Relationship between Resolution Blur and Stochastic Defect of Chemically Amplified Resists Used for Extreme Ultraviolet Lithography

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The stochastic defect generation such as pinching and bridging is a serious concern in extreme ultraviolet (EUV) lithography. The resolution blur (caused by secondary electrons) as well as the shot noise of EUV photons is considered to affect the stochastic defect generation. In this study, the relationship between resolution blur and stochastic defect generation in chemically amplified resists was investigated assuming two virtual sensitization mechanisms to clarify the effects of resolution blur. For the non-sequential radiative model, the increase of quantum efficiency from 2 to 4 is considered to be effective for the sensitivity enhancement, when the sensitization distance is shorter than 3 nm.

Keywords: EUV lithography, Chemically amplified resist, Stochastic defect, Sensitivity, Resolution blur, Shot noise

1. Introduction

The development of extreme ultraviolet (EUV) lithography has significantly progressed in the past few years. However, the defects of resist patterns such as pinching and bridging are a problem [1]. The defects caused by the contamination and inadequate filtering of chemicals are a problem in the production lines of semiconductor devices. In addition to such defects, it was pointed out that the defects caused by the stochastic effects in the sensitization processes are a serious concern in EUV lithography in 2013 [2].

In lithography, photons carry the information and energy needed for the fabrication of resist patterns. The relationship between information and energy has been investigated [3-8]. In the relationship between stochastic defects and sensitivity, there are two regions, namely, information- and energy-deficit regions [3]. In the information-deficit region, the sensitivity cannot be increased without increasing stochastic defects unless the quantity or quality of information is increased. On the other hand, the sensitivity can be increased by increasing the quantum efficiency of acids without increasing stochastic defects in the energy-deficit region [3]. However, the effect of quantum efficiency on sensitivity is limited because an increase in quantum efficiency essentially induces resolution blur in the initial acid distribution before postexposure baking (PEB) through further acid generation [6-8]. The resolution blur is induced because two molecules cannot occupy the same place.

The methods of increasing the quantum efficiency of acid generation have been investigated for the sensitivity enhancement. Increasing the reduction potential of an acid generator [9], an acid amplification system [10], a photosensitized chemically amplified resist (PSCAR™) [11,12], and an acid generation promoter [13] are typical means of enhancing the real or apparent quantum efficiency. For LER, the effect of resolution blur in an acid distribution induced by an increase in quantum efficiency has been investigated assuming two types of virtual sensitization mechanisms [6-8].

In this study, sensitivity enhancement in the energy-deficit region was investigated in terms of
its relationship with stochastic defect, assuming virtual sensitization mechanisms, in which the sensitization distances were defined as the distance from the last sensitization (or ionization) point [6,7] and the distance from the EUV absorption point [8]. Understanding the relationship between the stochastic defects and the blur accompanying quantum efficiency enhancement is important in assessing the feasibility of improving resist performance through an increase in real or apparent quantum efficiency. Hereafter, both real and apparent quantum efficiencies are simply referred to as quantum efficiency.

2. Simulation model and method

The resist pattern formation was calculated, assuming two types of virtual cases [6-8], to clarify the relationship between the resolution blur and the stochastic defect generation. The model system was a partially protected polymer with acid generators and photodecomposable [14] quenchers. Figure 1 schematically depicts the relationship between the real and virtual cases for sensitization of acid generators (AGs) and photodecomposable quenchers (PDQs) in chemically amplified EUV resists.

Fig. 1. Schematic of the relationship between the real and virtual cases for sensitization of acid generators (AGs) and photodecomposable quenchers (PDQs) in chemically amplified EUV resists.
II (non-sequential radiative model) [8], acid generator or photodecomposable quencher molecules nearest a position at a distance of \( r_s \) from the EUV absorption point were intentionally decomposed in accordance with the quantum efficiency. In these sensitization models, \( r_s \) was defined as a sensitization distance. The quantum efficiency was defined as the total number of acid generators and photodecomposable quenchers that are decomposed by an absorbed EUV photon.

The exposure dose distribution of line-and-space patterns with a half-pitch of 11 nm, \( I \) \((x: \) perpendicular to line pattern, \( y: \) parallel to line pattern), was approximated using the cosine function,

\[
I(x, y) = \frac{A}{2} \left[ 1 + C \cos \left( \frac{\pi x}{11} \right) \right]. \tag{1}
\]

Here, \( A \) and \( C \) represent the exposure dose and the contrast of the optical image, respectively. The optical contrast was assumed to be 1. The exposed line length was 1000 nm. The initial average number of protected units per polymer molecule before PEB and its standard deviation were 12 and 0, respectively. The absorption coefficient was set to 3.8 \( \mu m^{-1} \) [17]. The total sensitizer concentration (the sum of the acid generator and photodecomposable quencher concentrations) was 0.2 \( nm^{-3} \). The sensitization processes shown in Fig. 1 were calculated by a Monte Carlo method.

The preneutralization of acids before PEB [18,19] was assumed. The proton migration range at room temperature was set to 2.4 nm [20]. Using the acid distribution after the preneutralization as the initial condition, the catalytic chain reaction during PEB was calculated by a Monte Carlo method. This calculation method has been reported in detail elsewhere [5,20]. The effective reaction radius for deprotection was set to 0.1 nm; current high-performance EUV resists have values of 0.06-0.16 nm [21-26]. The effective reaction radius for neutralization was set to 0.5 nm. The parameters used in the simulation are summarized in Table 1 [17,27].

| Table 1. Simulation parameters. |
|---------------------------------|
| \( \rho \) \( 1/2 \) (nm)       | 11 |
| Optical contrast                | 1.0 |
| Resist thickness (nm)           | 25 |
| Absorption coefficient \(( \mu m^{-1} )\) [17] | 3.8 |
| Resist film density \(( g \ cm^{-3} )\) [27] | 1.2 |
| Total sensitizer concentration \(( nm^{-3} )\) | 0.2 |
| Number of monomer units per polymer | 40 |
| Number of protected units per polymer | 12 |
| Acid diffusion constant \(( nm^{2} \ s^{-1} )\) | 1.0 |
| Effective reaction radius for neutralization (nm) | 0.5 |
| Effective reaction radius for deprotection (nm) | 0.1 |

3. Results and discussion

The probability of the stochastic generation of pinching and bridging is considered to decrease with an increase in the difference between the number of protected units per polymer molecule after PEB and the dissolution point (threshold), \( |N-N_{DP}| \), and to increase with an increase in the protected unit fluctuation, \( \sigma \) [2]. Here, \( N \) and \( N_{DP} \) is the number of protected units connected to a polymer molecule after PEB and \( N \) at the boundary between lines and spaces. \( \sigma \) is the standard deviation of the number of protected units per polymer molecule after PEB. The relationship between stochastic defect generation and \( \sigma|N-N_{DP}| \) has been investigated, using the first EIDEC standard resist (ESR1), a typical high-performance EUV resist. For ESR1, \( \sigma|N-N_{DP}| \) was required to be smaller than 0.50–0.67 at the center of the space to eliminate bridging within a 6.8 \( \mu m \) line length. Also, \( \sigma|N-N_{DP}| \) was required to be smaller than 0.63–0.83 at the center of the resist line pattern to eliminate pinching within a 6.1 \( \mu m \) line length [2].

Assuming Model I, the relationship between sensitivity and \( \sigma|N-N_{DP}| \) was calculated for quantum efficiencies of 2, 4, 6, 8, and 10. The quantum efficiency of current chemically amplified EUV resists is approximately 2 [28,29]. The process parameters were set to minimize LER. Figure 2 shows the relationship between sensitivity and \( \sigma|N-N_{DP}| \) at \( x=\pm 11 \) nm (pinching), calculated with a total sensitizer concentration of 0.2 \( nm^{-3} \), where the sensitization distance was set to 0 to 1, 2, and 3 nm. The graph for the quantum efficiency of 2 was shifted in the horizontal direction to discuss the possibility of twofold sensitivity enhancement from the case with the quantum efficiency of 2 without increasing pinching (a dashed line). Figure 3 shows the relationship between sensitivity and \( \sigma|N-N_{DP}| \) at \( x=0 \) nm (bridging), calculated under the same condition for the case of pinching. The graph for the quantum efficiency of 2 was shifted to discuss the possibility of twofold sensitivity enhancement without increasing bridging (a dashed line). For both cases, the minimum value of \( \sigma|N-N_{DP}| \) for each quantum efficiency increased with the increase of quantum efficiency. The increment of \( \sigma|N-N_{DP}| \) increased with the increase of sensitization distance. At the sensitization distance of 1 nm, the twofold
stochastic defects when the sensitization

Fig. 2. Relationship between sensitivity and $\sigma / |N - N_{DP}|$ at $x = \pm 11$ nm (pinching) in Model I, calculated for sensitization distances of (a) 0, (b) 1, (c) 2, and (d) 3 nm. Numerical values following “$Q$” denote quantum efficiencies. The total sensitizer concentration was 0.2 nm$^{-3}$. The arrows with “1/2” indicate the parallel shift in the horizontal direction (the sensitivity of the corresponding curve was reduced by half for comparison).

Fig. 3. Relationship between sensitivity and $\sigma / |N - N_{DP}|$ at $x = 0$ nm (bridging) in Model I, calculated for sensitization distances of (a) 0, (b) 1, (c) 2, and (d) 3 nm. Numerical values following “$Q$” denote quantum efficiencies. The total sensitizer concentration was 0.2 nm$^{-3}$. The arrows with “1/2” indicate the parallel shift in the horizontal direction (the sensitivity of the corresponding curve was reduced by half for comparison).
enhancement in the energy-deficit region was feasible. However, it was not feasible at the sensitization distance of 3 nm. This means that the enhancement of quantum efficiency is meaningless for the suppression of stochastic defects when the sensitization distance is 3 nm. Assuming Model II, the relationship between sensitivity and $\sigma/[N-N_{DP}]$ was calculated for quantum efficiencies of 2, 4, 6, 8, and 10. The process parameters were set to minimize LER. Figure 4 shows the relationship between sensitivity and $\sigma/[N-N_{DP}]$ at $x=\pm 11$ nm (pinching), calculated with a total sensitizer concentration of 0.2 nm$^{-3}$, where the sensitization distance was set to 0 to 1, 2, and 3 nm. Figure 5 shows the relationship between sensitivity and $\sigma/[N-N_{DP}]$ at $x=0$ nm (bridging), calculated under the same condition for the case of pinching. The graph for the quantum efficiency of 2 was shifted in the horizontal direction to discuss the possibility of twofold sensitivity enhancement from the case with the quantum efficiency of 2 without increasing pinching or bridging (dashed lines). For both cases, the minimum value of $\sigma/[N-N_{DP}]$ for each quantum efficiency increased with the increase of quantum efficiency. The increment of $\sigma/[N-N_{DP}]$ was significantly smaller than that for Model I. At the sensitization distance of 3 nm, the twofold enhancement in the energy-deficit region was feasible. However, these results indicate that the stochastic defect cannot be decreased from the minimum value for the quantum efficiency of 2 by increasing the quantum efficiency.

The real sensitization mechanism is closer to Model II than Model I, because the inelastic mean free path of 20-80 eV electrons is significantly shorter than the thermalization distance [30]. A 92.5 eV photon produces 4-5 ion pairs (pairs of radical cation and thermalized electrons). As described before, the quantum efficiency of acid generation is approximately 2 in a typical chemically amplified resist. This is because some of thermalized electrons recombine with radical cations and because some of radical cations are not converted to protons. In principle, the quantum efficiency can be increased to 4-5, by suppressing the recombination and improving the conversion efficiency from radical cations to protons. The results obtained in this study suggest that the sensitivity can be increased twofold.
with the slight increase of defects by increasing the quantum efficiency close to the initial ion pair yield, although the information is not increased by increasing the quantum efficiency.

4. Conclusion

The relationship between resolution blur and stochastic defect generation in chemically amplified resists was investigated assuming two virtual sensitization mechanism to clarify the effects of resolution blur. For the sequential model (Model I), the enhancement of quantum efficiency was meaningless for the suppression of stochastic defects when the sensitization distance was 3 nm. For the non-sequential radiative model, the increase of quantum efficiency from 2 to 4 was effective for the sensitivity enhancement when the sensitization distance was shorter than 3 nm.

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