Detailed Monte-Carlo simulation of PMMA chain scissions in e-beam lithography

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Abstract. Detailed Monte-Carlo simulation of e-beam events in PMMA/Si system has been carried out. Polymer chains are modeled using random walk algorithm with subsequent assignment of simulated e-beam events to certain monomers. The processes leading to PMMA chain scission are determined to be ionization events on C atoms of PMMA backbone bond due to analysis of resist weight distributions, obtained by gel permeation chromatography.

1. Introduction
The Monte-Carlo is a widespread technique for the study of e-beam interaction with solid in single and multi-layered samples of sub-micron size. In the common approach, the spatial contours developed in the polymer resist film are determined by two separate processes: (1) electron scattering and energy deposition within the film and (2) differential solubility of the electron-irradiated volume with an organic solvent [1]. Resist solubility rate could be determined from resist number average weight after exposure, which is originally determined by the characteristics of inelastic e-beam events leading to resist molecule scissions. Resist average weight is usually calculated using formula [2]

\[ M_f = M_n \left( 1 + \frac{g \varepsilon M_n}{\rho N_A} \right)^{-1}, \]  

(1)

where \( M_n \) and \( M_f \) are resist number average weights before and after exposure, correspondingly, \( \varepsilon \) is absorbed energy density, \( \rho \) is resist density.

The parameter \( g \), determined as number of resist chain scissions per 100 eV of deposited energy, defines the contribution of all inelastic e-beam events in resist to the resist chain scissions. The most widely used \( g \) value is 1.9, but values in range 0.75–4.3 were also obtained [1, 3], which may lead to the inaccuracy of this approach. Besides, energy loss-based model of resist chain scissions and development could be hardly used for modern simulation purposes such as line edge roughness study due to complexity of application one-dimensional solubility rate to three-dimensional structures.

More comprehensive approach for the simulation of e-beam lithography profiles for sub-\( \mu \)m dimensions is based on the diffusion-like model for resist dissolution process [4]. It provides the dependence of resist solubility on local resist chain length, which requires the distribution of resist chain scission events caused by e-beam exposure. Several algorithms for the simulation of resist chain
scission have been already presented [3, 5], but they characterize scission rate using general theoretical assumptions. In our study, resist chain scission rate is for the first time determined directly from experimental resist chain weight distributions. This approach is based on Direct Monte-Carlo simulation of e-beam interaction events in resist and analysis of gel permeation chromatography data.

2. Simulation of e-beam events in resist
In our research, Direct Monte-Carlo algorithm with discrete loss approximation is applied for simulation of 20 keV electron trajectories in poly- methyl methacrylate (PMMA) layer on a silicon wafer (Fig. 1(a)). Dominant processes in energy range of our interest are elastic scattering, excitation, ionization and secondary electron generation [6] (Fig. 1(b)). During the simulation, for an electron in PMMA layer, the type of atom which provides scattering potential is determined first. Then, the cross sections of elastic scattering, excitation and ionization events are calculated and which allows to determine the process type, mean free path and next interaction position. The characteristics of elastic processes are defined by Mott differential cross sections [7], while cross sections and energy loss for inelastic processes are determined using Seltzer’s model of close and distant collisions [8] and Moller’s binary collision cross sections [9]. Secondary electrons originated from ionization events are then tracked using the same scheme.

PMMA chains are modeled using ideal chain model based on random walk simulation with 0.28 pitch and 109° between successive monomers [5] (Fig. 2(a)). PMMA chains are combined in the required volume until needed PMMA density (1.19 g/cm³) is achieved (Fig. 2(b)). Electron events and PMMA monomers are saved in histograms with 2x2x2 nm³ cells. This approach provides relaxed PMMA state and allows us to match each electron interaction event and monomer its position in certain chain.

3. PMMA chain scission simulation
Our study of PMMA chain scission events caused by e-beam exposure is based on the analysis of PMMA weight distributions before and after exposure obtained by gel permeation chromatography (GPC) [10]. We simulate e-beam interaction events in 100x100x500 nm³ PMMA volume with the parameters, corresponding to experimental ones: electron initial energy and dose are 10 keV and 10⁴ C/cm², correspondingly, initial PMMA number average weight is 5.63×10⁵, PMMA layer thickness is 500 nm. Then different PMMA chain scission mechanisms based on general assumption were
considered. PMMA scission events are presumably caused by inelastic e-beam events on carbon atoms in methyl methacrylate (MMA) molecule that form C–C backbone bond in PMMA (Fig. 3), so we investigated the influence on final PMMA weight distribution, caused by various combinations of excitation and ionization processes on several carbon atoms in MMA molecule (Fig. 4). The simulated mass distribution corresponds to the experimental one for the scission model consisted in the scission events due to ionization e-beam events on the equivalent number of carbon atoms in MMA from 2 to 2.5. These parameters refer to room temperature and they could be varied for the simulation of resist chain scissions for the higher exposure temperatures. PMMA chain scission simulation results for the exposure in series of parallel lines are presented in Fig. 5.

The required scission rate could be also achieved for the model considering both excitation ionization events with equivalent carbon atoms number less than 2, or excitation events with equivalent carbon atoms number higher than 3. These models have weaker physical interpretation, but they still result in some freedom in PMMA scission model choice.

Figure 2(a, b). (a) PMMA chain obtained using ideal chain model; (b) combination of PMMA chains for the simulation of PMMA layer (some chains are omitted for visibility).

Figure 3. Methyl methacrylate (MMA) monomer structure, C1 and C2 atoms form C–C backbone bond in PMMA.
Figure 4(a, b, c, d). Comparison of experimental PMMA chain weight distribution before exposure (initial) and after exposure (final) obtained by gel permeation chromatography (label “GPC”) with simulated distributions (label “SIM”) for several possible PMMA chain scission mechanisms.

Figure 5. Simulated PMMA chain scission events distribution for the exposure in series of parallel lines. Initial electron energy is 20 keV, exposure dose is 100 µC/cm², PMMA layer thickness is 100 nm.
4. Conclusion
Simulation algorithm of e-beam interaction events in resist and PMMA chain scission events is presented. It provides the most detailed information on processes in resist during exposure and avoids usage of $g$ value for resist chain scission simulation. The processes leading to PMMA chain scission at are determined from experimental GPC mass distribution for the first time. Scission events are supposed to occur due to ionization events on carbon atoms in MMA molecule with equivalent number from 2 to 2.5. The distribution of PMMA chain scission events in PMMA layer could be used as a starting point for the subsequent simulation of resist development using diffusive resist development model or simulation of temperature effects in resist such as thermal depolymerization or monomer diffusion. However, the deeper insight into polymer chemistry is desirable for the clarification of scission mechanism.

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