Acid Quantum Efficiency of Anion-bound Chemically Amplified Resists upon Exposure to Extreme Ultraviolet Radiation

Yoshitaka Komuro 1, Daisuke Kawana 1, Taku Hirayama 1, Katsumi Ohmori 1, and Takahiro Kozawa 2

1: Tokyo Ohka Kogyo Co., Ltd., Samukawa, Kanagawa 253-0114, Japan
2: The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan.

EUV lithography is one of candidates for the high-volume manufacturing of semiconductor devices with sub-10 nm critical dimension. An anion-bound polymer, in which the anion part of onium salts is introduced into main chain polymer, has attracted much attention for sub-10 nm fabrication. We have modeled the acid generation of anion-bound resists and developed a simulation code for facilitating the development and improvement of resist materials and processes for EUV lithography [1]. In this study, the acid quantum efficiency of acid generation was investigated using the developed simulation code. The quantum efficiency did not depend on the thermalization distance. The increase in the efficiency of acid generation from an electronically excited state of the resist and the suppression of the reaction between phenyl radicals are important for the improvement of quantum efficiency.

Keyword: Anion-bound polymer, EUV, Acid quantum efficiency, Sensitivity, Monte Carlo simulation

1. Introduction

Extreme ultraviolet (EUV) lithography that extends photolithography to extremely shorter wavelength (13.5 nm) is capable of achieving sub 20-nm half pitch resolution by single exposure [2]. EUV lithography is the leading candidate to succeed 193 nm immersion lithography. Deep ultraviolet (DUV) light energy (wavelength of 193 nm or 248 nm) is lower than the ionization potential of resist materials. Therefore, the acid generation mechanism of 193 nm immersion lithography is the direct excitation of acid generators.

On the other hands, the energy of EUV (92.5 eV) exceeds the ionization potential of resist materials. When EUV photons are irradiated on the resist matrix, the radical cations of matrix molecules and photoelectrons are generated through ionization. The photoelectrons generated further induce ionization until their energy is lost sufficiently. And then, the low energy electrons react with acid generators [3,4]. Therefore, EUV lithography presents new challenges in nature of the EUV radiation and requires the development of new platform which is different from the traditional DUV lithography system.

The main issue for developing EUV resists is to satisfy the ITRS targets of resolution, line-width roughness (LWR), sensitivity, and outgassing simultaneously [5-9]. Currently, the achievement of 15 nm half-pitch line-and-space pattern by using a commercially available EUV exposure tool...
(ASML NXE:3300) has been reported [10], although the sensitivity and LWR have not met the requirements yet. The increase in acid generator concentration and the suppression of the subsequent acid diffusion are a way to simultaneously improve resolution, LWR and sensitivity [11-16]. The incorporation of the anion part of acid generators into polymers (anion-bound polymer : ABP) is expected to enable high concentration loading of acid generators and achieve a high resolution fabrication with low LWR by reducing acid diffusion length. The ABP is also expected to improve the uniformity of the acid generator distribution in resist matrices. Many attempts to incorporate ionic and nonionic acid generators into the backbone or pendant groups of polymers have been reported [17-21].

We have investigated the acid generation mechanisms induced in ABP by secondary electrons, considering that the acid generation mechanism is a reason for low sensitivity [22,23]. On the basis of experimental results, we have modeled the proposed acid generation mechanisms of anion-bound resists and developed a simulation code for facilitating the development and improvement of resist materials and processes for EUV lithography [1]. The experimental quantum efficiencies were well reproduced by the developed simulation code. The best fit parameters for the thermalization distance ($r_0$), the effective reaction radius for the reaction between phenyl radicals ($R_b$) and acid generation efficiency from the excited states ($\varepsilon_E$) were 0.3 nm, 0.15-0.40 nm and 0.20-0.50, respectively. The blur of proton distribution intrinsic to the reaction mechanisms of anion-bound chemically amplified resists was estimated to be roughly 4.5-6.5 nm.

In this study, the quantum efficiency of acid generation was investigated, using the developed simulation code, to improve the quantum efficiency of acid generation.

2. Simulation model

In the simulation, EUV photons were randomly injected into the target area. The exposed area was set to be 50×50 nm². The injected EUV photons were randomly absorbed by ABP in accordance with Lambert’s law and photoelectrons were emitted:

$$\text{TPS}^+-\text{ABP}^- \rightarrow (\text{TPS}^+-\text{ABP}^)- + e^-.$$  (1)

Here, $\text{TPS}^+-\text{ABP}^-$, $(\text{TPS}^+-\text{ABP}^-)^+$, and $e^-$ are ABP, its radical cation, and a secondary electron (including a photoelectron), respectively. The secondary electrons with excess energy ionize or electronically excite ABP:

$$\text{TPS}^+-\text{ABP}^- + e^- \rightarrow (\text{TPS}^+-\text{ABP}^-)^+ + e^-.$$  (2)

$$\text{TPS}^+-\text{ABP}^- \rightarrow (\text{TPS}^+-\text{ABP}^-)^*.$$  (3)

Here, $(\text{TPS}^+-\text{ABP}^-)^*$ is an electronically excited ABP. The electron trajectories after EUV absorption were calculated in accordance with the reported procedure until the electron energy is reduced to less than 21 eV [24].

In ABP films, the secondary electrons are thermalized through the interaction with the surrounding molecules. The thermalized electrons migrate under the electric fields produced by other charged species until they find localization sites. The main localization sites are polymer radical cations and acid generator units. Therefore, the thermalized electrons, $e^-_{\text{th}}$, either recombine with polymer radical cations or react with acid generator units [3,25]:

$$e^-_{\text{th}} + (\text{TPS}^+-\text{ABP}^-)^+ \rightarrow (\text{TPS}^+-\text{ABP}^-)^* \text{ or } \text{TPS}^+-\text{ABP}^-,$$  (4)

$$e^-_{\text{th}} + \text{TPS}^+-\text{ABP}^- \rightarrow \text{Ph}_2\text{S} + \text{Ph}^- + (\text{TPS}^+-\text{ABP}^-)^*.$$  (5)

Here, $\text{Ph}_2\text{S}$ and $\text{Ph}^-$ are diphenylsulfide (DPS) and a phenyl radical, respectively.

The subsequent reactions for the generation of the protons of acids are [23]:

$$(\text{TPS}^+-\text{ABP}^-)^+ + \text{Ph}_2\text{S} \rightarrow \text{Ph}_2\text{S}^+ + (\text{TPS}^+-\text{ABP}^-)^*,$$  (6)

$$\text{Ph}_2\text{S}^+ + \text{Ph}^- \rightarrow \text{Ph}\text{-Ph}_2\text{S} + \text{H}^+.$$  (7)

Here, $\text{Ph}_2\text{S}^+$ and $\text{Ph}\text{-Ph}_2\text{S}$ are a DPS radical cation and a phenyl-substituted DPS, respectively. DPS radical cations are generated through the hole transfer from ABP radical cation to DPS. Protons and phenyl-substituted DPS are generated through the reaction of DPS radical cations and phenyl radicals.
The reaction between phenyl radicals was taken into account because biphenyl has been reported as a decomposition product of ABP upon exposure to $\gamma$-rays [23].

$$\text{Ph}^+ + \text{Ph}^- \rightarrow \text{Ph-Ph.} \quad (8)$$

Here, Ph-Ph is biphenyl. This reaction leads to the decrease of the quantum efficiency of acid generation, because the phenyl radicals required for acid generation [reaction (7)] are terminated.

The acids are also generated through the decomposition of acid generator units from their electronic excited states, although this path is minor [23]:

$$\text{(TPS}^+\text{-ABP}^-)^* \rightarrow \text{(TPS}^+\text{-ABP}^-) + \text{Ph-Ph}_2\text{S} + \text{H}^+. \quad (9)$$

$$(\text{TPS}^+\text{-ABP}^-)^*$$ is generated through the reactions (3) and (4). The quantum efficiency of the electronic excited state of each monomer unit and the efficiency of energy transfer between monomer units are unknown. In this simulation model, the acid generation efficiency from the electronic excited state was simply assumed to be proportional to the concentration of acid generator units. The other details parameter have been reported elsewhere [1].

3. Results and Discussion

The molecular structure is shown in Fig. 1. The parameters used are summarized in Table 1. The composition ratio of triphenylsulfonium difluoroalkylsulfonate units was changed from 5.4 to 10.9 and 14.3 mol%, which are hereafter called 5, 10, and 14 mol% ABP, respectively. The exposure doses were set to be 3.86, 7.73, and 11.6 mJ cm$^{-2}$.

![Figure 1. Molecular structure of anion-bound polymer.](image)

**Table 1. Parameters used in the simulation.**

| Parameter                        | Value          |
|----------------------------------|----------------|
| Absorption coefficient ($\mu$m$^{-1}$) | 5.45, 5.49, 5.55 |
| Resist film density (g cm$^{-3}$) | 1.25, 1.259, 1.275 |
| Dielectric constant              | 4.05, 4.20, 4.55 |
| Acid generator concentration     | 5.4, 10.9, 14.3 |
| Exposure dose (mJ cm$^{-2}$)     | 3.86, 7.73, 11.6 |
| Thermalization distance (nm)     | 3-7            |
| Effective reaction radius of reaction (4) (nm) | 0.5 |
| Effective reaction radius of reaction (5) (nm) | 0.5 |
| Effective reaction radius of reaction (6) (nm) | 0.5 |
| Effective reaction radius of reaction (7) (nm) | 0.5 |
| Ratio of (TPS$^+\text{-ABP}^-)$ and TPS$^+\text{-ABP}^-$ of reaction (4) | 1:1 |

a) 5 mol% ABP, b) 10 mol% ABP, c) 14 mol% ABP

Figure 2 shows the representative relationship between the $r_0$ and quantum efficiency. The quantum efficiency was almost unchanged when $r_0$ was changed. In the case of 5 mol% ABP, the quantum efficiency was slightly increased with the increase in the thermalization distance. In the case of 10 mol% and 14 mol% ABPs, the quantum efficiency was slightly decreased. The decomposion efficiency of TPS units increases by increasing $r_0$ [reaction(5)]. On the other hands, the efficiency of reaction (6) after the decomposition of TPS units decreases by increasing $r_0$ because the distance between ABP radical cations and diphenylsulfide increases. In the low ABP concentration region, the quantum efficiency is considered to be increased with the thermalization distance, because the decomposition of TPS units was more important for the acid generation than the hole transfer. In the high ABP concentration region, the quantum efficiency is considered to be decreased with the thermalization distance, because the hole transfer was more important for the acid generation than the decomposition of TPS units.

![Figure 2. The relationship between quantum efficiency and $r_0$ for $R_b = 0.35$ nm and $\varepsilon_E = 0.5$.](image)
Figure 3. The relationship between quantum efficiency and $\varepsilon_E$ for $R_B = 0.35$ nm and $r_0 = 0.4$ nm.

Figure 3 shows the representative relationship between the $\varepsilon_E$ and quantum efficiency. $\varepsilon_E$ includes the energy transfer from randomly generated excited species to TPS units. The quantum efficiencies increased by increasing $\varepsilon_E$. The slopes of first order approximation of 5 mol%, 10 mol%, and 14 mol% ABP were 1.09, 1.55, and 1.71, respectively. For example, if $\varepsilon_E$ was increased from 0.3 to 0.5, the quantum efficiency was estimated to increase by 15%. The increase in the efficiency of energy transfer to TPS units as well as the conversion efficiency from excited TPS units to protons is important for the improvement of the quantum efficiency of acid generation.

Figure 4 shows the representative relationship between $R_B$ and quantum efficiency. The quantum efficiencies were decreased by increasing $R_B$.

By decreasing $R_B$ from 0.5 to 0.3 nm, the quantum efficiency can be increased by 17-18%.

Figure 5 shows the representative relationship between the exposure dose and quantum efficiency. When AG concentration was increased, the quantum efficiency was increased. The quantum efficiency was increased slightly by increasing exposure dose. This is because the probability of the encounter of diphenylsulfide with ABP radical cations increased with the exposure dose. Note that the further increase of exposure dose leads to the decrease of quantum efficiency because the concentration of AG decreases due to the decomposition during the exposure.

4. Conclusion

The quantum efficiency of acid generation was investigated using the developed simulation code for ABP. The dependence of quantum efficiency on the thermalization distance, the efficiency of acid generation from electronically excited states, the efficiency of the reaction between phenyl radicals, and exposure dose was calculated. The quantum efficiency did not significantly depend on the thermalization distance. The increase in the efficiency of acid generation from an electronically excited state of the resist and the suppression of the reaction between phenyl radicals are important for the improvement of quantum efficiency.
References
1. Y. Komuro, D Kawana, T Hirayama, K Ohmori, T. Kozawa, Jpn. J. Appl. Phys., 54 (2015) 036506.
2. Y. Ekinci, M. Vockenhuber, M. Hojejij, L. Wang, N. Mojarad, Proc. SPIE, 8679 (2013) 867910.
3. T. Kozawa, Y. Yoshida, M. Uesaka, S. Tagawa, Jpn. J. Appl. Phys., 31 (1992) 4301.
4. T. Kozawa, S. Tagawa, Jpn. J. Appl. Phys., 49 (2010) 030001.
5. G. M. Gallatin, Proc. SPIE, 5754 (2005) 38.
6. D. Van Steenwinckel, R. Gronheid, J. H. Lammers, F. V. Roey, P. Willems, J. Micro/Nanolithogr. MEMS MOEMS., 7 (2008) 023002.
7. H. Oizumi, K. Matsumaro, J. Santillan, T. Itani, Proc. SPIE, 7636 (2010) 106.
8. K. R. Dean, K. E. Gonsalves, M. Thiagarajan, Proc. SPIE, 6153 (2006) 61531E.
9. I. Pollentier, J. Photopolym. Sci. Technol., 5 (2010) 605.
10. R. Peeters, presented at EUV Symp., 2013.
11. Y. Utsumi, T. Seshimo, Y. Komuro, A. Kawaue, K. Ishiduka, K Matsuzawa, H. Hada, J. Onodera, Jpn. J. Appl. Phys., 48 (2009) 06FC07.
12. H. Tsubaki, T. Tsuchihashi, T. Tsuchimura, Proc. SPIE, 7273 (2009) 72731K.
13. D. Van Steenwinckel, J. H. Lammers, L. H. Leunissen, J. A. J Kwinten, Proc. SPIE, 5753 (2005) 269.
14. B. D. Vogt, S. Kang, V. M. Prabhu, A. Rao, E. K. Lin, S. K. Satija, K. Turnquest, Proc. SPIE, 6153 (2006) 615316.
15. G. M. Wallraff, C. E. Larson, N. Fender, B. Davis, D. Medeiros, J. Meute, W. M. Lamanna, M. J. Parent, T. Roveledo, G. Young, Proc. SPIE, 4690 (2002) 160.
16. S. Yoshizawa J. Moriya, J. Vac. Sci. Technol B., 20 (2002) 1342.
17. S. Tarutani, H. Tsubaki, H. Takahashi, T. Itou, K. Matsunaga, G. Shiraishi, T. Itani, Proc. SPIE, 7639 (2010) 76391O.
18. R. D. Allen, U. Schaefdeli, D. R. McKean, S. A. Macdonald, Polym. Mater., Sci. Eng., 61 (1981) 185.
19. J. E. Hanson, E. Reichmanis, F. M. Houlihan, T. X. Neenan, Chem. Mater., 4 (1992) 837.
20. G. M. Wallraff, W. D. Hinsberg, Chem. Rev., 99 (1999) 1801.
21. M. D. Stewart, H. V. Tran, G. M. Schmid, T. B. Stachowiak, D. J. Becker, C. G. Willson: J. Vac. Sci. Technol., B 20 (2002) 2946.
22. Y. Komuro, H. Yamamoto, Y. Utsumi, K. Ohmori, T. Kozawa, Appl. Phys. Express, 6 (2013) 014001.
23. Y. Komuro, H. Yamamoto, K. Kobayashi, Y. Utsumi, K. Ohmori, T. Kozawa, Jpn. J. Appl. Phys., 53 (2014) 116503.
24. T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, M. J. Leeson, J. Vac. Sci. Technol. B., 25 (2007) 2481.
25. K. Natsuda, T. Kozawa, K. Okamoto, A. Saeki, S. Tagawa, Jpn. J. Appl. Phys., 48 (2009) 06FC05.