Study on Dissolution Behavior of Poly(4-hydroxystyrene) as Model Polymer of Chemically Amplified Resists for Extreme Ultraviolet Lithography

Masaki Mitsuyasu, Hiroki Yamamoto*, and Takahiro Kozawa

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
*E-mail address: hiroki@sanken.osaka-u.ac.jp

It is challenging to implement extreme ultraviolet (EUV) lithography in mass production because of strict requirement for EUV resist materials. Under this circumstances, it is important in EUV resist design to clarify the dissolution behavior of the resist film in the alkaline developer. In particular, the dissolution in exposed areas of resist films is one of the most critical processes. However, the details of the dissolution process of EUV resists have not yet been clarified. In this study, the dissolution of poly(4-hydroxystyrene) (PHS) polymer, which is a model polymer of EUV chemically amplified resists, with and without additives such as acid generators and amines was studied by a quartz crystal microbalance (QCM) method. The effects of the acid generator concentration and the addition of amines on the dissolution behavior of PHS films were investigated by varying the exposure dose with the aim of obtaining a systematic understanding of the effect of each resist component on dissolution. Differences in the experimentally observed dissolution behaviors were associated with the effect of each resist component on dissolution. The decrease in the development rate caused by the addition of an acid generator suggests that the solubility in the developer depends on the concentration of the remaining acid generator and its structure. In particular, the electrostatic interaction between the acid generator and the hydroxyl groups in PHS has a strong effect on the solubility in tetramethylammonium hydroxide (TMAH) developer. It is important in EUV resist design to take into account the concentration of undecomposed acid generator.

Keywords: Quartz Crystal Microbalance, Chemically amplified resist, Quencher, EUV lithography

1. Introduction

Beyond the 16 nm node, extreme ultraviolet (EUV) lithography is regarded as the most promising next-generation lithography (NGL) technology. The deployment of EUV is expected to have a great impact on the resist design because the energy of exposure tools has exceeded the ionization potential of resist materials used for mass production for the first time. It has been reported that the acid generation mechanism changes above the ionization potential of the resist materials (typically about 10 eV). [1, 2] Therefore, the ionization process preferentially occurs in the acid generation processes in EUV lithography.

It is difficult to implement EUV lithography for mass production because of the severe requirements for the EUV resist materials. In the development of EUV resists, the trade-off relationships between sensitivity, resolution, and line width roughness (LWR) are the most serious problem. In order to overcome this problem, it is essential to understand the basic chemistry of the resist matrices in each resist process. The aqueous base development process plays one of the most critical roles. The dissolution properties of resists strongly affect lithographic performances such as resolution, sensitivity, and LWR. Therefore, it is essential in EUV resist design to clarify the dissolution behavior of the resist film in the alkaline developer.

So far, optical interference measurement has generally been used to study the time evolution of
the resist film thickness during development. [3-5] However, it is difficult to obtain a precise value for the film thickness when the resist film thickness is less than the optical wavelength. Also, it is difficult to observe the swelling behavior during development by optical interference measurement. The quartz crystal microbalance (QCM) method was first applied to microlithography and showed excellent results for observing polymer dissolution. [6] Since then, the QCM method has been used to obtain precise information about the dissolution behavior of resist polymers. The dissolution behaviors of a resist, such as swelling and solvent penetration, have been investigated using this method. [6-9] It has also been extensively utilized to investigate the dissolution kinetics of phenolic resists [6, 10]. Furthermore, the QCM method has been used to study the dissolution of molecular resists for EUV and F_2 lithography. [11-13] In our previous work, we investigated the dissolution behavior of polymer-bound and -blended photoacid generator (PAG) by the QCM method. [14]

The dissolution of a variety of species within a resist film can play an important role in controlling the behavior and imaging performance of a resist. In particular, high dissolution contrast at the boundary between exposed and unexposed areas is required for ultrafine patterning. Therefore, the dissolution in exposed areas of resist films is one of the most critical processes for EUV resist development. However, the details of the dissolution process of EUV resists have not yet been clarified. In particular, these have been no fundamental studies on isolating the effects of the acid generator type, acid generator concentration, and amine addition on the dissolution behavior in thin resist films. In this study, the dissolution behavior of a poly(4-hydroxystyrene) (PHS) film, which is a model polymer of chemically amplified EUV resists, with acid generators was investigated using the QCM method with the aim of clarifying the effect of each resist component on the dissolution behavior. This method was employed since it can be readily applied to the measurement of rapid dissolution phenomena. In particular, the dissolution behavior of thin resist films was investigated by varying the exposure dose and the acid generator concentration.

2. Experimental

In the sample preparation for the QCM experiment, PHS was used as a polymer for chemically amplified resist. Triphenylsulfonium triflate (TPS-tf) and Triphenylsulfonium nonaflate (TPS-nf) were used as the acid generator. Propylene glycol monomethyl ether acetate (PGMEA) was used as the casting solvent. Resist solutions were prepared by dissolving PHS with and without the acid generator in PGMEA to evaluate the resist performance and carry out QCM measurement. Also, quenchers such as amines were added to the resist solutions.

The resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating onto QCM wafers to ensure the formation of clean films. Quartz crystal substrates with a frequency of 5 MHz were used. The resist solutions were spin-coated onto QCM substrate at 3000 rpm for 30 s to form thin films with ca. 100 nm thickness. Then, they were exposed to EUV radiation (Energetic, EQ-10M). [15] The exposed area was approximately 1 × 1 cm² and the exposure dose ranged from 0 to 15 mJ/cm². After the exposure, the spin-coated wafers were baked at 90 °C for 60 s. The dissolution behaviors of the PHS films with and without additive compounds such as acid generators and amines were investigated using a QCM-based analyzer (RDA-Qz3). [16] The exposed films were subjected to QCM analysis in a TMAH aqueous solution (NMD-3, Tokyo Ohka Kogyo Co. Ltd.). They were developed by dipping in TMAH solution for 60 s at 23 °C. After development, they were rinsed in water before drying. The resist film thickness was measured by spectroscopic ellipsometry (UVISEL, Horiba).

3. Results and Discussion

![Fig. 1. Dissolution behavior of PHS containing different concentrations of TPS-tf before EUV exposure.](image-url)
In order to investigate the effect of each resist component on dissolution, the dissolution behavior of PHS with and without the acid generator was observed using the QCM. We first investigated the effect of the acid generator concentration on the dissolution before EUV exposure. Figure 1 shows the dissolution behavior of PHS containing different concentrations of TPS-tf before EUV exposure. The relationship between resist thickness and development time was obtained by fitting the relationship between the development time and the resonance frequency obtained in the QCM experiments. It was found that the dissolution speed in the PHS resists film decreased with the increasing TPS-tf concentration. Three steps occur in the dissolution. Firstly, the developer solvent penetrates the PHS film. Secondly, the TMAH diffuses into the PHS film. Thirdly, the PHS polymer chains disentangle and dissolve in the developer. It has been reported that a penetration zone is formed during dissolution by the diffusion of developer into the polymer film. At the start of polymer dissolution, water and TMAH ions enter the polymer film and PHS molecules are simultaneously dissociated. Thus, a small number of phenol groups in the resin are dissociated to form phenolate ions. [17] Then, the dissociated polymer molecules are solvated by water. Some of cations of the developer base are also solvated to maintain electroneutrality. In the thin layer of resin adjacent to the interface with the developer solution, a low concentration of phenolate and mobile cations accumulates. As more base enters the polymer films, the solubility limit of the phenolate in the matrix is reached and a new phase is formed. This is followed by the rearrangement of the multiply ionized polymer chains, their detachment from the polymer film, and their eventual transfer into the solution. Considering this mechanism, the inhibition of dissolution by acid generators is considered to be caused by the interaction between the phenolic OH groups and the acid generators, and the reduced availability of phenolic protons is the fundamental cause of dissolution inhibition, as previously reported. [18-20] Therefore, the electrostatic interaction between the acid generator and hydroxyl groups in PHS has a strong effect on the solubility in the TMAH developer.

Next, we investigated the effect of the acid generator concentration on dissolution before and after EUV exposure. Figures 2 (a) and (b) show the relationship between resist thickness and development time in PHS films containing 10 wt% and 20 wt% TPS-tf, respectively. The exposure doses ranged from 0 to 15 mJ/cm². With increasing exposure dose, the dissolution rate in these resist films increased in both cases. This is due to the decomposition of the acid generators. Also, the dissolution rate in these resist films after EUV exposure decreased with the increasing TPS-tf concentration. These results indicate that the solubility of PHS containing acid generators in the developer after EUV exposure depends on the concentration of remaining acid generator.

The EUV reaction mechanism has been reported to be as follows. [1,2] The energy of the EUV is mostly deposited on the polymer matrices via ionization processes, and radical cations and secondary electrons are generated. The counter anions of acids are generated from acid generators after the reaction with these secondary electrons. Protons originate from the radical cations of polymers generated by the ionization. Finally, the counter anions recombine with protons to form acid. During postexposure baking (PEB), the acid diffuses in the resist material. Thus, it is easily
dissociated at the interface of the developer because the acid generator does not interact with the hydroxyl groups of PHS in the decomposition of the acid generator. The dissolution in positive resists is inhibited by the inductive polarization effect of strong hydrogen acceptors, which create hydrogen strings of OH groups. [18] It is generally accepted that inhibition of dissolution in phenolic resins is linked to hydrogen bonding between the acceptor groups (S=O or C=O) of the inhibitor and the polymer-bound OH groups of the resin. The dissolution inhibition effect of acid generators has been correlated with the interaction between the phenolic OH group and the acid generator molecules, as studied by 13C NMR. [19] Actually, the strong interaction of acid generators with phenol was clearly observed in the IR spectra of copolymer films.

We also investigated the effect of a quencher on dissolution before and after EUV exposure. We expected that a hydrophobic compound such as a base quencher would affect the dissolution behavior of polymer films. Figure 3 shows the relationship between resist thickness and development time in PHS films with and without 5 wt% TOA and no other additives. It was observed that the dissolution rate slightly decreased upon adding the quencher.

Figures 4 (a) and (b) show the relationship between resist thickness and development time in PHS films with 5 wt% TOA containing 10 wt% and 20 wt% TPS-tf, respectively. The exposure doses ranged from 0 to 15 mJ/cm.

The average dissolution rate was estimated from the results of QCM measurements. Figure 5 shows the relationship between average dissolution rate and exposure dose before and after EUV exposure.

The average dissolution rate was estimated from the results of QCM measurements. Figure 5 shows the relationship between average dissolution rate and exposure dose before and after EUV exposure.

The average dissolution rate was estimated from the results of QCM measurements. Figure 5 shows the relationship between average dissolution rate and exposure dose before and after EUV exposure.

The average dissolution rate was estimated from the results of QCM measurements. Figure 5 shows the relationship between average dissolution rate and exposure dose before and after EUV exposure.
penetration of the developer into the resist decreased because TOA is hydrophobic. In the PHS films with and without TOA, no dependence of the dissolution rate on exposure dose was observed. This suggests that some resist components inhibit dissolution. Hydrophobic molecules such as TOA can block some of the OH channels, changing the dissolution rate of the PHS films. From these results, it is thought that the dissolution rate corresponds to the density of hydrophilic channels in polymer films, which is reduced when inhibitor compounds such as TOA are added to the polymer film. Also, these results imply that the solubility in the developer depends on the concentration of remaining PAG.

The structural factors of dissolution inhibitors on their inhibition characteristics were also studied. In particular, we investigated the effect of the anion size of the acid generator on dissolution. Figure 6 shows the relationship between dissolution rate and exposure dose in TPS-tf and TPS-nf. The molecular concentration of the acid generators was kept constant relative to that of PHS. It was observed that the dissolution rate in the PHS film with TPS-nf was faster than that in a PHS film with TPS-tf in the presence of the same concentration of acid generators both before and after EUV exposure. It is important in EUV resist design to take into account the concentration of undecomposed PAG.

4. Conclusion

The dissolution behavior of thin resist films was investigated with the QCM method with the aim of obtaining a systematic understanding of the effect of each resist component on dissolution. The dissolution rate decreased with increasing TPS-tf concentration in PHS. The solubility in the developer depends on the concentration of remaining PAG and the structure of the acid generators and quencher. Thus, some resist components inhibit dissolution. Also, it was observed that the dissolution rate in a PHS film with TPS-nf was higher than that in a PHS film with TPS-tf in the presence of the same concentration of acid generators both before and after EUV exposure. It is important in EUV resist design to take into account the concentration of undecomposed PAG.

References
1. S. Tagawa, S. Nagahara, T. Iwamoto, M. Wakita, T. Kozawa, Y. Yamamoto, D. Werst, and A. D. Trifunac, Proc. SPIE 3999, 204 (2000).
2. T. Kozawa, Y. Yoshida, M. Uesaka, S. Tagawa, Jpn. J. Appl. Phys. 31, 4301 (1992).
3. T. Itani, H. Yoshino, S. Hashimoto, M. Yamane, N. Samoto, and K. Kasama, J. Photopolym. Sci. Technol. 22, 73 (2009).
4. A. Sekiguchi, Y. Kono, M. Kadoi, Y. Minami, T. Kozawa, S. Tagawa, D. Gustafson and P. Blackborow, Proc. SPIE 6519, 651946-1 (1996).
5. M. Toukhy, K. Schlicht, B. Maxwell and S. Chanthalyama Proc. SPIE 3999, 638 (2000).
6. W. Hinsberg, C. Willson and K. Kanazawa, J. Electrochem. Soc. 133, 1448 (1986).
7. W. Hinsberg, F. A. Houle, S.-W. Lee and H. Ito, K. Kanazawa Macromolecules 2005 38 1882-1898.
8. M. Toriumi, T. Ohfuji, M. Endo, and H. Morimoto, J. Photopolymer. Sci. Technol. 12, 545 (1999).
9. T. Wallow, W. Chan, W. Hinsberg, and S-W. Lee, SPIE 4690, 299 (2002).
10. H. Ito, E. Flores and A. F. Renaldo, J. Electrochem. Soc. 135, 2328 (1988).
11. M. Toriumi, J. Santillan, T. Itani, T. Kozawa, and S. Tagawa J. Vac. Sci. Technol. B 27, 2622 (2009).
12. M. Toriumi, J. Santillan, T. Itani, T. Kozawa,
124

J. Photopolym. Sci. Technol., Vol. 28, No. 1, 2015

and S. Tagawa J. Vac. Sci. Technol. B 25 2486 (2007).
13. M. Toriumi, T. Yamazaki, T. Furukawa, S. Irie, S. Ishikawa, and T. Itani, J. Vac. Sci. Technol. B 20, 2909 (2002).
14. H. Yamamoto, T. Kozawa, and S. Tagawa, Microelectron. Eng. 129 65 (2014).
15. S. F. Horne, M. M. Besen, D. K. Smith, P. A. Blackborow, R. D’Agostino, Proc. SPIE 6151, 61510P (2006).
16. A. Sekiguchi, J. Photopolym. Sci. Technol. 23 421 (2010).
17. P. C. Tsiartas, L. W. Flanagan, C. L. Henderso, W. D. Hinsberg, I. C. Sanches, R. T. Bonnecaze and C. G. Willson Macromolecules 4656 (1997).
18. Zhenglin Yan and Arnost Reiser Macromolecules 31 7723 (1998).
19. H. Ito, D.-F. Alexander, and G. Breyta, J. Photopolymer. Sci. Technol. 10 397 (1997).
20. H.-Y. Shin, A. Reiser, Macromolecules 28 5595 (1995).