Stochastic Simulation of Pattern Formation for Negative-Type Chemically Amplified Resists in Extreme Ultraviolet Lithography

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A stochastic simulation of the pattern formation process for negative-type chemically amplified resists in extreme ultraviolet (EUV) lithography has been performed. The initial structures of the resist polymers are formed by randomly bonding monomers. The deposited energy distribution in the resist by EUV light exposure is calculated by Monte Carlo simulation of the photoelectron scattering. The activation of acid generators is introduced according to the deposited energy distribution. Acid diffusion and the polymer crosslinking reactions during the post-exposure bake (PEB) are then simulated. Development of the resist is modeled by removing the polymers with a polymerization degree below the threshold value from the resist. The effects of EUV light exposure and PEB conditions on the pattern shapes are investigated by the simulation.

Keywords: Extreme ultraviolet lithography, Stochastic simulation, Acid diffusion, Polymer crosslinking reaction, Line edge roughness, Critical dimension error

1. Introduction

Research and development for the practical use of extreme ultraviolet (EUV) lithography [1,2] in the high-volume production of semiconductor devices have actively been conducted. There are various issues to be solved in terms of the optical system, mask, resist materials and resist processes. The stochastic effect in the pattern formation process is one of the serious problems. Absorption of EUV light, scattering of photoelectrons, and chemical reaction of the resist are stochastic processes that cause uncertain variations in the pattern shape and size. In the case of a chemically amplified resist [3,4], the stochastic effect is more evident because the exposure dose is small. Various studies [5–12] have been conducted to address this issue, but this problem has not yet been sufficiently resolved.

Computational simulation considering the molecular structure of the resist is effective for studying the stochastic effect of the pattern formation process. We recently proposed molecular-scale simulations and studied the effects of the molecular behavior on pattern formation in various lithography processes [13–20]. In the case of a chemically amplified resist, it is necessary to consider not only the behavior of the resist molecule but also the acid diffusion and the catalytic reaction.

In our previous studies [19,20], we introduced the processes of acid diffusion and deprotection, and developed a stochastic simulation of the pattern formation process for a positive-type chemically amplified resist. In those studies, we analyzed the effects of the resist molecular size and post-exposure bake (PEB) time on the pattern shape. In the present study, we introduce the polymer crosslinking reaction instead of deprotection and apply our stochastic simulation technique to the pattern formation process for negative-type chemically amplified resists in EUV lithography. The acid diffusion and crosslinking density distributions in the resist during the PEB process are analyzed. We also evaluate the pattern shapes obtained in various conditions with the simulation.
2. Simulation model

The trajectories of the photoelectrons generated by EUV light exposure in the resist were calculated by a Monte Carlo simulation of the electron scattering. The same simple simulation model as in the previous work was used [20]. Here, we briefly review the model. The depth of photoelectron production was determined by the photon absorption probability in a sample using the ionization cross-section. The scattering angle of the photoelectron was determined by the screened Rutherford cross-section. The energy loss of the photoelectron was calculated as being inversely proportional to the square root of its energy. Secondary electron generation was not included in the present study. The deposited energy distribution in the resist was obtained by the photoelectron trajectory calculation.

In the present study, the wavelength of EUV light was 13.5 nm. The dose distribution was assumed to be a delta function. The composition of the elements and density of the resist for poly(methyl methacrylate) (PMMA) were used to calculate the photoelectron trajectories, as in the previous study. Schematic illustrations of the stochastic models of acid diffusion and polymer crosslinking are shown in Fig. 1. In this study, we modeled an alkali-soluble negative-type resist. An illustration of the initial resist structure is shown in Fig. 1(a). The method of creating the initial structure model was the same as that reported in a previous study [20]. The resist contained monomer and acid generator molecules. All of the molecules were expressed as a unit particle. Each monomer and acid generator was a virtual molecule with a molecular weight of 332. The density of the resist was 1.1 g/cm³. These values were adjusted with those from our previous studies [15-20]. The monomers were randomly placed in space. Their positions were relaxed and optimized by using a molecular mechanics method using a Lennard-Jones potential before the polymer chain formation. The polymer chains were formed by connecting randomly selected monomers in sequence until the degree of polymerization reached the set value, which was 30 in the present study. Quenchers were not expressed as explicit particles, and were assumed to be uniformly distributed in the resist. In the present study, the resist contained 5 weight percent of acid generators and 0.5 weight percent of the quencher.

The effect of EUV light exposure on the chemically amplified resists was introduced by the activation of the acid generator (Fig. 1(b)). Activation of the acid generator in the resist was randomly determined in proportion to the deposited energy distribution calculated by the Monte Carlo simulation of the photoelectron scattering.

The models of acid diffusion in the resist during the PEB process are shown in Fig. 1(c). We assumed that the acid diffusion process was Brownian motion. Acid diffusion was introduced by the random-walk model with a step length according to the Gaussian probability distribution. The initial positions of the acid molecules were the same as those of the activated acid generators. The acid molecules randomly diffused at each step. The standard deviation of the diffusion step length was set to 0.1 nm. The termination of the acid diffusion by the quencher was introduced by the stochastic removal of the acids according to the quencher mass fraction. When the termination of the acid diffusion occurred, the quencher mass fraction at the position was reduced.

At each step of the random walk, when the nearest neighbor monomer was within the critical reaction radius, as shown in Fig. 1(d), the acid reacted with the monomer and crosslinking occurred. The partner monomer to be cross-linked was randomly selected from monomers within another critical reaction radius, as shown in Fig. 1(e).
and (f). Here, the critical radius of the crosslinking was the distance at which the radial distribution function of the initial resist structure was minimized. The critical reaction radius of the acid reaction was set to be half that of the crosslinking. Crosslinks were not always formed, but were formed with the assumed probability, which was 0.1% in the present study.

In the development simulation, the resist polymers with a polymerization degree below the threshold value, which was 150 in the present study, were removed from the resist structure. By removal of the polymer chains, some parts of the resist departed from the part fixed to the substrate. These floating parts of the resist were also removed in the development simulation.

3. Results and discussion

Cross-sectional views of the acid positions and crosslinking densities in the 20-nm-thick resist for a 14-nm-wide line pattern at several PEB step numbers are shown in Figs. 2(a) and (b), respectively. A PEB step number of 1 corresponded to approximately 0.017–1.7 ms, as estimated in our previous studies [19,20]. The acid molecules more widely diffused and the region with high crosslinking density also broadened with increasing PEB step number.

An example of a 14-nm-wide line pattern on a Si substrate obtained by the simulation is shown in Fig. 3. The resist film thickness was 20 nm. Acid diffusion and the crosslinking reaction stopped at PEB step number 1000.

The developed pattern width was approximately 16 nm, which was slightly wider than the design size.

As in the case of the positive resist, the pattern edges were rough and several polymer chains at the edge stuck out of the resist. The line edge roughness (LER) of this pattern was estimated to be approximately 5 nm.

The LER and critical dimension (CD) error were then evaluated for the 14-nm-wide line pattern obtained by the simulation. The resist film thickness was 20 nm. The resist was a virtual one as in our previous studies. Therefore, we expressed the dose as the relative value. We defined the case where all of the acid generators were activated in the maximum deposited energy region of the resist as a relative dose of 1.0. The other doses were defined as the ratio of the number of activated acid generators to that of the relative dose of 1.0.

The LER as a function of the PEB step number for various EUV light doses is shown in Fig. 4. Although statistical fluctuation is large, basic features appear. With increasing PEB step number, the LERs first decreased and then increased. With a larger EUV light dose, the LER reached the minimum at a smaller PEB step number. For each dose, there was an optimum PEB step number to minimize the LER of the pattern. These trends agree

Fig. 2. Cross-sectional views of (a) the acid positions and (b) crosslinking densities for a 14-nm-wide line pattern exposed to EUV light at PEB step numbers of 50, 2000, and 4000.

Fig. 3. Bird’s-eye view of the 14-nm-wide line pattern in the negative-type resist exposed to EUV light.

Fig. 4. Effect of the PEB step number on the LER of the 14-nm-wide line pattern for various doses ($M_n = 9960$).
with those obtained by the simulation in the case of a positive resist.

The CD error as a function of the PEB step number for various EUV light doses is shown in Fig. 5. The CD errors monotonically increased with an increasing PEB step number. The line width of the pattern becomes wider with larger dose. Acid generation became greater when the dose was large. Therefore, the crosslinking reaction proceeded earlier for a larger dose. These trends also agree with those of a positive resist.

Fig. 5. Effect of the PEB step number on the CD error of the 14-nm-wide line pattern for various doses \((M_n = 9960)\).

4. Conclusion

A stochastic simulation of the pattern formation process for negative-type chemically amplified resists in EUV lithography has been performed. The polymer molecule structure, acid diffusion, and polymer crosslinking process were included in the simulation.

The acid diffusion and crosslinking density distributions in the resist during the PEB process were visualized. With increasing PEB step number, the LER first decreases and then increases. The LER reaches the minimum at a smaller PEB step number with a larger dose. The CD error monotonically increases with increasing PEB step number. These trends agree with those obtained by the simulation in the case of a positive resist.

Together with the previous research, we were able to show that our simulations can qualitatively reproduce the fundamental characteristics of pattern formation in a chemically amplified resist. To improve the simulation accuracy by comparison with experiments and to make the simulation quantitatively usable are important future subjects.

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