

Simulation of roughness in chemically amplified resists using percolation theory

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A simulator for e-beam exposure and development (SELID) is combined with molecular modeling in order to investigate the various side effects of the gelation process in the case of chemically amplified resists (CARs). The procedure is demonstrated in the case of the negative tone epoxy resist but the method is equally applicable for other resist systems (positive and negative tone) and development mechanisms. A conventional resist simulator is not sufficient for the description of characteristics related to the detailed gel structure of the resist film and it needs to be combined with a molecular model. Molecular modeling is a suitable method for the simulation of the microscopic changes occurring during the post-exposure bake and development processes in the case of CARs. Macroscopic feature changes such as free volume size, cluster formation, and surface roughness can be effectively described using percolation theory. In order to construct a molecular model of a complex resist system a 3D square lattice is considered. The lattice size is equal to the mean radius of the spherical volume occupied by a monomer, in our case about 1 nm. The lattice is filled with the polymer chains by a random walk process and the photoacid generator is randomly distributed in the lattice according to its percent content in the actual material. In the case of an actual resist pattern exposure, SELID provides the energy deposition profile after e-beam exposure. The deposited energy stored into each cell of the lattice induces acid generation and subsequent reactions. Reaction progress is simulated using the molecular model. Using the above process it has been possible to reproduce the actual experimental contrast curves and to simulate line edge roughness. © 1999 American Vacuum Society. [S0734-211X(99)11506-3]

I. INTRODUCTION

As lithographic demands for the next decade are focused in the region below 100 nm it will be crucial to investigate the resolution limits and quality of lithography. Roughness in the resist patterns is a significant limiting factor affecting both line size and critical dimension control. The key factors that affect roughness depend upon the exposure tool which is used, e.g., the shot noise for electron and ion beams and upon the resist itself such as the polymer size, the polymer configuration, the thermal processing steps, and the developer selectivity.

The shot noise effect is particularly important in the case of ion beam lithography.¹ Nanoedge roughness in electron beam lithography for dimensions below 20 nm has been experimentally observed and investigated in the case of a few conventional²⁻⁴ and chemically amplified resist (CAR) systems.³ The reaction-diffusion mechanism activated during post-exposure bake (PEB) has a major effect on line roughness. In the case of negative tone CAR SAL601 (Shipley) it has been demonstrated that roughness increases with increasing PEB time.³ In the case of positive tone Apex-E (IBM) it has been argued that roughness depends mainly upon the degree of deprotection.⁵ The same deprotection degree may be obtained either by varying the PEB conditions or by varying the exposure dose.

Edge roughness analysis is also expected to be important for the development of top surface imaging technologies necessary for 193 and 157 nm lithographies.⁶

Atomic force microscopy (AFM) is being used specially for surface roughness measurements. In order to identify surface roughness, two parameters may be used, rms surface deviation and fractal dimension.⁷

Process modeling in small dimensions requires a more detailed account of the microscopic changes of the resist material. A percolation model to account for the developer selectivity in the case of PMMA has been tested.⁸ In this article

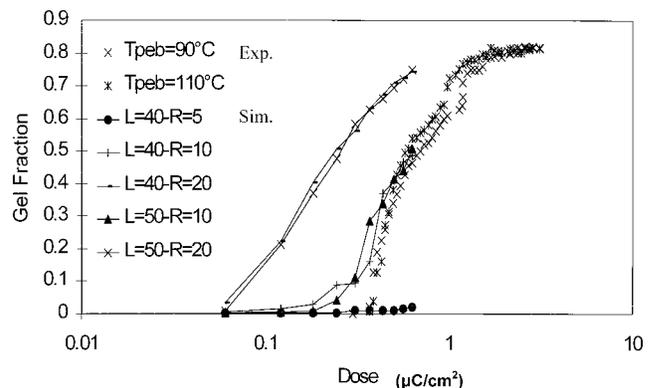


Fig. 1. Comparison of experimental and simulation contrast curve results.

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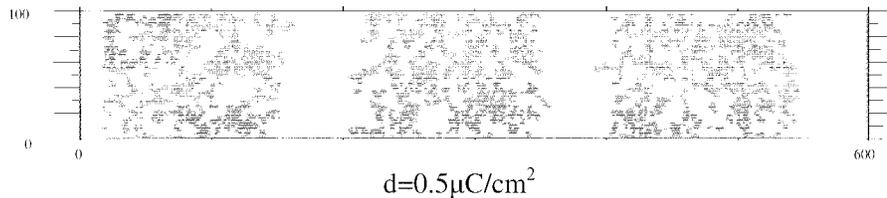


FIG. 2. Crosslink density for a line edge profile.

a molecular model⁹ for CARs will be presented and applied in the case of an epoxy based resist (EPR). This model will be used in combination with exposure models in order to simulate edge roughness.

II. EXPERIMENT

The negative tone chemically amplified resist EPR was selected for this work.¹⁰ This resist has a known composition, therefore it can be modeled precisely. EPR is a two component system consisting of fractionated cresol epoxy novolac polymer chains and hexafluoroantimonate triphenyl-sulphonium salt as the photoacid generator molecules. In the case examined, the concentration of the photoacid generator is 5%. Experiments with EPR were carried out with a Leica EBPG-3 electron-beam vector scan system at 50 keV, 10 MHz, and a beam diameter less than 40 nm. The resist was spun on silicon 4 in. wafers at 4000 rpm for 30 s. The wafers were prebaked at 120 °C for 60 s. Large pads (50 μm×50 μm) were exposed for a dose range of 0.2–8.0 μC/cm² and variable PEB conditions. Film thickness was measured with a Dektak profilometer. Surface roughness in 1 μm² fields was examined with a Digital Nano Scope II, AFM.

III. MOLECULAR MODELING SIMULATION

Two- and three-dimension simulations with lattice constant equal to the monomer radius are considered. In the case of EPR, taking into account the ionic radius, the bond length and the possible molecular conformations, a monomer molecule occupies a spherical volume of 2 nm mean radius.

Polymer chains and initiator's molecules were placed randomly on that lattice under the following restrictions: (a) The chains should be self-avoiding and populate the lattice to the same density as the actual material; (b) the polymerization length was assumed to be a uniform distribution in accordance with experimental data; (c) each lattice site can be occupied by no more than one monomer and one initiator molecule; and (d) the chains are subject to periodic boundary conditions.

The radiation induced effects were simulated through the use of an initiation probability attributed to each of the initiator's molecules. The formation of a cross link is acceptable in the simulation procedure if the cross-linked monomers belong to different chains (no cyclization effects are allowed in accordance with experimental evidence) and their distance is within one lattice constant from an active initiator's molecule.

The effects of chain reaction and acid diffusion occurring during PEB have been taken into account through parameters

describing the diffusion length and the reaction probability at a given site. Developer selectivity is controlled by determining the minimum cluster size interacting with the developer.

Graph theory is used in order to count the final configuration of clusters formed after exposure. Each monomer is represented by a node in a graph and the lines connecting different monomers nodes represent the links between monomers in a chain. In computer language each node is a structure containing information about the position in the lattice and the chain identity. The implementation of the interchain connections is based on the formation of a sparse array using linked lists. Each node in this representation is a head of a list which contains information about the chain and links to its monomers. In order to determine the characteristics of the clusters that are formed during PEB, the cycles in the graph must be evaluated.

The code has been integrated in a convenient graphical environment and the selection of the input parameters allows the use of this code for more general use. Indeed the problem is not necessarily limited to cross-linking systems, no special change is needed for the consideration of systems based on protection/deprotection chemistry. In this case the clusters are interpreted as regions in the material where solubility change has occurred due to exposure.

IV. RESULTS AND DISCUSSION

A. Contrast curve analysis

Experimental results were compared with simulation in the case of EPR containing 5% photoacid generator and two different PEB temperatures 90 and 110 °C. Lattices of size 40³ and 50³ cells were considered. The results are shown in Fig. 1. The actual dose d in the experiment was related to the activation probability P_{init} used in the Monte Carlo procedure through the relation

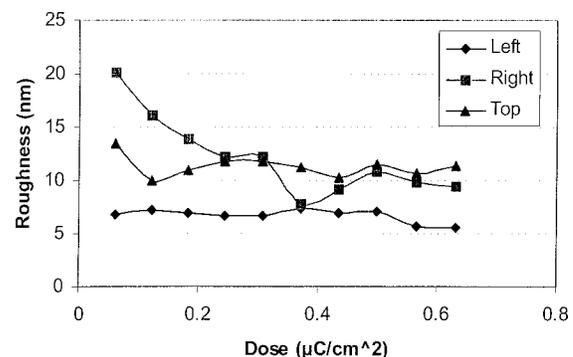


FIG. 3. Line edge roughness vs dose.

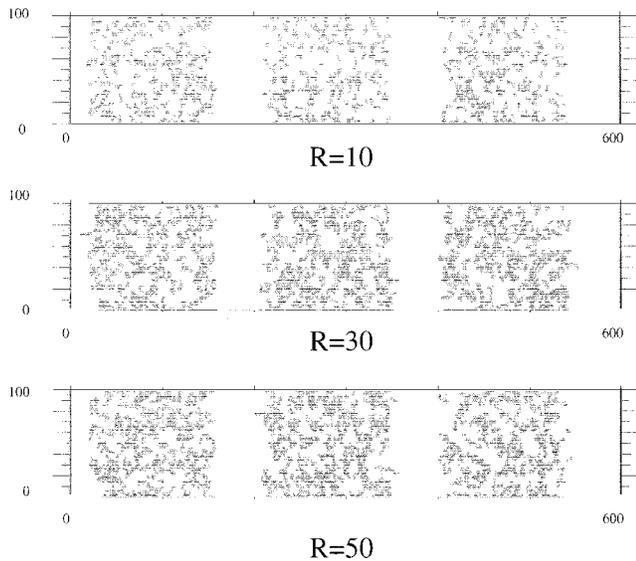


FIG. 4. Simulated line edge for different diffusivities.

$$P_{\text{init}} = 1 - e^{-Kd}, \quad (1)$$

where K is the experimental sensitivity. The tail appearing in the low dose regime is due to the fact that the effect of the developer has not been taken into account in the simulation curves. The action of the developer results in the removal of the small clusters formed in lower doses.

The diffusion range R was tested between the limits of 5 and 20 steps. The simulation curves are very sensitive in respect to a change of the diffusion range parameter R . The best fit with experimental results was obtained for $R=10$ steps which is equivalent to a main diffusion length of ≈ 10 nm and a diffusion coefficient $D=0.83 \times 10^{-6} \mu\text{m}^2/\text{s}$. This value is in good agreement with previous results obtained by other methods.¹¹ Thus, it is demonstrated that a microscopic parameter may be obtained from a simple experimental result such as the contrast curve using a molecular model. The low value of the diffusion length is due to the high sensitivity of EPR and the cage effect. EPR has a very high sensitivity and the cross-linked environment soon inhibits further diffusion of the acid.

B. Line edge roughness

In order to simulate line edge roughness using the same method, it is necessary to start with the evaluation of the energy deposition profile for a line pattern. In the current work the energy deposition profile is obtained through the use of SELID¹² and then it is transformed into a photoinitiator initiation probability profile. The simulated structure is a series of lines/spaces with nominal width of 100 nm, pitch of 200 nm, and resist height of 100 nm. The exposure simulation was carried out for an energy beam of 50 keV, a beam step size of 20 nm, and a point size of 20 nm.

In Fig. 2 the simulated results for a dose of $1 \mu\text{C}/\text{cm}^2$ are shown. In this figure only the cross-linked sites are plotted, the polymer chains have been omitted for clarity. The beam size and the diffusion effect caused the broadening of the

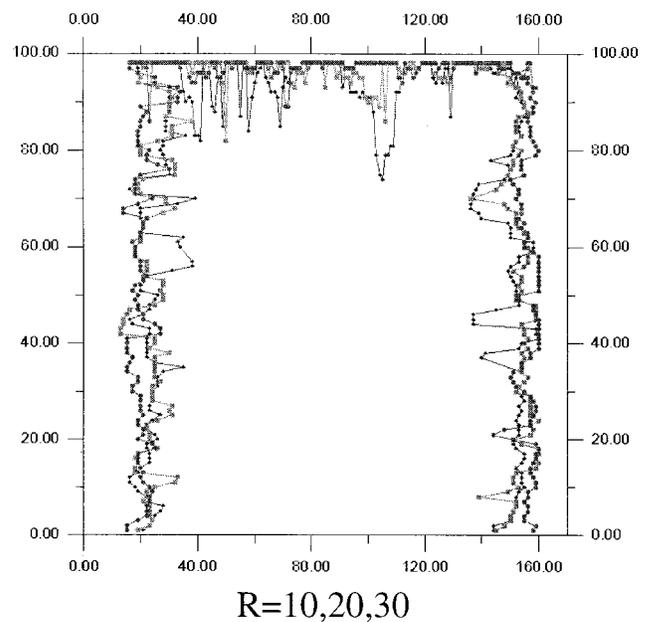


FIG. 5. Variation of edge roughness with the diffusion length.

linewidth to the value of 135 nm. It should be noted that the effect of the developer has not been taken into account in Fig. 2.

In Fig. 3 the surface roughness of the left-hand side line in Fig. 2 is plotted versus dose. It is obvious that the roughness of the right-hand side is much larger due to the proximity effect. Roughness seems to saturate for larger dose values. In Fig. 4 the line edge profiles have been overlapped to demonstrate the diffusion effect. In Fig. 5 the dependence of the line edge roughness upon the number of diffusion steps (i.e., the thermal processing conditions) is demonstrated. The prediction of simulation is that the top surface roughness is generally larger than side roughness. This is shown in Fig. 6.

C. Surface roughness

Surface roughness was separately examined experimentally by AFM measurements. Fields of $1 \mu\text{m} \times 1 \mu\text{m}$ of exposed resist were scanned using the AFM tapping mode and the roughness was measured by software. In Fig. 7 the dependence of surface roughness Z_R upon dose and PEB time

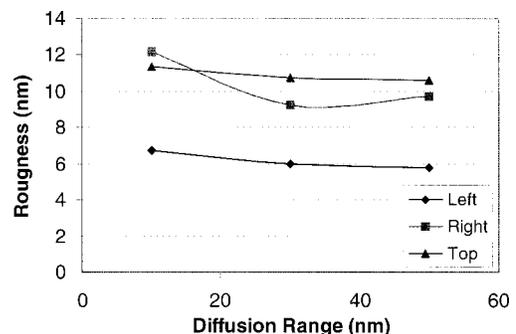


FIG. 6. Roughness vs diffusion range.

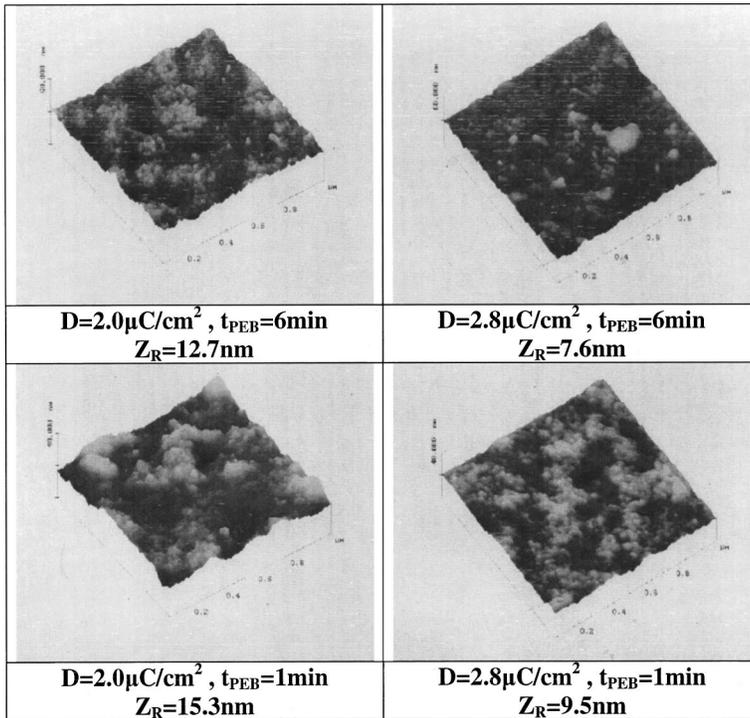


FIG. 7. Experimental surface roughness for different PEB and exposure conditions.

is demonstrated for a PEB temperature of 90 °C. The doses in Fig. 7 correspond to the saturation part of the contrast curve as may be compared with Fig. 2. The minimum roughness is obtained for the higher dose and the longer PEB time. The surface roughness is in the range 5–15 nm in accordance with the simulation results of Fig. 6 for line edge simulations.

V. CONCLUSIONS

It has been demonstrated that a molecular model can sufficiently describe the contrast curve of a CAR. The combination of experimental results with the model is adequate for the estimation of the diffusion length. Results have been proved to be compatible with point beam exposure measurements. Furthermore the molecular model has been combined with exposure simulation in order to obtain results for the line edge roughness. It has been shown that roughness in high resolution patterns is more enhanced on the surface than on the sides.

Experimental surface roughness measurements have proved that roughness decreases with PEB time and increas-

ing dose. The grain size does not increase significantly due to the high sensitivity of this specific resist which blocks the diffusion paths.

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