Inhomogeneity of PAGs in Resist Film studied by Molecular Dynamics Simulations

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Extreme ultraviolet (EUV) resist materials continue to gain attention as one of the most critical components for EUV lithography. An ideal EUV resists must simultaneously improve the resolution, line-edge roughness (LER), and sensitivity (RLS). In a resist film the inhomogeneous structures in the nanometer region tend to have significant direct influence on the resolution and LER, and indirect influence on the sensitivity. Therefore in this study, we have investigated the inhomogeneity of photoacid generators (PAGs) in a hybrid resist for EUV lithography using molecular dynamics simulations. The simulation results indicate the inhomogeneous positions and motions of the PAG cations and anions in the hybrid resist film. The distance between the PAG cation and anion does not play an important role in influencing the positions and motions of PAG. The correlation between the appearance frequency and the distance between the PAG cation and anion was very weak.

Keyword: inhomogeneity, PAG, resist, molecular dynamics

1. Introduction

Extreme ultraviolet (EUV) lithography is an advanced semiconductor manufacturing technique that offers great promise for manufacturing devices of a half-pitch 20 nm node and below. An ideal EUV resist material is expected to simultaneously meet the requirements of resolution, line-edge roughness (LER), and sensitivity (RLS), the trade-off of which restricts the resist performance.

Inhomogeneity in the nanometer regions of additives such as Photoacid generators (PAGs) and quenchers directly influences the resolution and LER of resist patterns. Therefore, the surface morphology of such additives is often studied by atomic force microscopy to understand the self-organization of ionic groups of PAG unit was suggested [1]. Resist sensitivity maybe influenced by the inhomogeneity of the additives, thereby affecting reaction efficiency such as in acid diffusion and deprotection of protected functional groups.

To this end, several studies have analyzed the effect of thin film structure on resist performance. For example, a resist polymer film was studied by time-resolved total-internal-reflection spectroscopy, which revealed the surface segregation of additives. Furthermore, the study indicated differences in the chemical properties and energy-transfer kinetics between the surface and the bulk region [2]. Recently depth profiles of resist components were measured by time-of-flight secondary-ion mass spectrometry, in combination with gas cluster ion beam milling [3]. This essentially determines the depth profile on the order of nanometers. However, the measured data are averaged in a horizontal plane. In reality, it is difficult to measure nanometer-sized structures directly....
in the plane.

Another method to study the inhomogeneity in a resist film is a molecular dynamics simulation. Molecular dynamics is a computer simulation of physical movements of atoms and molecules, where the trajectory of motion is determined by numerically solving Newton’s equations of motion under the given force fields. Although a previous attempt has been made to apply molecular dynamics for analyzing a resist film [4], in reality, the actual resist polymer is too large to be simulated using the computer hardware available at that time. Now, the recent advancements in workstations enable the simulation of real resist systems including polymers with weight-average molecular weight of 10,000. Accordingly, in our previous study, we performed molecular dynamics simulation to analyze inhomogeneity of PAG in terms of positions and motions in a resist system [5]. The study demonstrated the inhomogeneity of PAGs in a resist system. However the results were simulated from single configuration. Hence we could not arrive at a comprehensive understanding without the dependence of the initial configuration.

Therefore, in the present study, we have performed several simulations different configurations, to gain deeper insights on the inhomogeneity of PAGs in a resist system improve the simulation accuracy.

2. Simulation

2.1. Simulated resist system

As a model EUV resist, a hybrid resist consisting of a random hybrid polymer with methacrylate monomer and phenol monomer, triphenylsulfonium nonaflate (TPS-Nf) was investigated as shown in Fig. 1.

2.2. Simulation system and procedure

The simulation was performed on a Dell Precision T7600 workstation with a Xenon processor ES-2687W (8 cores, 3.10 GHz, 20 MB, 8.0 GT/s) and 192 GB memory. The molecular dynamics code LAMMPS was utilized on the Materials and Processes Simulations (MAPS®) platform developed by SCIENOMICS SARL and was conducted on parallel processing of the Linux workstation.

Figure 1. Molecular structures of the hybrid resist model

Amorphous resist models with two chains of the hybrid polymers and seven PAG molecules were built in a simulation box using the MAPS®. The resist model in the amorphous cell was simulated under three-dimensional periodic boundary conditions, to simulate the bulk interactions of the resist film.

TEAM force field was used on the MAPS® for the molecular dynamics simulations.

The initial geometrical structures of the resist model and the cell parameters were optimized by minimizing the energy of the system using the steepest descent and conjugated gradient methods. Furthermore, geometrical relaxation of the system was conducted by monitoring the bond energies by molecular dynamics calculations within the NVT ensemble for 100 ps and density variations within the NPT ensemble for 500 ps at 300 K and 1 atm. After confirming the geometrical relaxation, the molecular dynamics calculations were performed within the NPT ensemble for 5 ns at 300 K and 1 atm.

Time development of film and molecular properties, such as density, bonding energy and geometries, and dynamic trajectories were analyzed on the MAPS® using the time development of the molecular coordinates simulated by the molecular dynamics. Further analysis was conducted by home-made programs.

3. Results and Discussions

3.1. Simulation accuracy

Before studying the inhomogeneity of PAGs in the resist film, the accuracy of the molecular dynamics simulation was validated by comparing the measured density of the resist film with the corresponding simulation results.
Figure 2. Snap shots of (a) hybrid resist system packed into an amorphous cell, (b) chains of hybrid polymers extending into the neighboring cells.

The simulation of the hybrid polymer under the above-mentioned normal condition indicated a density of 0.96 g/cm$^3$. Meanwhile, the density of the same polymer film was experimentally measured by grazing-incidence X-ray diffraction, which indicated a value of 1.08 g/cm$^3$. The simulated value is ca. 11% smaller than the measurement value. The volume accuracy was assumed to be approximately 10% and the one-dimensional accuracy of length was approximately 4%.

3.2. Inhomogeneity of PAGs in a resist

Figure 2 shows the optimized structure of an amorphous basic cell of a hybrid resist, wherein the basic cell is indicated in gray dashed lines. The cell is a cube with a dimension of 3.36 nm on each side. Figure 2(a) shows the resist packed into the amorphous cell. As is shown in Fig. 2(b), two chains of hybrid polymers extended out from the basic cell to the neighboring cells of which frames are no invisible here. Additionally, some PAGs are scattered out into the regions of neighboring replica cells. Figure 2(b) indicates the inhomogeneous distribution of PAGs in the hybrid resist.

Figure 3(a) shows the snapshot of PAGs and TPS-Nf in the base cell, wherein the other polymers are hidden to facilitate visualization of PAGs. Figures 3(b) and (c) show the ellipsoids that indicate the trajectory spaces of the PAG cations and anions obtained from the molecular dynamics simulations of NPT ensembles under the condition of 300 K and 1 atm. The coordinates of a gravity center were calculated; the changes in the rotational or directional motions of PAG cations are not considered here.

Trajectory domains show characteristic shapes, varying from a sphere to a flat ellipsoid. The shape of the trajectory domain typically reflects the molecular environment surrounded by the neighboring molecules of polymers and PAGs. Furthermore, the PAG cations show the inhomogeneity of their motions in addition to their positions.

Table 1 shows the relative domain sizes of the trajectory of PAG cations and anions, where the domain sizes are normalized to the size of the PAG cation, C1. Here it is to be noted that there is no relation between the cation and anion numbers. The correlation between the PAG cations and anions will be discussed in the forthcoming section.

As evidence from Table 1, PAG cation #4 and anion #3 have the largest domain size of trajectory. According to the detailed analysis of polymer configurations the larger domain sizes of trajectories for the cation #4 and anion #3 could be attributed to the larger free volumes [4].
The abovementioned analysis is based on the motion of the center of gravity of PAGs. Atomic trajectories of PAG anion #1 are analyzed and shown in Fig. 4. The right part consists of a central sulfur atom and three surrounding oxygen atoms, which are respectively recognized as isolated domains. On the other hand, the left part consists of three terminal fluorine atoms, which cannot be recognized as isolated atoms but as a mixed state. This implies that the strong interaction between sulfur and oxygen atoms makes them localize at their positions, but the weak interactions of fluorine atoms make their delocalization easier. Therefore, the chemical properties of PAG anions significantly influence the position and motions of PAG anions, and further determine the inhomogeneity of PAG anions.

These inhomogeneities, in turn, may influence resist properties such as resolution, and LER.

### Table 1. Relative sizes of trajectory domains of PAG cations in a hybrid resist.

| Cation and Anion # | C1 | C2 | C3 | C4 | C5 | C6 | C7 | A1 | A2 | A3 | A4 | A5 | A6 |
|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Relative size     | 1.0| 1.9| 2.7| 5.8| 0.9| 0.4| 0.7| 0.9| 1.1| 13.6| 1.0| 1.7| 0.4|
calculated during every time-step of the molecular dynamics simulations. The correlation between the cations and anions of PAGs was then studied from the histogram of distances between them. There are seven PAGs in the hybrid resist systems, and hence $7 \times 7 = 49$ correlations should be considered as a possible pair of a cation and an anion of PAG. Figure 5 shows the typical method adopted to determine the pair of PAG cation and anion. All histograms were calculated, and the pair with the highest frequency or shortest distance was selected as the most possible pair of cations and anions. For instance, the pair of cation #3 and anion #2 was selected in Fig. 5(a) because it shows the largest frequency and shortest distance of trajectories. Sometimes a single cation interacts with two anions, for instance the interaction among cation #3, anion #1 and anion #6 shown in Fig. 5(a). In such cases, two pairs of cation #3 and anion #1 and cation #3 and anion #6 were selected.

![Figure 5](image)

Figure 5. Typical histograms of distances between the cation and anion of PAGs in a hybrid resist.

Furthermore we performed molecular dynamics simulations of different initial amorphous cell structures using the same procedure mentioned above. The correlation of selected cations and anions is shown in Fig. 6.

![Figure 6](image)

Figure 6. Dependence of frequency on the distance between the cation and anion of PAG in a hybrid resist.

The correlation is weak, although it shows negative correlation with the correlation coefficient of -0.29. The distance between the cation and anion of PAG does not seem to play an important role in influencing the positions and motions of PAG. This tendency agrees well with the histogram profiles show broad distribution with short distances [4].

4. Conclusions

We have investigated the inhomogeneity of PAGs in a hybrid resist for EUV lithography using molecular dynamics simulations. Analysis of the locations and motions of PAGs in a hybrid resist showed an inhomogeneous profile in the nanometer regions. This inhomogeneity is considered to influence resist properties such as resolution and line-edge roughness (LER).

The molecular structures and chemical structures of PAGs produce the inhomogeneity, in addition to the ionic interaction. Furthermore, the free volume generated in resist matrix also makes a significant contribution to the motions of PAGs, where the distance between the PAG cation and anion does not play an important role in influencing the positions and motions of PAG.

The atomistic information obtained in this study should be beneficial for controlling the homogeneity in nanometer regions of resist films and for breaking the RLS tradeoff.
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