Effect of Inhomogeneous Acid Distribution on Line Edge Roughness - Relationship to Line Edge Roughness Originating from Chemical Gradient

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Line edge roughness (LER) is the critical issue in the development of chemically amplified resists used for extreme ultraviolet (EUV) lithography. The main cause of LER in state-of-the-art resists used at 22 nm node is the chemical inhomogeneity intrinsic to chemical reactions. This LER is expressed using the chemical gradient of chemical compounds which determine the solubility of resists. However, the inhomogeneity in the initial acid distribution possibly caused by the inhomogeneous distribution of acid generators becomes a concern with the reduction of feature sizes. In this study, the effect of acid distribution on LER was theoretically investigated on the basis of the reaction mechanisms of chemically amplified EUV resists. The fluctuation of line edge originating from the initial acid distribution was compared with LER originating from the chemical gradient. The microfluctuation in the initial acid distribution was sufficiently smoothed out through catalytic chain reaction. This indicates that the smoothing effect of acid diffusion is essential to the ultranfine patterning with high sensitivity.

Keywords: EUV lithography, chemically amplified resist, line edge roughness, inhomogeneity, chemical gradient

1. Introduction

Extreme ultraviolet (EUV) radiation will be the first ionizing radiation used for the main process of the mass production of semiconductor devices. EUV lithography is expected to be used at 22 nm node and below,[1] It has been demonstrated that EUV lithography has 11 nm resolution.[2] With the decrease of feature sizes, the reduction of line edge roughness (LER) becomes increasingly important.[3] The causes of LER have been intensively investigated during the past two decades.[4] Although many factors affect LER formation, the main cause of LER in state-of-the-art resists is the chemical inhomogeneity at image boundary.[5-8] Upon exposure to EUV radiation through photomask, optical modulation is transferred to resist materials as the modulation of acid concentration. Through catalytic reactions, the modulation of acid distribution is transformed to that of the concentration of chemical compounds that determine the solubility of resists into developer. In this process, the inhomogeneity in the distribution of chemical compounds is generated at the image boundary between solubilized and insoluble regions (intermediate region). This chemical inhomogeneity is intrinsic to chemical reaction because the chemical reaction is a stochastic process. LER is proportional to the width of the intermediate region. Because the width of the intermediate region can be approximated by using the chemical gradient (the gradient of the concentration of chemical compounds that determine the solubility of the resist), LER is expressed as[9]

\[ LER_{lg} = f_{\text{LER}} \frac{dm}{dx} \]  

(1)

Here, \( f_{\text{LER}} \), \( m \), and \( \frac{dm}{dx} \) are a constant, the
of chemical compounds normalized by its initial concentration, and the chemical gradient. It has been demonstrated using an EUV exposure tool that eq. (1) is valid in the wide range of exposure dose and half-pitch.[9]

Besides LER expressed by eq. (1), the microfluxuation of acid concentration possibly caused by the inhomogeneous distribution of acid generators such as molecular clustering is another concern when the feature sizes are reduced. The clustering of acid generators has been investigated. Although the evidence of clustering has not been found yet because of the difficulty of detection,[10,11] the possibility of the clustering of acid generators has not been excluded as a cause of LER. In this study, the effect of inhomogeneous acid distribution on LER was theoretically investigated by adding virtual microfluctuation to the acid distribution calculated with the assumption of uniform acid generator distribution. In particular, the relationship of LER caused by microfluctuation of initial acid distribution to LER expressed by eq. (1) is discussed.

2. Simulation method

In the simulation, the aerial image of incident EUV photons, \( I(x) \) (perpendicular to line pattern, \( y \): parallel to line pattern, \( z \): depth direction) was approximated using a cosine function.

\[
I(x, y, z) = A \left[ \frac{1}{2} \left( 1 + C \cos \left( \frac{\pi x}{P_{x/2}} \right) \right) \exp(-\alpha |z|) \right]
\]  
(2)

Here, \( A, C, P_{x/2}, \) and \( \alpha \) represent the exposure dose, the contrast of the aerial image, the half-pitch of a line-and-space pattern, and the absorption coefficient of the resist, respectively. The details of the sensitization mechanisms of EUV resists have been reported elsewhere.[12-14] The resolution blur induced by secondary electrons[15-17] was incorporated using the spherically symmetric point-spread function for EUV resists.[18,19] The acid distribution was calculated by convoluting the point-spread function with the aerial image of EUV photons. The preneutralization of acids before postexposure baking (PEB)[20-22] was assumed. Using the acid distribution after the preneutralization as a boundary condition, the subsequent reaction diffusion was calculated using the following equations.

\[
\frac{\partial C_{\text{acid}}}{\partial t} = \nabla(D_{\text{acid}} \nabla C_{\text{acid}}) - k_N C_{\text{acid}} C_q
\]  
(3)

Here, \( C_{\text{acid}}, C_q, D_{\text{acid}}, D_q, \) and \( k_N \) represent the concentrations (probability densities) of acids and quenchers, the diffusion constants of acids and quenchers, and the rate constant for neutralization, respectively. The deprotection was calculated as

\[
\frac{\partial C_p}{\partial t} = -k_p C_{\text{acid}} C_p.
\]  
(5)

Here, \( k_p \) represents the rate constant for deprotection.

The details of the point-spread function and the parameters used for calculation have been reported elsewhere.[18] The reported parameters are those of PHS-based chemically amplified resists with triphenylsulfonium triflate and have been proved to reproduce the acid yields generated in resist films.[23,24] The acid generator concentration was assumed to be constant during exposure. The error in the estimation of acid concentration caused by this assumption is less than 3%.[25] This error does not significantly affect the following discussion. The rate constant for neutralization between acids and quenchers is equal to the diffusion-controlled rate.[26] The rate constant for deprotection \( k_p \) was calculated using \( k_p = 4\pi R_{\text{eff}} D \) where \( R_{\text{eff}} \) and \( D \) are the effective reaction radius and the sum of the diffusion constants of related molecules. The effective reaction radius has been investigated for a typical chemically amplified EUV resists and estimated to be approximately 0.1 nm.[9] The initial protection ratio of the polymer is 30%. In chemically amplified resists used for ionizing radiation, the protons of acids are generated through the deprotonation of polymer radical cations.[27,28] The hydroxyl groups are the major proton source.[29-32] The protection of hydroxyl groups has been reported to reduce acid yields.[27,33] Although the deprotonation efficiency depends on the molecular structures of the protecting groups, the deprotonation efficiency of protected units is set to be a typical value of 0.3.[33] The diffusion constants of acids and quenchers were assumed to be 1 nm$^2$ s$^{-1}$. The quencher diffusion constant was assumed to be the same as the acid diffusion constant. The effect of the quencher diffusion constant has been reported and this assumption does not significantly affect the following discussion.[34] The effect of matrix-dependent diffusion on the chemical gradient has been also reported.[35,36] The half-pitch and resist
thicknesses were assumed to be 23 and 50 nm, respectively. The contrast of the aerial image was assumed to be 1 for simplicity. The effect of contrast on chemical gradient has been also reported.[37,38]

The absorption coefficient and acid generator concentration were set to be typical values for chemically amplified EUV resists (3.8 \( \mu \)m\(^{-1}\) and 10 wt %), respectively. The contribution of the direct electronic excitation of acid generators to acid generation was incorporated using the excitation factor (1.4 \( \times \) 10\(^{-2}\) dm\(^3\) mol\(^{-1}\) eV\(^{-1}\)).[39] The other parameters associated with basic material properties were determined mainly by the quantitative analysis of acid yields generated in model resists upon exposure to EUV and an electron beam.[40]

3. Results and discussion

The microfluctuation of acid concentration was generated by multiplying the acid concentration distribution by Gaussian function \( f_{\text{mod}}(x,y) \) using the following equation.

\[
f_{\text{mod}}(x, y) = \frac{I_c}{2\pi \sigma_s^2} \exp\left(-\frac{x^2 + y^2}{2\sigma_s^2}\right)
\]

\[
C'_{\text{acid}}(x, y) = C_{\text{acid}}(x, y) \times \prod_{i=0}^n \left[1 + (-1)^m f_{\text{mod}}(x-x_i, y-y_i)\right]
\]

Here, \( m \) is a random number which gives 0 or 1. \( C'_{\text{acid}}, I_c, \) and \( \sigma_s \) are a modulated acid distribution, the intensity of microfluctuation, and the size of microfluctuation, respectively. The coordinates of microfluctuation \((x_i, y_i)\) were randomly generated. \( n \) is the number of microfluctuation and calculated using \( n = A_{\text{calc}} \times D \), where \( A_{\text{calc}} \) and \( D \) are the area for simulation and the density of microfluctuation.

Figure 1 shows the relationship of the parameters \((I_c, \sigma_s, \) and \( D)\) to the modulated acid distribution. While the inhomogeneity was increased with \( I_c \), and \( D \), it was decreased with the increase in \( \sigma_s \).

Using the modulated acid distribution shown in Fig. 1, the subsequent neutralization and deprotection were calculated. By changing quencher concentration, dissolution point, and PEB time, the condition, under which the highest average chemical gradient is obtained at the intended boundary, was surveyed. The optimum
The quencher concentration did not depend on the extent of microfluctuation within the parameter ranges assumed in this study. Similarly, the optimum PEB time and dissolution point did not significantly depend on the extent of microfluctuation. The latent images corresponding to the acid images in Fig. 1 are shown in Fig. 2. The dissolution point is indicated by light green. With the increase in the inhomogeneity of acid distribution, the fluctuation of line edge was increased.

The deviation of line edge from the intended line edge ($x=p_{1/2}/2$, LER$_{MF}$) was calculated and $3\sigma$ ($\sigma$: dispersion) is plotted in Fig. 3. LER originating from the chemical gradient (LER$_{CG}$) was calculated using eq. (1) with the calculated chemical gradient. $f_{LER}$ reported for the third Seltec Standard Resist (SSR3)[9] was used in the estimation. LER$_{CG}$ was 4.5 nm when a smooth acid distribution was assumed. The total LER is expressed as

$$\text{Total LER} = \sqrt{\text{LER}^2_{CG} + \text{LER}^2_{MF}}. \quad (8)$$

The calculated total LER is also plotted in Fig. 3. For $\sigma = 1$ and 2 nm, LER$_{MF}$ exceeds LER$_{CG}$ at $D = 0.2$ nm$^2$ and $I_c = 4$. For $\sigma = 5$ nm, LER$_{MF}$ exceeds LER$_{CG}$ at $D = 0.2$ nm$^2$ and $I_c = 6$. This indicates that the effect of microfluctuation in the initial acid distribution is sufficiently suppressed through the catalytic chain reaction unless the initial acid distribution is significantly degraded. The smoothing effect of acid diffusion is effective to suppress the effect of microfluctuation.

4. Conclusion

The effect of acid distribution on LER was theoretically investigated on the basis of the reaction mechanisms of chemically amplified EUV resists. The fluctuation of line edge originating from the initial acid distribution was compared with LER originating from the chemical gradient. It was found that the microfluctuation in the initial acid distribution is sufficiently smoothed out through catalytic chain reaction. This indicates that the smoothing effect of acid diffusion is effective to suppress the effect of microfluctuation. The acid diffusion is essential to the ultrafine patterning. The control of acid diffusion is a key to the development of high performance resists below 22 nm node.
Fig. 3. Effect of microfluctuation of initial acid distribution on LER. Fig. (a), (b), and (c) shows the results calculated with $\sigma_s = 1$, 2, and 5 nm, respectively. The unit of density is nm$^{-2}$.

References