Jpn. J. Appl. Phys. Vol. 42 (2003) pp. 16–22
Part 1, No. 1, January 2003

Approach for High-resolution of Chemically Amplified Resists Using Rate Editor Software

Atsushi SEKIGUCHI, Yoshihisa SENSU and Yasuhiro MIYAKE

Litho Tech Japan Corp., 2-6-6-201 Namiki, Kawaguchi, Saitama 332-0034, Japan

(Received May 14, 2002; revised manuscript received September 5, 2002; accepted for publication September 6, 2002)

In discussions of resist resolution and process margins, knowledge of the resist development characteristics is more important than of primary importance. However, at present, there is insufficient understanding of the extent of the impact of various development characteristics on different process margins. The authors therefore analyzed photoresist development rate data obtained for various exposure doses, and developed rate analysis software that allows the development, and hence characteristics, of the resists to be modified freely. The design rule of VLSI devices is expected to reach the 70 to 100 nm scale by 2005 through lithography using F_2 excimer lasers (157 nm). The software developed in this study was used to determine which development characteristics need be changed and to what extent, to obtain high resolution and a broad defocus margin for processes involving chemically amplified positive resist for use with ArF excimer lasers. The resist was improved based on the findings of this study, and the validity of the results was confirmed. [DOI: 10.1143/JJAP.42.16]

KEYWORDS: photo-resist, development characteristics, F_2 excimer lasers, profile simulation

1. Introduction

In discussions of resist resolution and process margins, knowledge of the resist development characteristics is essential.[1,2] There have been numerous studies regarding ideal development characteristics for increasing resolution.[3] However, there are many development characteristics, each influencing the other characteristics in complicating the optimization of resolution and defocus margin. The development characteristics may be described as follows.

- Resist contrast (γ): A measure of resolving power of a photoresist, the photoresist contrast is defined in one of two ways. The measured contrast is the maximum slope of a plot of log-development rate versus log-exposure energy. The photoresist contrast is usually defined by the symbol γ.[4]
- Dose to clear (E_{th}): The amount of exposure energy required to just clear the resist in a large area for a given process.[4]
- Development contrast ($\tan\theta$): Equal to the rising slope of the development rate curve, indicated by $\tan\theta$.[5]
- Development discrimination: Difference in resist development rates for unexposed areas and completely exposed areas.[6]
- Surface inhibition effect: A reduction effect of the development rate at the top surface of a resist relative to bulk development rate.[7]
- Bulk effect: Depth-direction development rate distribution resulting from optical absorption by the base resin of the resist.
- Film thickness effect: Change in development characteristics due to changes in film thickness (standing-wave effect due to changes in film thickness).
- Effect of acid diffusion length: Diffusion during post-exposure baking (PEB) of acid generated by the photo-acid generator (PAG); appears as reinforcement of the standing-wave effect in the resist film.[8]

However, as yet, it is not well known which of these characteristic elements affect process margins and resolution and to what extent. We therefore developed, based on measured development rate data for different exposure doses, a software rate analyzer that enables analysis and free adjustment of each of these characteristic elements. This paper describes the results of studies on development contrast, development discrimination, and the bulk effect, and the effects on resolution and focus margin.

The minimum design rule for very large scale integrated (VLSI) devices is anticipated to reach 70 to 100 nm in or around 2005 consequent to the development of lithography by using F_2 excimer lasers (157 nm).[9–12] The present analysis system was employed to study which development characteristics should be changed, and to what extent, to obtain high resolution and a broad defocus margin for F_2 excimer laser processes involving chemically amplified positive resist, 2-methyl-2-adamantyl-mathacrylate (2-Methytriclo[3.3.1.13.7]dec-2-yl methacrylate: 2MAdMA), (hereafter "2MAdMA resist" made by Sumitomo Chemical)[13] suitable for use with ArF excimer lasers. Specifically, the VUVES-4500 exposure system[14,15] for photochemical analysis, equipped with an F_2 excimer laser for 2MAdMA resist, was used to measure development rate distributions at various exposure doses using an existing development rate analyzer.[16] The rate analyzer was then used to separate the development rate data obtained into individual components corresponding to resist characteristics, and the values were varied. The newly obtained development rate data was then used for profile simulation.[17] The simulation results clarified the relationships of the different development characteristics with resolution and focus margin. Based on the knowledge obtained in this study, the resist was improved, patterning was performed using F_2 excimer laser exposure, and studies were conducted to determine the validity of the result of the future.

2. Configuration of Analysis System

This analysis system consists of the following three units.

(1) A unit for measuring resist development rates for different exposure doses (resist development analyzer).
(2) Software to analyze and edit for resist development rate (Rate Editor).[16]
(3) A simulation unit to perform numerical calculations of resist profiles and process margins, using modified development rate files (SOLID-C).[17]

2.1 *Unit for measurement of resist development rates (resist development analyzer)*

The resist development analyzer was developed previously by the present authors.[16] Resist development rates are measured by irradiating a developing resist thin film with monochromatic light. When the monochromatic light is incident on the developing resist, the light reflected from the resist surface interferes with the light reflected from the substrate surface. As the resist film thickness changes with development, the reflection intensity changes sinusoidally. The resist film is expected to be thinner in F_2 excimer laser processes. A 470-nm light-emitting diode (LED) light source, for which adequate interference waveforms can be obtained even from thin films, was therefore adopted as the monitor light source. In order to prevent degradation of the interference waveform due to the non-uniform dissolution characteristic of chemically amplified resists,[18] an optical pickup system capable of focusing the monitor light to a spot of less than 1 mm diameter was developed, allowing highly localized measurements. Light reflected from the sample enters and passes through a receiving lens and optical fiber to a phototransistor, and the output signal is digitized and analyzed by a computer. By converting the development time and reflected light intensity data into development rate data, the development rate $R(E,Z)$ at different depth positions in resist films can be determined for a range of exposure doses.[5] Here R is the development rate, E is the exposure dose, and Z is the depth position in the resist.

2.2 *Software to editing resist development rate data (rate editor)*

2.2.1 *Edit of bulk effect*

The bulk effect represents the decrease in development rate with depth in the film due to optical absorption by the base resin of the resist. The resist development analyzer was used to measure the development rate distribution in the resist, and the B_{Dill} values were used to calculate the theoretical accumulated energy distribution in the resist film as a result of exposure.[19] By comparing these two sets of data and eliminating the depth term, the relationship between accumulated energy and development rate can be obtained. It is thought that the accumulated energy is proportional to the density of acid generated by the PAG.[20] Hence, the effect of optical absorption by the resist base resin is given by the B_{Dill} value, and the depth distribution of accumulated energy can be calculated. Using this relationship, and by converting the newly obtained accumulated energy at different depth positions into development rates, depth distributions of the development rate can be obtained for optical absorption by different base resins.

2.2.2 *Editing of development discrimination effect*

Development discrimination is the effect of the difference in development rates in unexposed areas and in areas that have been fully exposed. Development discrimination is modeled as follows. Photoresist development rates for various exposure doses are measured, and the data is used to derive the relationship between the average development rate and the exposure dose (the discrimination curve). The discrimination curve obtained is then divided into three development-rate regions with threshold values.

The first region is the low-development rate region, in areas with low exposure doses (the region including the minimum development rate $R_{\min}$); the second region is a narrow region representing intermediate development; and the third region is the high-development rate region, in areas with high exposure doses (the region including the maximum development rate $R_{\max}$). A function is then defined for the relationship between development rate and exposure dose in the first and third regions, which can then be modified via the intercept to alter the effect of development discrimination. The discrimination curve obtained is then stored over the original depth profile of development rate.

2.2.3 *Editing of development contrast effect*

Development contrast represents the slope of the development rate curve, expressed by $\tan\theta$, and is analyzed as follows. The method described in §2.2.2 is used to divide the discrimination curve into three development rate areas with thresholds. Data for the second (intermediate) area, representing the effect of development discrimination, is approximated by a straight line. The value of $\tan\theta$ is then determined from the slope of the line. The development contrast can be set freely by modifying the value of $\tan\theta$. The new discrimination curve is then stored over the depth profile of development rate.

2.2.4 *Editing of surface inhibition effect*

Surface inhibition represents the suppression of development of the surface layer of the resist, and is expressed by the following equation.[7]

$$R(d) = R_{\mathrm{B}}\left(1 - (1 - R_0)e^{\left(\frac{d}{\delta}\right)}\right) \tag{1}$$

R_{B}: Development rate in the bulk region (nm/s)
R_0: Minimum ratio of development rate in the resist surface layer to R_{B}
δ: Depth of surface inhibition layer (nm)
d: Depth position in the resist film

Equation (1) can be used to apply the surface inhibition effect to data already obtained for the depth distribution of development rate. However, in the present study, the surface inhibition effect is not considered.

2.3 *Lithography simulation unit*

The lithography simulation unit is based on SOLID-C (SIGMA-C, Germany).[17] This software simulates the basic steps in lithography, including image formation, resist sensitivity (acid generation), deprotection reaction in PEB, and development, to determine the final resist profile. In calculating the optical intensity, the extended source method can used, which is based on scalar diffraction theory, to calculate the optical intensity for a projection optical system that is partially coherent and diffraction-limited or has aberration, taking defocusing effects into account. In addition, corrections for a high NA are performed so as to reproduce the effect of defocusing in the resist film more faithfully.

The acid concentration distribution in the resist film induced by exposure is calculated. Dill's A, B and C parameters are used to convert the distribution of optical intensity in the film into an acid concentration distribution.

Calculations of the two-dimensional diffusion of acid due to PEB, and dissociation of the protective bases resulting from catalytic action of the acid, are calculated. The loss function of the acid can also be taken into consideration. Development calculations are performed after converting the distribution of the concentration of protective bases thus obtained into a resist development rate distribution using the development parameters. As a result of this series of calculations, the final resist profile is obtained. A calculation model such as this is called a physical calculation model.

A simulation method for development calculations in which the measured exposure energy and development rate data table $R(E, Z)$ is used directly to calculate the development rate distribution from the optical intensity distribution in the film without using Dill's A, B and C parameters or development parameters, is also applicable. This method, called the measurement development model,[14] is adopted in this study.[15] Using this method, development rate data modified using the Rate Editor can be directly transferred to the simulator, and simulations performed.

Using the above three analysis units, the effects of the resist contrast, discrimination, and transmittance (bulk effect due to differences in B value) of the base polymer, were modified using the Rate Editor, and simulations were performed. In this way, the process parameters that influence the resolution and focus margin in F_2 excimer laser processes were identified.

3. Experimental

3.1 *Measurement of basic characteristics*

The basic characteristics of F_2 excimer laser exposure and development of a positive CA resist for ArF excimer lasers, 2MAdMA resist,[13] were measured. The experimental conditions and the measured B_{Dill} value and acid diffusion coefficient appear in Table I. A VUVES-4500 F_2 excimer laser exposure system was used,[14] and exposure doses were varied up to 30 mJ/cm^2. The films were developed by dipping in NMD-3 (TMAH 2.38%) at 23°C. Table II shows

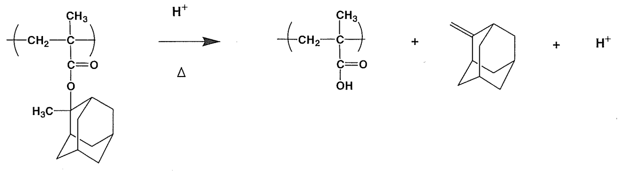


Fig. 1. Scheme of deprotection reaction for 2MAdMA resist.

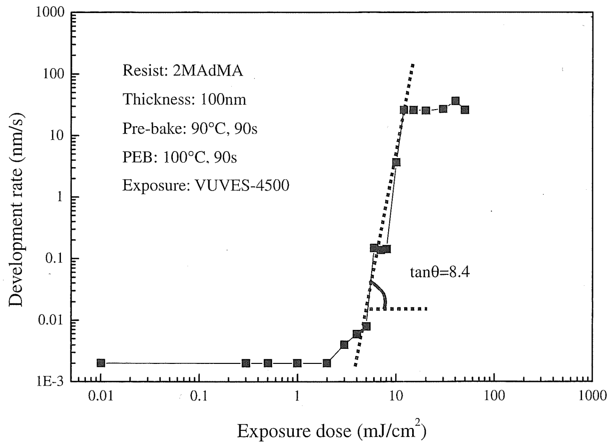


Fig. 2. Discrimination curves for 2MAdMA resist at F_2 exposure.

a list of development characteristics for F_2 excimer laser exposure of 2MAdMA resist. 2MAdMA resist is a chemically amplified resist, based on an acrylic resin, in which hydroxyl groups are protected by adamantyl groups. Figure 1 shows the anticipated scheme of the deprotection reaction depending on 2MAdMA resist; Fig. 2 shows the discrimination curve obtained.

3.2 *Editing development characteristics using the Rate Editor*

3.2.1 *Study of bulk effect*

The transmittance of a 2MAdMA resist film of thickness 100 nm was 23.3% ($B_{Dill} = 14.9$). Using the Rate Editor, the development rate data was generated for transmittances of 50% ($B_{Dill} = 6.93$) and 70% ($B_{Dill} = 3.56$) at 100 nm. The results calculated using the Rate Editor for the (normalized) accumulated energy distribution in the resist film under these conditions are shown in Fig. 3.

3.2.2 *Study of development discrimination*

The minimum and maximum development rates for 2MAdMA resist are $R_{min} = 0.04$ nm/s and $R_{max} = 30$ nm/s. The development discrimination value is therefore 10^4. The Rate Editor was used to change the area corresponding to R_{max}, without changing R_{min}. Three discrimination levels were used in these studies: 10^5, 7.5×10^5, and 10^6. The discrimination curves obtained are shown in Fig. 4.

3.2.3 *Study of development contrast*

The development contrast for 2MAdMA resist was $\tan\theta = 8.4$. Using the Rate Editor, the area corresponding to the ascending part of the curve was modified, without changing the areas including R_{min} or R_{max}. Three contrasts were used in these studies: $\tan\theta = 12.7$, 20.0, and 34.9. The resulting discrimination curves are shown in Fig. 5.

Table I. Examination conditions.

Resist	2MAdMA (Sumitomo Chem.) ($n_{157} = 1.80$)
Thickness	100 nm
Pre-bake	120°C, 60 s
PEB	120°C, 60 s
Substrate	Si without BARC ($n = 0.478$ $k = 2.000$)
Transmittance	23.3% (Measured by VUVES-4500 at 100 nm thickness)
B_{Dill}	14.59 μm^{-1}
Diffusion coefficient	46.7 nm^2/s

Table II. Resist development characteristic for 2MAdMA and HC-Resist.

	2MAdMA resist	HC-resist
E_{th}	9.20 mJ/cm^2	12.13 mJ/cm^2
γ (60 s development)	1.28	2.56
$\tan\theta$	8.40	11.10
R_{max}	30.21 nm/s	93.4 nm/s
R_{min}	0.0030 nm/s	0.0012 nm/s

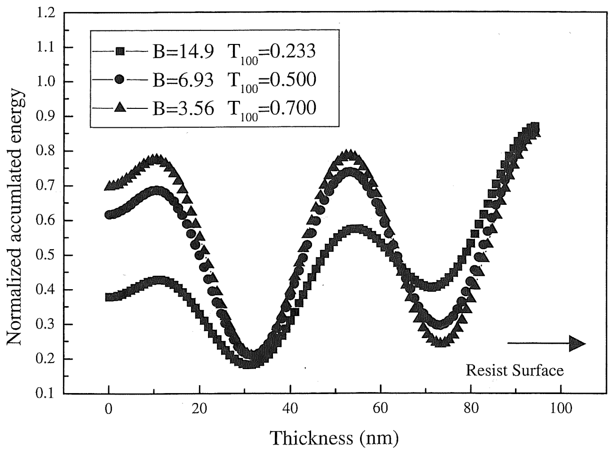


Fig. 3. Comparison of normalized accumulated energy in depth distribution for various transmittance depending on after PEB (T_{100} is transmittance at film thickness of 100 nm).

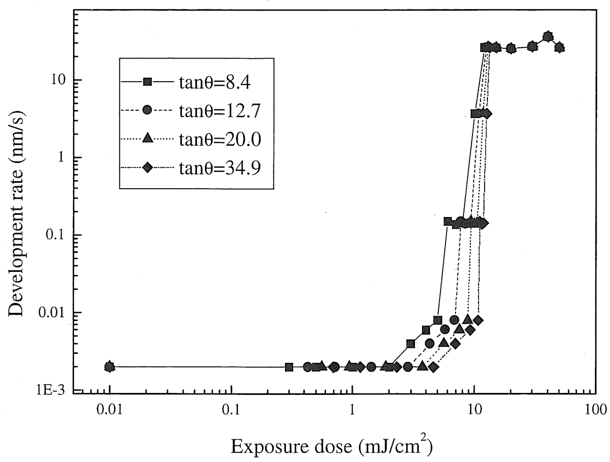


Fig. 5. Exposure dose-development rate curves for various resist contrast values ($\tan\theta$).

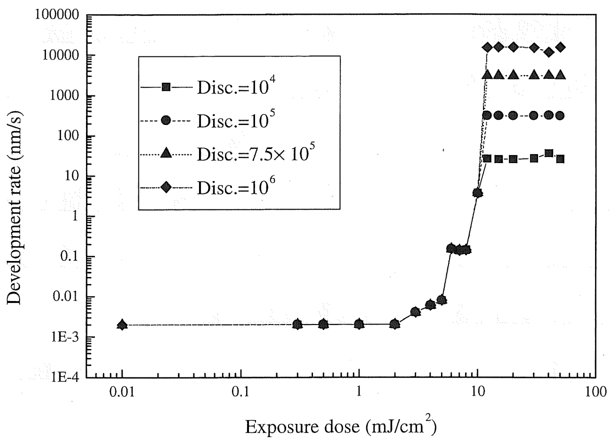


Fig. 4. Exposure dose-development rate curves for various discrimination values.

3.3 *Profile simulation*

Simulation conditions were as follows: exposure wavelength 157 nm, NA = 0.70, and coherence factor of illumination system 0.6. Studies were conducted for line and space widths of 100 nm, with defocusing at −0.3 to +0.3 μm. The development rate data tables $R(E, Z)$ obtained after editing were input into the simulator, and 100 nm line pattern profiles were calculated.

3.3.1 *Result of examined bulk effect*

Figure 6 shows the simulation results of focus latitude for a range of transmittances. When the transmittance rises, the pattern profile is deformed, and the focus characteristics are degraded. For the 100 nm thickness studied here, it was found that if the polymer transmittance is increased, the standing-wave effect is strengthened and resolution declines.

3.3.2 *Result of examined development discrimination*

Figure 7 shows the simulation result of focus latitude for various development discrimination values. It was found that increases in the development discrimination have no effect on the defocus characteristics.

3.3.3 *Result of examined development contrast*

Figure 8 shows the simulation result of focus latitude for a range of development contrasts. It was found that as the

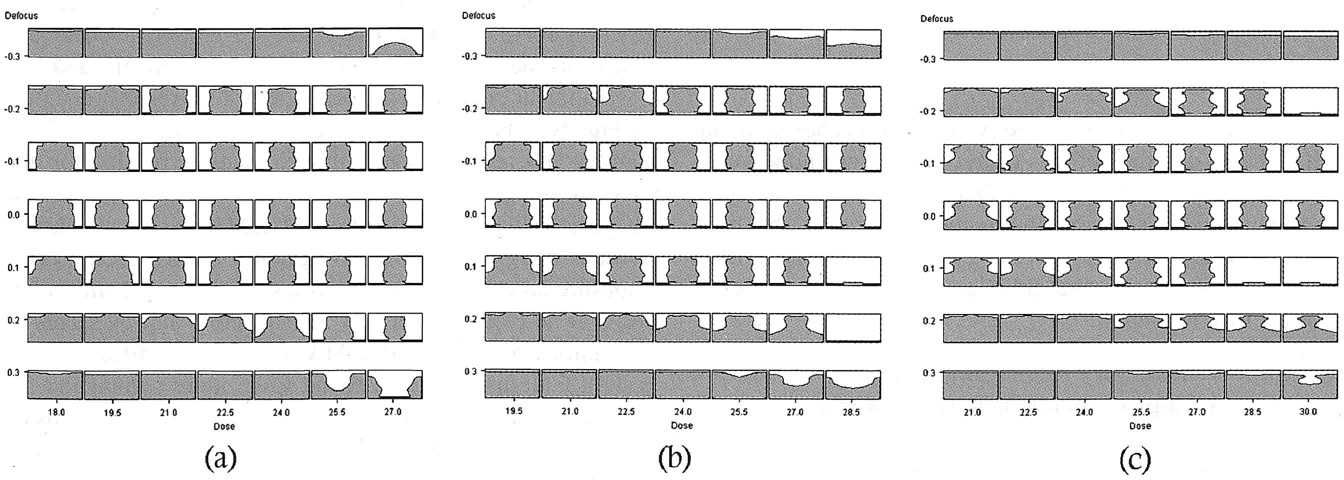


Fig. 6. Comparison of focus latitude at different exposure doses depending on B_{Dill} for simulation: (a) $B_{\text{Dill}} = 14.9$ ($T_{100} = 23\%$), (b) $B_{\text{Dill}} = 6.93$ ($T_{100} = 50\%$), (c) $B_{\text{Dill}} = 3.56$ ($T_{100} = 70\%$).

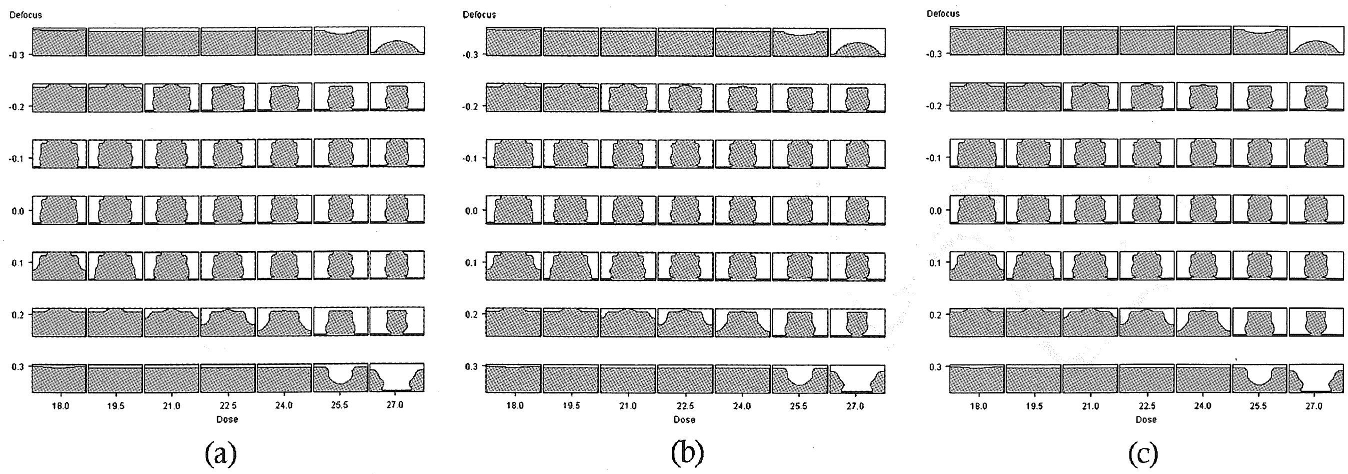


Fig. 7. Comparison of focus latitude at different exposure doses depending on discrimination for simulation: (a) Disc. $= 10^4$, (b) Disc. $= 7.5 \times 10^5$, (c) Disc. $= 10^6$.

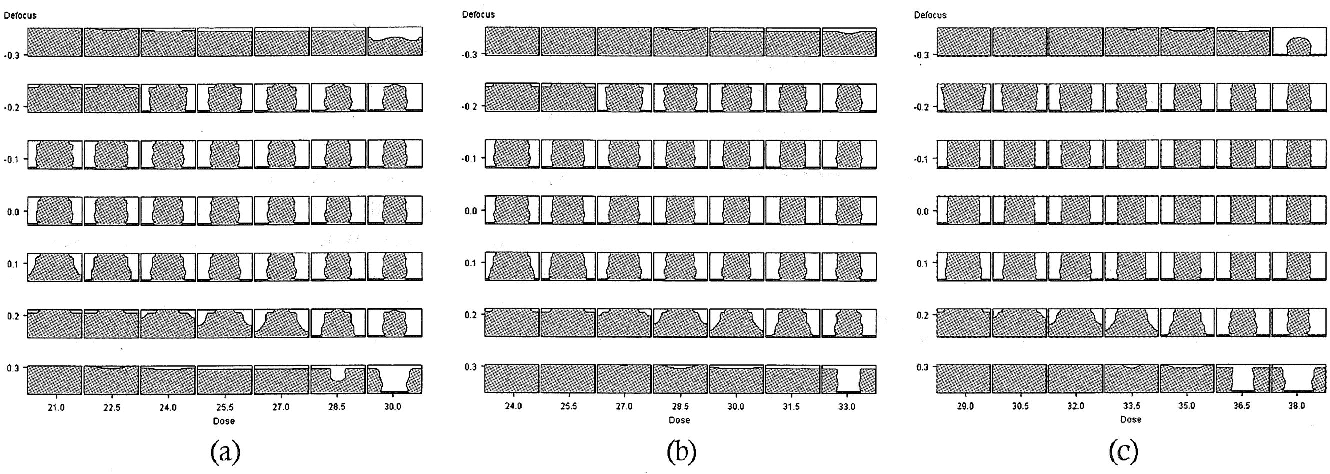


Fig. 8. Comparison of focus latitude at different exposure doses depending on resist contrast for simulation: (a) $\tan\theta = 12.7$, (b) $\tan\theta = 20.7$, (c) $\tan\theta = 34.9$.

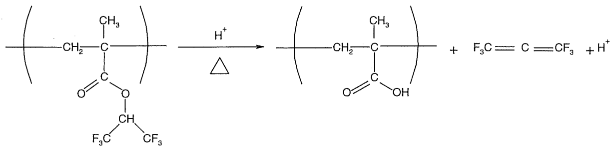


Fig. 9. Scheme of deprotection reaction for HC resist.

development contrast rises, the pattern approaches a rectangular shape, and the defocus characteristics are improved.

From the above, it was found that for the 100 nm thickness considered in this study, the focus margin can be most effectively improved by increasing the development contrast rather than increasing the polymer transmittance or development discrimination.

4. Improvement of Resolution and Focus Margin through Improvements in Resist Materials

It was discovered, through application of the Rate Editor and simulations, that the development characteristics for resist materials can be most effectively improved by increasing the development contrast rather than increasing the polymer transmittance or development discrimination. Protection groups were changed to obtain gat high contrast based on this knowledge. A new resist is called HC resist (HC resist: 1-trifluoromethyl-2.2.2-trifluoroethyl methacrylate: HFIPMA (hexafluoro-isopropanyl methacrylate)[21]). Figure 1 shows the anticipated scheme of the deprotection reaction for 2MAdMA resist. The development characteristics of the HC resist are listed in Table II, and the development curves for HC and 2MAdMA resist are shown in Fig. 10. The contrast for the HC resist was $\tan\theta = 11.1$. Figures 11 and 12 show the simulation results for the defocus margin and limiting resolution, respectively. The HC resist is improved over the 2MAdMA resist by 0.1 µm in defocus margin (-0.2 to $+0.2$ µm for TB/MA resist at an exposure dose of 27 mJ/cm^2, versus -0.2 to $+0.2$ µm for HC resist at an exposure dose of 32.5 mJ/cm^2) and by 10 nm in resolution (90 nm for 2MAdMA resist, versus 80 nm for HC resist). Patterns were also found to be more rectangular for the HC resist. Patterning studies based on contact exposure were conducted with the VUVES-4500 system; the scanning electron microscopy (SEM) observation results are shown in Fig. 13. Resolution is almost the same (120 nm) for both resists, but the HC resist yields a more rectangular pattern.

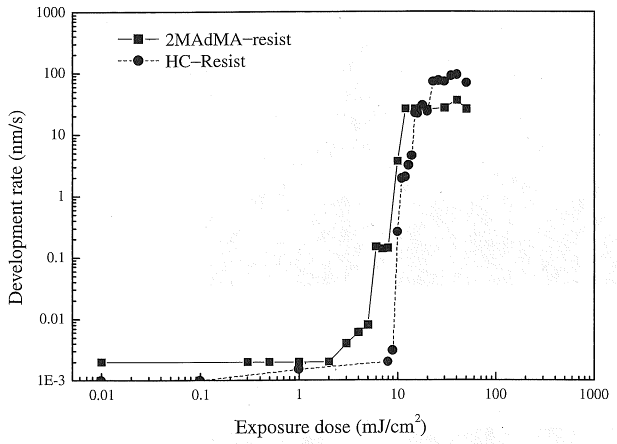
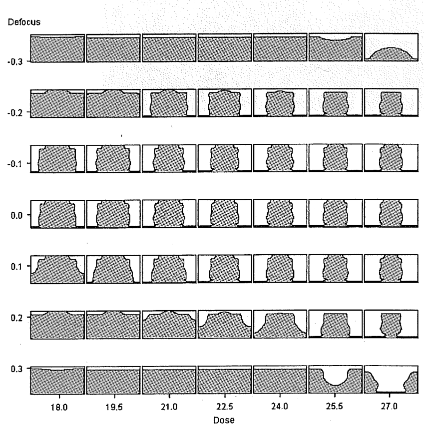
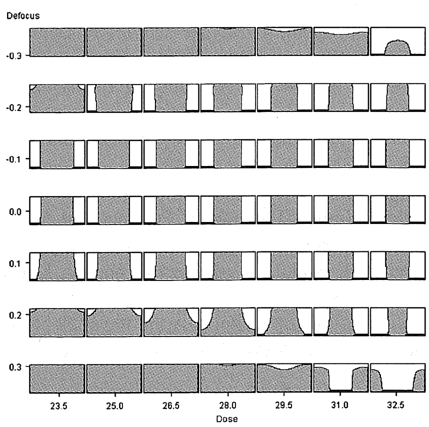


Fig. 10. Comparison of exposure dose-development rate curves for 2MAdMA resist and HC resist.



(a)

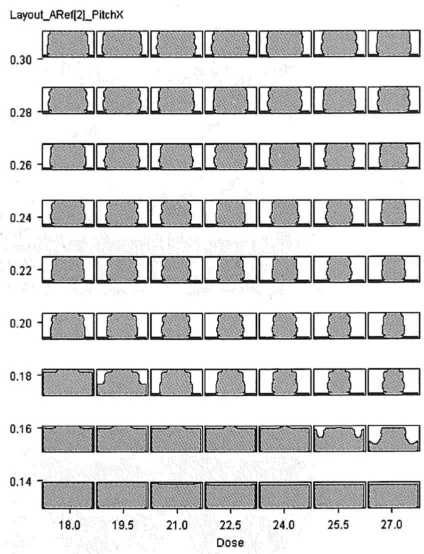


(b)

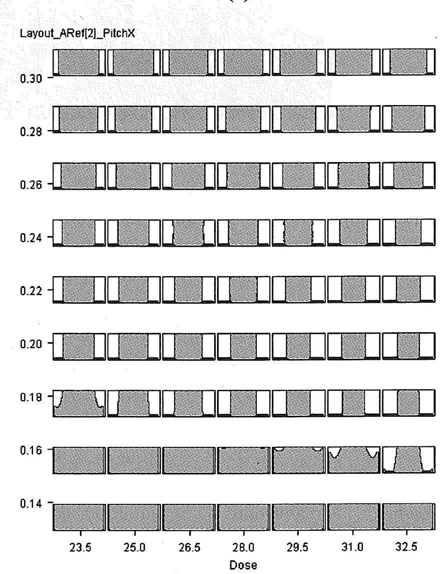
Fig. 11. Comparison of simulation result for focus latitude by (a) 2MAdMA resist and (b) HC resist for focus latitude at 100 nm L/S.

5. Conclusion

Rate analysis software was developed and used to analyze photoresist development rate data obtained for various exposure doses. The software allows the data to be decomposed into discrete characteristics, which can then be modified in order to identify the development characteristics that affect resist properties and to what extent they do so. Such tuning of the development process is expected to enable the production of high-resolution resists with broad defocus margin, taking into account the application of 2MAdMA chemically amplified positive resist for ArF excimer lasers in excimer laser processes. It was found that for the 100 nm thickness studied in this work, it is more effective to increase the development contrast to improve resolution and focus margin than to increase the polymer transmittance or development discrimination. Based on the knowledge obtained in this work, the resist was improved, and the validity of the study results was verified. The results of contact exposure evaluations indicated that, although the improved resist had the same resolution as the original resist, the pattern profile was improved. This system has been demonstrated to be useful for studies of resist materials for use with F_2 excimer lasers.



(a)

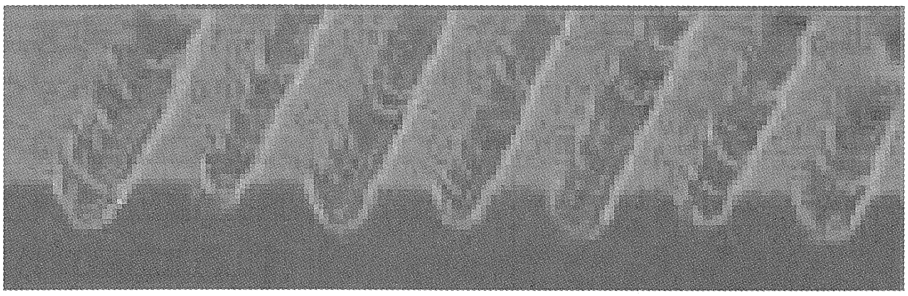


(b)

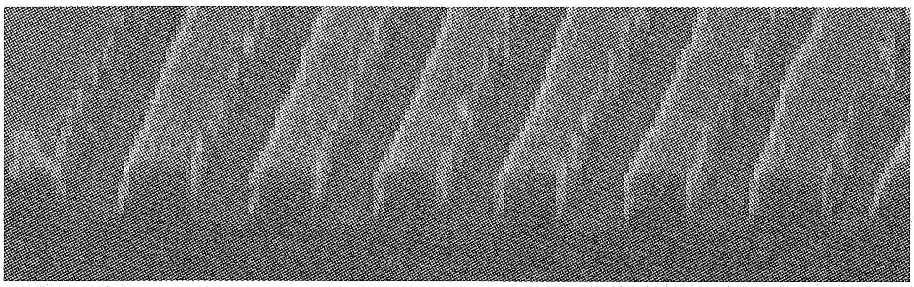
Fig. 12. Comparison of simulation result for resolution limit by (a) 2MAdMA resist and (b) HC resist for resolution at different exposure doses.

Acknowledgements

The authors wish to thank Senior Researcher Dr. Uetani of the Fine Chemicals Research Laboratory of Sumitomo



(a)2MAdMA-resist at 17mJ/cm^2



(b)HC-resist at 23 mJ/cm^2

Fig. 13. Comparison of patterning result by VUVES-4500 contact exposure module for (a) 2MAdMA resist and (b) HC resist at 120 nm line and space, 100 nm thickness.

Chemical Co., Ltd. for providing the resist, and Researcher Dr. Miya of the same laboratory for performing SEM observations. We would also like to thank Dr. Christian K. Kalus for valuable opinions on the lithography simulations.

1) A. Sekiguchi, Y. Minami and Y. Sensu: Proc. 42nd Symp. Semiconductors and Integrated Circuits Technology, 1992, Vol. 42, p. 109.
2) A. Sekiguchi, C. A. Mack, Y. Minami and T. Matsuzawa: Proc. SPIE **2725** (1996) 49.
3) P. Trefonas: Proc. SPIE **771** (1987) 194.
4) G. N. Taylor: Solid State Technol. **8** (1984) 56.
5) T. Kokubo: Fuji Film Res. Dev. **34** (1989) 21.
6) S. Kishimura, S. Uoya, A. Yamaguchi and K. Nagata: J. Photopolym. Sci. Technol. **1** (1988) 105.
7) C. A. Mack: J. Electrochem. Soc. **134** (1987) 148.
8) D. Seligson, S. Das, H. Gaw and P. Pianetta: J. Vac. Sci. Technol. B **6** (1988) 2303.
9) M. Sasago: J. Photoplym. Sci. Technol. **12** (1999) 585.
10) Int. SEMATECH: Int. Technol. Roadmap for Semicon. (1999).
11) S. Kishimura, M. Sasago, M. Shirai and M. Tsunooka: J. Photopolym. Sci. Technol. **12** (1999) 717.
12) S. Kishimura, A. Katsuyama, M. Sasago, M. Shirai and M. Tsunooka: Jpn. J. Appl. Phys. **38** (1999) 7103.
13) Y. Uetani and K. Fujishima: J. Photopolym. Sci. Technol. **8** (1999) 9.
14) A. Sekiguchi, C. A. Mack, M. Kadoi, Y. Miyake and T. Matsuzawa: Proc. SPIE **3999** (2000) 395.
15) A. Sekiguchi, M. Kadoi, Y. Miyake and T. Matsuzawa: Jpn. J. Appl. Phys. **39** (2000) 1920.
16) A. Sekiguchi, C. A. Mack, Y. Minami and T. Mastuzawa: Proc. SPIE **2725** (1996) 49.
17) A. Erdmann, C. L. Henderson, C. G. Willson and W. Henke: Proc. SPIE **3048** (1997) 114.
18) T. Ushirogouchi, T. Naito, K. Asakawa, N. Shida, M. Nakase and T. Tada: Microelectronics Technology: Polymers for Advanced Imaging and Packaging, (1995) ACS Symp. Ser. No. 614, p. 240.
19) A. Sekiguchi, M. Kadoi, T. Matsuzawa and Y. Minami: Electron. Commun. Part 2 **82** (1999) 30.
20) H. Fukuda and S. Okazaki: Jpn. J. Appl. Phys. **28** (1989) 2104.
21) Y. Uetani: 157 nm Int. SEMATECH Resist Work Shop (2000).