Microelectronic Engineering xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Molecular simulation of pattern formation in electron beam lithography

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ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Electron beam lithography
Molecular dynamics
PMMA
Line edge roughness

ABSTRACT

We performed molecular simulation to investigate the pattern formation in electron beam lithography. We introduced the effect of electron exposure by the chain scission of the polymer molecules. In the development process, the small segments of polymer molecules are removed from the resist structure. Our present simulation reveals the typical structure of atomic scale line edge roughness, i.e., the prominences of a molecular chain superimposed on an undulating molecular network. It also indicates that electron scattering in the resist is more dominant for determining the line edge roughness than the molecular behavior for PMMA resist even in atomic scale lithography.

1. Introduction

In the recent progress of nanodevices, required feature size in pattern formation has become smaller than ever. Among many pattern formation methods, electron beam lithography is one of the leading candidates as a tool for single-nano-scale patterning from a long time ago [1,2].

In electron beam lithography, numerical simulations such as Monte Carlo simulation of electron scattering are powerful tools for evaluating pattern profiles and correcting proximity effects [3–8]. However, with a decrease in pattern size, the behaviors of the polymer molecule in the resist become crucial to understand the pattern formation process. Conventional simulations for electron beam lithography do not introduce the resist's molecular structure. Recently, discrete or stochastic resist model is used in the simulation to raise the precision of the evaluation of the line edge and line width roughness for optical and electron beam lithography [9–12].

Molecular dynamics (MD) simulation is one of the powerful tools and takes on a growing importance for the analysis in such an atomic-scale region. Several MD studies are performed to analyze the pattern formation in Nanoimprint lithography [13–15]. However, few are reported for electron beam lithography. In the present work, we performed MD simulation of pattern formation in electron beam lithography. We modeled both the electron exposure and development process and analyzed the features of atomic scale line edge roughness.

2. Simulation model

Fig. 1 shows a schematic diagram of the present simulation. The simulation sample is a PMMA resist on a Si substrate. The film thickness of the PMMA resist is 4 nm. The molecular weight (Mw) of the initial PMMA polymer is 5000. A 2-nm-wide line pattern is exposed by the electron beam. There are some resists with improved performance like ZEP. However, the exact chemical reaction of polymer during electron exposure is not modeled in the present simulation. The difference of the resist performance does not clearly appear in the result.

The simulation consists of two basic parts: an electron exposure and a resist development. The effect of electron exposure is introduced by the chain scission of the PMMA polymer in the MD simulation. The breaking positions in the polymer chain are randomly selected. The development process is modeled by removing the small segments of polymer molecules from the resist structure.

The chain scission and structural relaxation processes are alternately repeated in electron exposure simulations. For PMMA polymer, we adopted the force field by Okada et al. [16] in the present MD simulation. It consists of bond stretching, angular bending, torsion potentials, and nonbonding interaction including Lennard-Jones and Coulomb potentials. Lennard-Jones potential is used between the PMMA polymer and the Si substrate. We adopted a periodic boundary condition in the horizontal direction and kept the temperature constant at 300 K. Because the distance between the segments of the chain is too small just after the chain scission, an extremely large repulsive force acts between the segments. Therefore, we relaxed the structure with the intermolecular force diminished by 20 orders of magnitude for the first 100 MD steps after chain scission. We increased the intermolecular force by two orders of magnitude every 50 MD steps, it became equal to

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http://dx.doi.org/10.1016/j.mee.2013.03.119

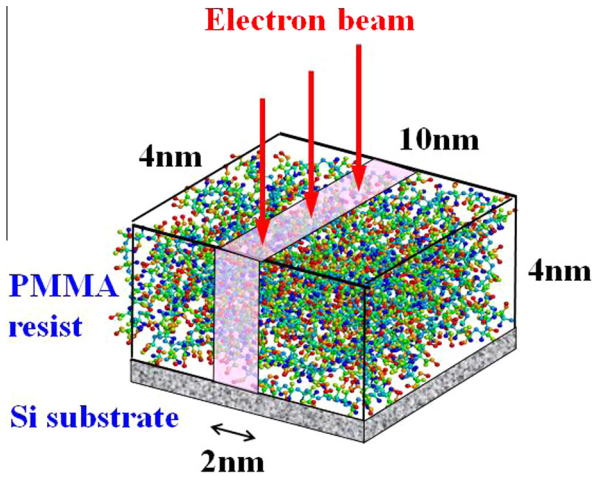

Fig. 1. Schematic diagram of present simulation. Simulation sample is PMMA resist on the Si substrate. A 2-nm-wide line pattern is exposed by the electron beam.

the original value after 500 MD steps. The resist structure is relaxed with the original intermolecular potential for more 500 MD steps. After these relaxation steps, we performed the next chain scission step.

When we performed the patterned exposure in the lithography, the chain scission rate was set proportional to the absorbed energy distribution in the resist calculated by the Monte Carlo simulation of the electron scattering. In the present work, we used the screened Rutherford cross section [17] and the Bethe equation [18] to calculate the elastic scattering and the electron energy loss in the Monte Carlo simulation [3].

In the development simulation, the PMMA molecules were removed from the structure in ascending order. First, the monomers were removed from the resist. Then, the dimmers and trimmers were removed in sequence. Because the resist film is very thin in the present simulation, the depth dependence of the resist solution was not considered. All the molecules in the resist structure were equally treated. After the removal of such small molecular segments, the structure was relaxed for 1000 MD steps at 300 K. The time step in the MD simulation is 1 fs.

Due to the CPU performance of our computing environment, we selected Mw of polymer of 5000, which is much smaller than usually used in electron beam lithography (350 K, 450 K, 996 K). We could increase Mw up to 50 K, which is the practical limit to perform the simulation. However, when Mw becomes 50 K, the volume of the resist also becomes larger and we require the improved model for the resist development process where the depth dependence of the resist solution is introduced. Recently, MD simulation of the development process of PMMA resist was reported [19].

3. Results and discussion

Fig. 2 shows snapshots of the electron exposure process of the PMMA resist in the present simulation. One PMMA molecule is highlighted as a marker molecule, which was segmented as the electron exposure progressed. Each segment of the molecule slightly moves from the original position. At the final chain scission stage, the original shape of the marker molecule is hardly recognizable from the constituent segments.

Fig. 3 shows the absorbed energy distributions in the PMMA resist film on the Si substrate for a 2-nm-wide line pattern at accelerating voltages of 1, 10, and 100 kV calculated by the Monte Carlo simulation of the electron scattering. With the decrease in the accelerating voltage, the absorbed energy in the resist becomes large and broad because of the electron scattering in the sample. The backscattering plays more important role than the forward movement of the electrons due to the small resist thickness.

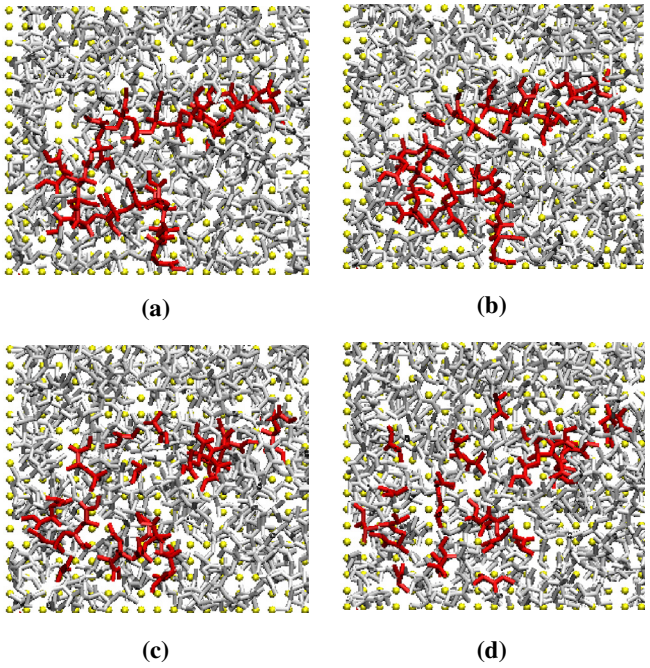

Fig. 2. Snapshots of electron exposure process of PMMA resist in present simulation. One PMMA molecule is highlighted as a marker molecule, which is segmented as the electron exposure progressed. Structures after (a) 0, (b) 1, (c) 3, and (d) 7 ps irradiation are shown. Chain scission rate is 0.34 bonds/(nm^{3}ps).

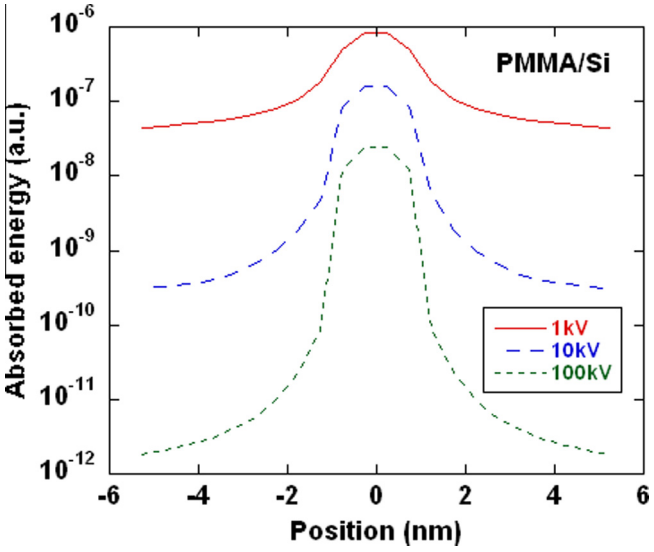

Fig. 3. Absorbed energy distributions in PMMA resist film on Si substrate for 2-nm-wide line pattern at accelerating voltages of 1, 10, and 100 kV.

Fig. 4 shows an example of the development process of the 2-nm-wide line pattern in the PMMA resist obtained by the present simulation. The chain scissions of the PMMA molecules are introduced based on the absorbed energy distribution at 100 kV. The average chain scission rate in the exposed center area and the exposure time are 1.5 bonds/(nm^{3}ps) and 8 ps, respectively. Therefore, the chain scission density is 12 bonds/nm^3 at the center area of the 2-nm-wide line pattern in Fig. 4. By removing the monomers in the development process, the molecular density around the line