the underlayer. The cross-sectional SEM image is shown in Fig. 11. A deep pillar pattern of 300 nm was obtained, with an etching selectivity of 24.

Table 1. CD-SEM images of OPAL-LC01 with pillar guide by each process.

| Phase Separation | After Treatment | Under Layer RIE |
|------------------|----------------|----------------|
| Center           |                |                |
| Middle           |                |                |
| Edge             |                |                |

3.4 Effect of hemicellulose
To confirm the effect of hemicellulose, the properties of the micro phase separation and R2H were studied.

3.4.1. Effect of micro-phase separation
Three kinds of OPAL-BCP were prepared for the L/S pattern ($M_w = 12.5k$), using different hemicellulose contents.

Figure 12 shows the results after the micro-phase separation and RIE of OPAL-BCP without R2H. By a 9-fold increase in the hemicellulose content, the micro-phase separation property exhibits improvement.

Fig. 12. Comparison of top view SEM images of micro-phase separation with hemicellulose relative content.

3.4.2. Effect of R2H
Two kinds of OPAL-BCP were prepared for the cylinder pattern ($M_w = 16.4k$) with different hemicellulose contents.

Figure 13 shows the results after R2H and RIE of OPAL-BCP. By a 5-fold increase in the hemicellulose content, the depth of fabrication into the underlayer has improved.

Thus, the hemicellulose content is a key parameter to achieve improvement in the micro-phase separation and fabrication properties via R2H.

Fig. 13. Comparison of cross-sectional SEM images of fabrication property of R2H with relative content of hemicellulose.

3.5 Experimental results for other types of OPAL-BCP
Two cylinder types and one line-and-space-type BCP were also fabricated as underlayers.

Figures 14(a) and (b) show the result for OPAL-LC02 (CD 42 nm hole with hole guide) and OPAL-LC03 (CD 48 nm pillar pattern), respectively. The pattern depths in Fig. 14(a) and (b) exceed 300 nm, with an etching selectivity of 24.

The L/S pattern of OPAL-LS01 (hp 18.5 nm)
with a physical guide is shown in Fig. 15. The image confirms that a pattern depth of 311 nm is successfully obtained.

4. Conclusion

Fabrication technology for underlayers was newly developed using hemicellulose block copolymers (OPAL-BCP) and reactive hemicellulose hardening (R2H) for wide-range DSA. The dry etching resistance of OPAL-BCP improved with R2H. Underlayer RIE with R2H was successfully performed to achieve a depth over 300 nm and etching selectivity of 24. Hence, OPAL-BCP with R2H is promising for next-generation lithography.

Acknowledgements

The authors would like to thank Dr. Y. Tanaka and Dr. H. Tanaka from Oji Holdings Corporation for detailed discussion on the process and materials.

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