Multiscale Simulation of the Development Process in Electron Beam Lithography

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Multiscale simulations are performed to study the development process in electron beam lithography. The whole pattern profiles are calculated with the cell removal simulation. The pattern profiles are shown to reflect the electron scattering manner in the resist. The local pattern structures are then studied by molecular dynamics simulation. The residual layer with a lot of voids, the residual polymer chains and concave sidewall reflecting the molecular structures are observed as typical atomic-scale pattern structures. The size of the pattern roughness is observed to be comparable with the molecular size of the resist. The diffusion process of the resist molecules among the developer molecules is also analyzed.

Keywords: Multiscale simulation, Electron beam lithography, Cell removal simulation, Molecular dynamics, Monte Carlo simulation

1. Introduction

Electron beam lithography (EBL) is a well-established method for nanopatterning. A flexible and high resolution patterning is easily achieved with EBL. However, the electron scattering phenomena makes it difficult to realize well-controlled patterning using EBL. Techniques to optimize the patterning conditions would be indispensable.

Numerical simulations have been widely used to evaluate and predict the pattern profiles in EBL [1-8]. Monte Carlo simulation of electron scattering is a typical tool for the electron exposure process. The development simulations such as cell removal simulation are used to predict the developed pattern profiles. However, when the pattern size becomes less than several tens of nanometers, the behavior of the polymer molecules in the resist determines the pattern formation process. Conventional simulations that do not consider the resist molecular structure fail to predict the pattern profiles at such a scale.

Molecular dynamics (MD) studies have become increasingly important in such atomic-scale pattern analysis [9-12]. However, MD simulations require long calculation times. It is difficult to calculate the large pattern profiles with an MD simulation. Selecting the simulation type according to the required scale is important. In the present work, we performed multiscale analyses of the development process in EBL. Whole pattern profiles at a relatively large scale and local pattern structures at an atomic scale were simultaneously analyzed with the use of both cell removal and MD simulations.

2. Simulation model

The sample in the simulations was a polymethylmethacrylate (PMMA) resist on a silicon substrate. The absorbed energy distributions in the electron exposed resist were calculated by a Monte Carlo simulation of the electron scattering. The effects of electron exposure were introduced using the energy distributions in the all scale simulations. In the present Monte Carlo simulation, the screened Rutherford cross section was used for the elastic scattering. The energy loss was calculated by the continuous slowing-down approximation using a modified Bethe equation. The secondary electron generation was not included in the present simulation. The beam edge blur of the electron beam was assumed to be zero.

The development process of the relatively large patterns was calculated by the cell removal...
model. In this model, the resist pattern was divided into small cells and the cells were removed from the resist surface according to the solubility rate of each cell. In this work, we calculated the solubility rate of each cell from the absorbed energy using the equation given in Ref. 3.

The local pattern structures were calculated by the MD simulation. The model used in the MD simulation was the same as that described in our previous work [9-12]. The PMMA film was divided into several thin layers. The effect of electron exposure was introduced by chain scission of the PMMA polymer molecules. The rate of chain scission in the resist was set to be proportional to the absorbed energy distribution of each layer. The breaking positions in the polymer chain were randomly selected. The chain scission and structural relaxation processes were alternately repeated in the exposure simulation.

The development process in the MD simulation was modeled by removing small segments of the polymer molecule from the resist structure. The resist was developed from the surface to the bottom layer. The molecule removal and structural relaxation processes were also alternately repeated in the development simulation. After development of the surface layer was complete, the second layer was developed in the same manner. This procedure was repeated until the bottom layer was developed.

The force field reported by Okada et al. [13] was used for the PMMA resist. The Lennard–Jones potential was used between the resist polymer and substrate. The width and depth of the unit structure of the PMMA resist were 10 and 4 nm, respectively. A periodic boundary condition was applied in the horizontal direction. The molecular weight ($M_w$) of the initial PMMA polymer was 5000. The temperature was kept constant at 300 K. The time step in the MD simulation was 1 fs.

Finally, the early stage of the development process was calculated considering the diffusion of PMMA molecules into isopropyl alcohol (IPA) developer molecules. The electron-exposed PMMA resist was contacted with the IPA molecules. The interactions of the PMMA and IPA molecules were calculated with the MD simulation. The force field for a hydroxyl group in IPA molecules was not given in the original work by Okada et al. [13], so we used the force field for oxygen instead.

3. Results and discussion

3.1. Absorbed energy distribution

All the development simulations in the present study were performed based on the absorbed energy distribution calculated by Monte Carlo simulation of electron scattering. Figure 1 shows examples of the calculated absorbed energy distributions in the PMMA resist on the Si substrate used in the present study. The film thickness was 40 nm. A 20-nm-wide line pattern was exposed by electrons at an acceleration voltage of 5 kV. Because of the low acceleration voltage, the distribution at the bottom of the resist film broadened widely.

![Fig. 1. Absorbed energy distributions at top and bottom of the 40-nm-thick PMMA resist on a Si substrate. A 20-nm-wide line pattern is exposed by electrons at an acceleration voltage of 5 kV.](image1)

3.2. Pattern profile

First, we calculated the whole pattern profiles using the cell removal model. Figure 2 shows the development process of a 20-nm-wide line pattern calculated by the cell removal model. The thickness of the resist film was 40 nm. The acceleration voltage and electron dose were 5 kV and 100 μC/cm², respectively. The developer was a 1:1 solution of MIBK and IPA. Because of the substantial forward scattering of electrons in the resist, the pattern width broadens with increasing resist depth. The edge roughness of the pattern arises from the fluctuation of the absorbed energy owing to the stochastic effects of electron scattering.

![Fig. 2. Development process of 20-nm-wide line pattern exposed at 5 kV calculated by the cell removal model. T = 0.1 sec.](image2)
3.3. Local pattern structure

Atomic-scale structures of the resist pattern can be calculated by the MD simulation. The development process obtained by the cell removal simulation is shown in Fig. 3. The electron exposure and development conditions were the same as those used for Fig. 2. The one side pattern profiles at later development stages are indicated. The local structures indicated by symbols A to D were simultaneously calculated by the MD simulation using the same absorbed energy distributions.

Figure 4 shows the MD simulation results. The snapshots of one side edge of the line pattern are shown. Figure 4(a) shows the structures of the pattern edge and residual layer indicated by A in Fig. 3. The thickness of the residual layer was 2 nm. As shown in the top view, this residual layer possessed many voids and the layer was not a uniform film. Some parts of the PMMA molecules were removed and the structures formed by the residual molecular chains were clearly observed.

Figure 4(b) shows the structures of the bottom edge of the pattern indicated by B in Fig. 3. At this stage of the development, the pattern width on the substrate became a little narrower in the cell removal simulation. In the MD simulation, the residual polymer chains were observed on the substrate. The residual polymer chains hanging in the air were also observed. The length of the protruding polymer chain was approximately 2 nm from the present result. This size was close to the PMMA polymer size estimated in the following section for a $M_w$ of 5000.

Figure 4(c) shows the structures of the bottom edge of the pattern indicated by C in Fig. 3. At this stage of development, the pattern width broadened with an increase of the resist depth. In the MD simulation, the pattern had a concave sidewall because of the forward scattering of electrons in the resist. The concave sidewall structure arose from the fluctuation of the absorbed energy arising from the stochastic effects of electron scattering as mentioned in the previous section. While the cell removal simulation showed the relatively smooth side wall, the MD simulation showed a complicated structure reflecting the molecular structure of the resist.

Figure 4(d) shows the structures of the top edge of the pattern indicated by D in Fig. 3. The top edge of the pattern exhibited a much smoother sidewall than the bottom edge. This is because the effects of the forward scattering of electrons were smaller at the top of the resist as shown in Fig. 1. Hence, the polymer molecular structure did not reflect the pattern shape at the top as well as at the bottom.

3.4. Early stages of the development process

Finally, we introduced the interaction between the PMMA and IPA molecules to analyze the diffusion process of the resist molecules among the developer molecules. MD simulation of the interaction of short PMMA chains with common developer components have already been reported [14]. Because the simulation of the whole development process requires a large computational time, we only simulated the early stages of the development process in the present work.
Snapshots of the interface between the PMMA resist and IPA developer during the development process, obtained by the MD simulation, are shown in Fig. 5. Some PMMA molecules were gradually removed from the resist surface and diffused among the developer molecules. The diffusion length of the IPA molecules in the PMMA resist at this stage was approximately 1 nm.

The lateral distribution of the developed PMMA molecules from the resist is shown in Fig. 7. A 2-nm-wide line pattern was exposed at 5 kV. The development time was 1 ps. The resist molecules were removed only from the center 3-nm-wide region. Distribution of the removed molecules corresponded to the width of the exposed region.

3.5. Resist molecular size

The molecular size of the polymer is an important value for the discussion of the roughness structures of the pattern. Therefore, we estimated the molecular size of the polymer chain as follows. First, we calculated the average volume of each polymer chain by dividing the original resist volume by the number of constituent polymer chains. We assumed the shape of the polymer to be a sphere, and the diameter of polymer was calculated from the average polymer volume. The estimated diameters of the PMMA molecules are shown in Fig. 8. The size of PMMA molecules with a Mw of 5000 is approximately 2.5 nm. The size of the pattern roughness in Fig. 4 became comparable with the molecular size of the resist.
4. Conclusions
Multiscale analyses of the development process in EBL were performed. The whole pattern profiles were calculated with the cell removal simulation. The pattern shape reflected the electron scattering manner in the resist. The edge roughness of the pattern arose from the fluctuation of the absorbed energy owing to the stochastic effects of electron scattering. The local structures of the resist pattern were studied by the MD simulation. The residual layer possessing voids, the residual polymer chains on the substrate and concave sidewall reflecting molecular structures were observed as typical atomic-scale pattern structures. By introducing the interaction between PMMA molecules and the IPA molecules, the diffusion process of the resist molecules among the developer molecules was also analyzed. The diffusion length of the IPA molecules among the PMMA resist in the present simulation was approximately 1 nm. It is shown that the size of the pattern roughness became comparable to the molecular size of the resist.

The present MD simulations were performed based on a simple model. The simulation accuracy should be further improved, as the atomic-scale structures in the resist pattern are complicated. Further studies with the improved simulation model are required to understand the development process in nanopatterning with an electron beam.

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