Study on Resist Performance of Noria Derivatives Modified with Various Protection Ratios of Acetal Moieties by means of Extreme Ultraviolet Irradiation

Hiroki Yamamoto1*, Hiroto Kudo2, and Takahiro Kozawa1

1The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
2Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita-shi, Osaka 564-8680, Japan *hiroki@sanken.osaka-u.ac.jp

The requirements for next generation resist materials in extreme ultraviolet (EUV) lithography are very challenging. Therefore, the development of new resist materials has been expected to meet strict requirements. Molecular resists are promising resists owing to the small size of their building blocks. In this study, we examined lithographic performances, such as sensitivity and patterning, using noria derivative (noria-CHVEs, Resist 1-3) under EUV and a 75 keV electron beam (EB) exposure system. In particular, the effect of the protection ratio on the lithographic performances was studied by changing the protection ratio. The sensitivities of noria-CHVEs showed high values in the range between 1.8 and 3.0 mJ/cm². Resist 2 could provide a resist pattern with a higher resolution than Resist 1 and Resist 3, i.e., a semi-isolated pattern with a line width of 30 nm (pitch: 100 nm). These results indicate that the synthesized noria-CHVEs are promising EUV resist materials.

Keywords: Extreme ultraviolet, Molecular resist, Chemically amplified resist, Noria derivative, Protection ratio

1. Introduction

Nanolithography technologies have been widely used below the 100 nm node scale, including the 193 nm immersion, electron beam (EB) [1,2], extreme ultraviolet (EUV, 13.5 nm), nanoimprint methods [3,4], and focused ion beam (FIB) lithography [5]. Among these technologies, EUV lithography is one of the most promising nanolithographic technologies for advanced devices to achieve less than 16 nm nodes [6-8] and is a potential future lithographic technology for high-volume manufacturing in the microelectronics industry. For the feasibility of EUV lithography, EUV resist materials and their resist processes play a crucial role.

Currently, chemically amplified resists have been used for the mass production of semiconductor devices and are expected to work well in EUV lithography. However, the requirements for EUV resist materials are so strict that technical solutions are still unknown. In addition, there is a trade-off relationship among resolution, sensitivity, and line width roughness (LWR). Therefore, it is very difficult to meet these requirements simultaneously. Among them, LWR has become the most serious problem in resist processes as feature sizes continue to shrink. The LWR target has been set to be less than 1 nm for a 16 nm DRAM half pitch [9]. Although much effort has been devoted to the reduction of LWR, LWR remains too higher than the LWR target at present. To meet the strict demand for EUV lithography, new materials must be developed for chemically amplified resists.

With the reduction of the feature size of resist patterns, the molecular size of the resist materials becomes more important. Actually, some molecular resists show higher sensitivity or yield
higher resolution than polymer resists. Therefore, there is great potential for molecular resists to be used as the skeleton of EUV resists. Also, the reduction of the grain size is believed to lead to a fundamental improvement in the ability to consistently obtain a lower LWR. Therefore, the reduction of the molecular size is essential to resolve ultra-fine patterns. Thus, molecular resists have attracted much attention.

To date, several different materials have been investigated as potential molecular resist materials [10-12]. Recently, Kudo and coworkers have succeeded in the synthesis of a new ladder cyclic oligomer “noria” (water wheel in Latin) [13] and reported the synthesis and photochemical reactivity of noria derivatives containing t-butoxycarbonyl groups [14,15], t-butylerester groups [16], acetal groups [17,18], and adamantyl ester groups [19-23]. It was found that these noria derivatives have high photoreactivity and produce clear line and space patterns with resolutions of 50-70 nm using an EB exposure tool and 26 nm using an EUV exposure tool [15-23]. Moreover, we clarified that the sensitivity of the resist materials was consistent with the structure of the cyclic oligomers such as noria, calixarene dimer, cyclodextrin, and pillar[5]arene [24].

In this study, we examined the lithographic performances such as sensitivity and patterning of noria-CHVEs under EUV and EB exposure. In particular, the effect of the protection ratio on lithographic performances, such as sensitivity and patterning, was studied by changing the protection ratio.

2. Experimental

Noria derivatives (noria-CHVEs) were used as a resist. Noria derivative with different protection ratios of CHVE groups were synthesized by adjusting the reactant feed ratios and reaction concentration by a previously reported method [17]. We synthesized three types of noria-CHVEs (Resists 1-3) with pendant cyclohexyl acetal moieties as protection groups (protection ratios = 43, 50, and 59%) as shown in Fig. 1. Propylene glycol monomethyl ether acetate (PGMEA) was used as a casting solvent without further purification. Triphenylsulfonium trifluoromethanesulfonate (TPS-nf) was used as an acid generator without further purification. Noria derivatives and TPS-nf were dissolved in PGMEA. The weight ratio of the constituents was polymer/acid generator = 100/10.

In the sample preparation for the evaluation of resist performance, noria derivative resist solutions without amine were spin-coated on a bottom antireflective coating (BARC)-treated n-type Si wafer. Then, the resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating on silicon wafers. The resist solutions were spin-coated onto silicon substrates at 3000 rpm for 30 s to form thin films on the silicon wafers. Then, these spin-coated films were prebaked at 90 °C for 90 s. The film thickness was then adjusted to 100 nm. The films were exposed to EUV (Energetic, EQ-10M) [25]. The exposed area was approximately 1 × 1 cm². After the exposure, they were baked at 90 °C for 60 s. They were developed by dipping in tetramethylammonium hydroxide (TMAH) (2.38 wt%) solution for 30 s at 23 °C and then rinsed in deionized water before drying. The resist film thickness was measured with an ET200 surface profiler to obtain sensitivity curves.

In the sample preparation for the scanning electron microscope (SEM) observation of resist patterns, amine was added to noria derivatives resist solutions. Then the resist solutions were spin-coated on a BARC-treated n-type Si wafer. The spin-coating, prebaking, and development conditions were the same as those in the above sensitivity measurement. A water-soluble conducting polymer (Showa Denko, Espacer) was also spin-coated at 2000 rpm for 60 s before exposure. The films were exposed to a 75 kV EB (ELIONIX, ELS-7700). After the exposure, they were baked in the temperature range from 90 to 110 °C for 60 s. Resist patterns were recorded by an ultrahigh-resolution SEM (Hitachi-Hitec S-5500).

3. Results and discussion

For the evaluation of resist performance, we measured the sensitivity of noria-CHVEs resists containing 10 wt% TPS-nf and no amine using EUV exposure tools and compared their sensitivity.
Figure 2 shows the sensitivity curves of noria-CHVEs (Resists 1-3) upon exposure to EUV. The film thickness was normalized by that before development. The postexposure bake (PEB) temperature and time were 90 °C and 60 s, respectively. Their sensitivities showed high values in the range between 1.8 and 3 mJ/cm². In Resists 1 and 2, pattern formation occurred with a loss of resist thickness because Resists 1 and 2 have lower protecting ratios than Resist 3. The result indicated that the order of sensitivity was Resist 2 ≡ Resist 3 > Resist 1. It has been reported that noria derivatives with low protection ratios of cyclohexyl acetal moieties showed higher sensitivity [17]. Therefore, we expected that Resist 1 would exhibit higher sensitivity than the other resist materials. However, an increase in resist sensitivity with the decrease in the protection ratio was not observed in this experiment. This might be due to the use of a different acid generator and a slight difference in the process conditions, although this has not yet been proven.

Patterning experiments were also carried out using a 75 kV EB and changing the PEB temperature. Figure 3 shows SEM images of line and space patterns delineated on Resists 1-3 with PEB temperature at 90 °C. As predicted from the sensitivity results, the sensitivities of Resists 2 and 3 were higher than that of Resist 1. Relatively fine patterns in both Resists 2 and 3 were obtained upon exposure to an EB. In Resist 2, the best line width and pitch were 30 and 100 nm, respectively. On the other hand, the best line width and pitch were 40 and 120 nm in Resist 3, respectively. These patterns required a dose of 50 μC/cm². The resolution of Resist 2 is superior to that of Resist 3 at the same exposure dose. On the other hand, in Resist 1, the best line width and pitch were 30 and 170 nm with a dose of 50 μC/cm². However, the pattern contrast was lower than those of Resists 2 and 3 because resist thickness perhaps decreased as observed in Fig. 2.

Figures 4 and 5 show SEM images of line and space patterns delineated on Resists 1-3 with PEB temperature at 100 °C and 110 °C, respectively. As shown in Fig. 4, a semi-isolated pattern with a line width of 30 nm (pitch: 150 nm) was delineated in Resist 2. This pattern required a dose of 50 μC/cm² and had the best resolution among the resists with PEB temperature at 100 °C. Thus, Resist 2 has a higher resolution than Resists 1 and 3. The same tendency was also observed in the patterning results with PEB temperature at 110 °C. Resist 2 showed a semi-isolated pattern with a line width of 30 nm (pitch: 200 nm), which was obtained at a
dose of 45 μC/cm². Thus, Resist 2 had the best resolution at a lower dose. However, Resist 3 had the best resolution with a dose of 50 μC/cm². This might be explained in terms of differences in their glass transition temperature (Tg). It has been reported that Tg generally increases with an increase in the protection ratio for the same protecting group [26]. Unfortunately, the protection ratio dependence of lithographic performances such as sensitivity and resolution could not be clearly observed in this study. However, we clarified that noria-CHVE resists are promising candidates as EUV resist materials because of their high sensitivity and high resolution.

4. Conclusion

We examined the lithographic performances, such as sensitivity and patterning, of noria derivatives under EUV and 75 keV EB exposure. The sensitivities of noria-CHVEs showed high values in the range between 1.8 and 3 ml/cm². Also, we clarified that Resist 2 provides higher resolution than Resist 1 and 3. Resist 2 provided a semi-isolated pattern with a line width of 30 nm (pitch: 100 nm). We clarified that noria-CHVE resists were promising EUV resist materials because of their high sensitivity and high resolution. In addition, we investigated the effects of the protection ratio on lithographic performances such as sensitivity and resolution. However, the protection ratio dependence of lithographic performances was not clearly observed.

Acknowledgements

The authors wish to thanks Prof. Tadatomi Nishikubo for his guidance, helpful suggestions and warm encouragement through our research. This work was partly supported by Cooperative Research Program "Network Joint Research Center for Materials and Devices". Also, this work was supported in part by a Grant-in-Aid for Scientific Research (Project No. 25246036, 16K14439) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). A part of this work was supported by “Nanotechnology Platform Project (Nanotechnology Open Facilities in Osaka University)” of Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. M. S. Wei and S. Y. Chou, J. Appl. Phys., 76 (1994) 6679.
2. A. E. Grigorescu and C. W. Hagen, Nanotechnology, 20 (2009) 29200.
3. H. Schift, J. Vac. Sci. Technol., B 26 (2008) 458.
4. S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett., 67 (1995) 3114.
5. S. Matsui, Y. Kojima, and Y. Ochiai, Appl. Phys. Lett., 53 (1988) 868.
6. T. Itani and T. Kozawa, Jpn. J. Appl. Phys., 52 (2013) 010002.
7. J. V. Germans, D. Laidler, P. Foubert, K. D’havé, S. Cheng, M. Dusa, and E. Hendrickx, Proc. SPIE, 8322 (2012) 832202.
8. H. Shite, K. Matsunaga, K. Nafus, H. Kosugi, P. Foubert, J. Hermans, E. Hendrickx, M. Goethals, and D. van den Heuvel, Proc. SPIE, 8322 (2012) 83222Y.
9. International Technology Roadmap for Semiconductors. http://www.itrs.net/home.html. accessed May 2015.
10. F. Diederich and C. Thilgen, Science, 271 (1996) 317.
11. M. Yoshiiwa, H. Kageyama, Y. Shirotu, F. Wakaya, K. Gamo, and M. Takai, Appl. Phys. Lett., 69 (1996) 2605.
12. J. Fujita, Y. Ohnishi, Y. Ochiai, and S. Matsui, Appl. Phys. Lett., 68 (1996) 1297.
13. H. Kudo, R. Hayashi, K. Mitani, T. Yokozawa, N. C. Kasuga, and T. Nishikubo, Angew. Chem. Int. Ed., 45 (2006) 7948.
14. X. André, J. K. Lee, A. D. Silva, C. K. Ober, H. B. Cao, H. Deng, H. Kudo, and T. Nishikubo, Proc. SPIE, 6519 (2007) 65194B.
15. H. Kudo and T. Nishikubo, Polym. J., 41 (2009) 569.
16. H. Kudo, D. Watanabe, T. Nishikubo, K. Maruyama, D. Shimizu, T. Kai, T. Shimokawa, and C. K. Ober, J. Mater. Chem., 18 (2008) 3588.
17. H. Kudo, M. Jinguji, T. Nishikubo, H. Oizumi, and T. Itani, J. Photopolym. Sci. Technol., 23 (2010) 657.
18. H. Kudo, K. Mitani, S. Koyama, and T. Nishikubo, Bull. Chem. Soc. Jpn., 77 (2004) 819.
19. T. Nishikubo, H. Kudo, Y. Suyama, H. Oizumi, and T. Itani, J. Photopolym. Sci. Technol., 22 (2009) 73.
20. H. Seki, H. Kudo, H. Oizumi, T. Itani, and T. Nishikubo, Jpn. J. Appl. Phys., 50 (2011) 121602.
21. N. Niina, H. Kudo, H. Oizumi, T. Itani, and T. Nishikubo, Thin Solid Films, 534 (2013) 459.
22. H. Kudo, Y. Suyama, T. Nishikubo, H. Oizumi, and T. Itani, *J. Mater. Chem.*, **20** (2010) 4445.

23. H. Yamamoto, H. Kudo, S. Tagawa, K. Okamoto, and T. Kozawa, *J. Vac. Sci. Technol. B*, **34** (2016) 041606.

24. H. Yamamoto, H. Kudo, and T. Kozawa, *Microelectron. Eng.*, **133** (2015) 16.

25. S. F. Horne, M. M. Besen, D. K. Smith, P. A. Blackborow, and R. D’Agostino, *Proc. SPIE*, **6151** (2006) 61510P.

26. J. Dai, S. W. Chang, A. Hamad, D. Yang, N. Felix, and C. K. Ober, *Chem. Mater.*, **18** (2006) 3404.