Investigation of Discrimination Enhancement with New Modeling for Poly-Hydroxystyrene Positive Resists

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Discrimination enhancement of poly-hydroxystyrene based chemically amplified positive resists was investigated with acid and base neutralization model in Eq. 8. Relationship of deprotecting reactivity and discrimination property was reported in Fig. 7. Dissolution distribution in resist film depth was discussed to be important characteristic to fabricate fine sub-quarter micron pattern in Fig. 9.

Keywords: chemically amplified resist, discrimination enhancement, dissolution distribution, poly-hydroxystyrene

1. Introduction

Chemically amplified resists are being applied with KrF excimer laser illumination for mass production of device manufacturing. Recently, reduction of DRAM’s chip size is speeded up accelerated with the shift of design rule from quarter micron meter to sub 0.2 micron meter. KrF lithography technique is rapidly advanced, and even 0.13 μm rule device manufacturing process is now investigated.

To fabricate fine patterns being much smaller than wavelength, application of high NA lens, optical enhancement techniques and high contrast resist materials are indispensable. Chemically amplified system was superior invention because not only this have high speed property in the first viewpoint[1], but also this have variety to choose many catalyst and acid labile substrate and have possibility for contrast enhancement with control of chemical reaction and diffusion.

Simulation is an important tool not only for process optimization and estimation but also for resist development and optimization. It is well known that resist dissolution property, acid diffusion, and transmittance are closely related to resolution, exposure defocus margin, and pattern profiles. Many resist models were reported[2-11] and some of these were commercially available. So far models were based on first order kinetics of acid generation originated in Dill’s ABC parameter[3].

In this study, authors present a new model that supports non linear acid generation by acid and base neutralization reaction. At the same time, investigation of discrimination enhancement are suggested using neutralization model for high resolution resists.

2. Experimental

2.1. Materials

35mol % 1-ethoxy ethyl (EOE) blocked polyhydroxystyrene were prepared for resist base polymer. Mw and dispersion of base polymer were 10,000 and 1.10, respectively. Tri-phenyl sulfonium tosylate was prepared for photo acid generator (PAG).

Resist formulated with 2wt% of PAG and small amount of amine quencher in base polymer dissolved in propylene glycol 1-monomethyl ether 2-acetate (PGMEA) solvent.

2.2 Methods

Resist solvents were spun on anti-reflection layer coated Si wafer. Resist film thickness were 600nm after 100 degrees pre-bake. Wafer was exposed by KrF excimer laser stepper (Nikon 0.5NA lens) and baked (PEB) on 110 degrees. 2.38 wt% tetramethyl ammonium hydroxide (TMAH) water solution was applied for
development. Gray tone mask was used in less than 0.5mJ/cm² exposure.

Dissolution rate was measured by RDA780 (Lithotech Japan) and deprotection was monitored by FT-IR JIR-5500 (JEOL). Protection ratio of EOE polymer was measured at 940cm⁻¹ peak absorbance. Photo acid generation was monitored from absorbance at 618nm with 1wt% tetrabromophenol blue disodium salt added resist film on quartz substrate[12].

3. Results and Discussion

3.1 Proton Jump Model

In aqueous solution, acid generation with the existence of amine is calculated as follows.

\[
\begin{align*}
H^+ + B &\leftrightarrow HB^+ \\
X_0 &= 1 - \exp(C \cdot E) \\
K &= \frac{X_0 - \alpha}{\alpha(B_0 - X_0 + \alpha)} \\
\alpha &= \frac{(B_0 - X_0 + 1) + \sqrt{(B_0 - X_0K + 1)^2 + 4X_0K}}{2K} \\
P &= P_0 \exp(-\alpha t/kd)
\end{align*}
\]

H⁺: Photo-generated Acid  
B: Additive base  
C: Photo acid generation constant, 0.06(cm²/mJ)  
E: Dose (mJ/cm²)  
K: Equilibrium constant  
X₀: Quantity of photo generated acid (mol)  
B₀: Quantity of additive base (mol)  
α: Quantity of acid under equilibrium state (mol)  
P: Protection ratio (%)  
P₀: Initial protection ratio (%)  
t: PEB time (sec.)  
k₀: Rate constant in deprotecting reaction

The pKa value of p-toluene sulfonic acid is minus 7 and almost alkylamine is around 8 in water at 25 degrees. Equilibrium constant K is estimated to be 10¹⁵. Acid generation is calculated using eq. 3. In Figure 1, very sharp acid generation is shown at neutralization point. The sharp acid generation changes the deprotection slope dramatically (Fig. 2).

Figure 3 shows experimental result of EOE deprotection property with variety of additive amine quantity. Each curves change to be steep slope by addition of amine and sensitivity decrease exactly in proportion to amine quantity. Sufficient steep slopes are obtained with 10-20 molar % of amine.

From comparison of Figure 2 and 3, the slope angles in 10-20% protection range and steep deprotection dose points in each amine quantity are almost same. However experimental slopes in 25-35% protection range are smaller than calculated result. The gentle curve shows that substitution is deprotected in the range of smaller photo generated acid quantity than added amine.

First model in eq. 3 is supposed that added amine capture photo-generated acid very quickly and acid can be liberated just over neutralization point.

A new model suggest the competitive reaction of acid with amine and acid with substrate. Acid concentration are expanded from eq. 5. Protection ratio is calculated in eq. 8 that is arrived by eq. 6 and 7. The calculated curves express gentle curves in small deprotection area and good fitting with experimental result (Fig. 4).

To enhance the slope angle in initial deprotecting region, it is important to increase kamine(Fig. 5). Figure 6 shows deprotection curves with two kinds of amines. Amine 1 is superior to amine 2 for capturing rate of acid. A new amine quencher are developed to achieve maximum kamine value.

\[
\frac{dX_t}{dt} = -k_{amine}X_t[B - X_t \cdot X_t] \\
\frac{d[P]}{dt} = -k_x X_t[P] \\
X_t = \frac{(B_0 - X_0)^{\frac{X}{B_0}} \exp[-k_{amine}(B_0 - X_0t)]}{1 - \frac{X}{B_0} \exp[-k_{amine}(B_0 - X_0t)]} \\
[P] = \left[ P_0 \left( \frac{B_0}{X_0} - \frac{X}{B_0} \right) \exp[-k_{amine}(B_0 - X_0t)] \right] \exp[-k_{amine}(B_0 - X_0t) - 1]^{X_0/Bo}
\]

Xt : Acid concentration  
kamine : rate constant of acid and amine

3.2 Effect of Deprotection Reactivity on Proton-Jump Model
Difference of deprotection activation energy was discussed in several acid labile substitutions. Acid labile substitutions have strong effect on deprotection and dissolution properties.

Figure 7 shows calculated result with variation of $k_a$. High reactivity substitutions are steeper than low reactivity substitutions in the range of 0-20% protection ratio, while low reactivity substitutions are superior to high reactivity substitutions in the range of 25-30% protection ratio. Optimum deprotection property is expected to exist and combination of two or three kind of high and low reactivity substitutions is effective for optimization.

To introduce parameter of protection ratio and dissolution rate relationship (eq. 9), deprotection curves are conversed to dissolution curves (Fig. 8)

$$R = R_{max} \cdot \exp(-Inh \cdot P^C)$$  \hspace{1cm} (9)

R : Dissolution Rate  
Rmax : Dissolution rate of 0% blocked polymer  
Inh : Inhibition ability parameter  
C : Inhibition curvature parameter

High reactivity substitutions are steeper than low reactivity substitutions in the range of 100-1000 Å/s dissolution rate. Low reactivity substitutions are superior to high reactivity substitution in 1-10 Å/s rate range. The slope in 100-1000 Å/s dissolution rate is important for trench or contact hole pattern fabrication with more than 700nm thickness resists. The slope in getting off region (1-10 Å/s) is important for line pattern, especially for recent thin film process.

3.3 Dissolution Distribution in Film Depth

Simulation result of 0.2 μmL/S dissolution rate images with 0.4 μm defocus optical contrast are shown in Figure 9. Left side is surface dissolution in smaller dose and right side is surface dissolution in larger dose. Dissolution rate and slope angle are same in two resists, however image profiles are quite different.

This result shows that dissolution distribution in resist film is more important property in critical pattern size.

Experimental dissolution distribution property is shown in Figure 10 and 11. Types A and B have the same transmittance (60%/μm), however type B is smaller distribution than A. Lithographic performance of Type B is superior to type A with wide DoF margin and vertical side wall (Fig. 12).

Dissolution distribution in film depth shows different proton jumping point in film depth. For this reason, PAG or amine concentration distribution is considered.

Fig. 1 Acid generation with aqueous proton jump model

Fig. 2 Deprotection with aqueous proton jump model

Fig. 3 Experimental deprotection curves with variation of amine concentration
Figure 4  Calculated deprotection curves with new model

Figure 5  Calculated deprotection with effect $K_{amine}$

Figure 6  Experimental deprotection with variety of amines

Figure 7  Calculated deprotection with variation of $k_d$

Figure 8  Calculated dissolution rate curves with variation of $k_d$
Figure 9  Dissolution distribution in film depth

Surface dissolve in smaller dose (left), surface dissolve in larger dose (right)
Upper are dissolution property in film depth, middle are 0.2 µm L/S dissolution rate images
with 0.4 µm defocus to substrate side, under are 0.4 µm defocus to lens side.

Figure 10  Experimental dissolution distribution
Surface layer dissolve in smaller dose

Figure 11  Experimental dissolution distribution
Surface, middle and bottom layer dissolve in same dose
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**5. References**


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**Figure 12** Lithography performance of 0.2 μm L/S DoF profile