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Stochastic simulation studies of molecular resists

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Abstract

The influence of resist molecular weight as well as its architecture becomes important in lithographic scales aiming at sub-45 nm resolution. The effects of processing and resist molecular geometry on line-edge roughness (LER) should be well understood in order to meet the ITRS lithographic specifications. In this work, two-dimensional simulations and comparisons of the LER between films of molecular resists and resist films made of oligomers with the same molecular diameter, showed that in all cases molecular resists have lower LER. Explanations of this behavior are proposed based on molecular architecture and the free volume distribution in the resist film. It was also found that the size of free volume regions is less in molecular resist than in the corresponding oligomers.

Keywords: Molecular resists; High resolution lithography; LER

1. Introduction

As resist feature sizes get smaller towards the sub-45 nm nodes, resist thickness become less than 100 nm, which introduces non-bulk behavior on the physicochemical properties of the resist films, due to interfaces and also the decreasing number of polymer chains which comprise the film itself. Therefore, the influence of resist molecular weight as well as its architecture becomes important in these lithographic scales [1–5].

Experiments [6–11] and simulations [3–5], have shown that low molecular weight resist materials could result in low line-edge roughness (LER) which is a critical parameter for the next technology nodes.

Fig. 1 shows the effects of average degree of polymerization (for linear polymer chains) on LER as obtained from stochastic lithography simulations for a conventional type resist and a chemically amplified one [3]. It is seen that low LER levels are accomplished with short polymer chains and low acid diffusion lengths.

Motivated from this behavior, several molecular resists based on anthracene or other polycarbocycle derivatives, newly synthesized by our group, have been tested experimentally and characteristic main resist components are modeled with the stochastic lithography simulator in order to predict their LER behavior. One of the studied molecular resin architectures is shown in Fig. 2a and has code name M21. This molecule is one of a large series of similar polycarbocycles designed and synthesized by the Demokritos group [10], to be used as main components of molecular resists. Similar molecules had been also proposed few years ago as etch resistance additives [11]. Experimentally M21 molecular resist formulation resulted in sub-45 nm resolution under EUV exposure, [unpublished results; to be presented at MNC 2006].

In the current modeling level, only material properties closely related to dissolution are accounted explicitly and not other intermolecular or intramolecular properties, other than the excluded volume constraints. The effects of molecular geometry and size on LER will be investigated. Comparisons of the LER between films of molecular resists

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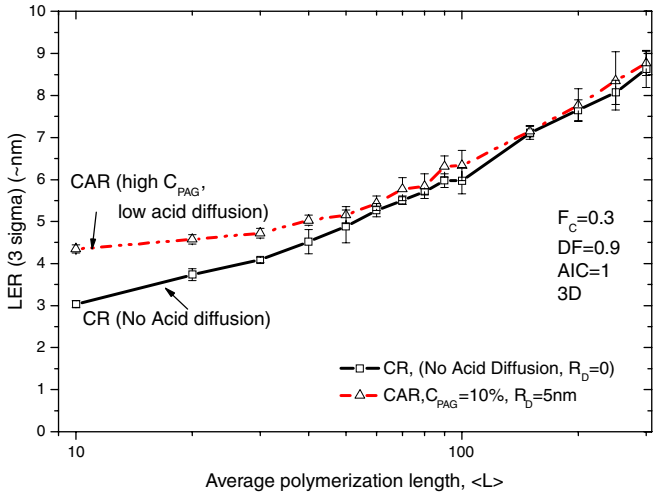

Fig. 1. Effect of average degree of polymerization on LER. One conventional resist (CR) and one chemically amplified (CAR) is shown. In all cases deprotection fraction is 0.9 in the exposure lattice. Critical ionization fraction for dissolution is 0.3. Results are from 3D simulations. RD is acid diffusion range and C_{PAG} is photoacid generator (PAG) concentration. Ideal aerial image contrast condition, AIC = 1.

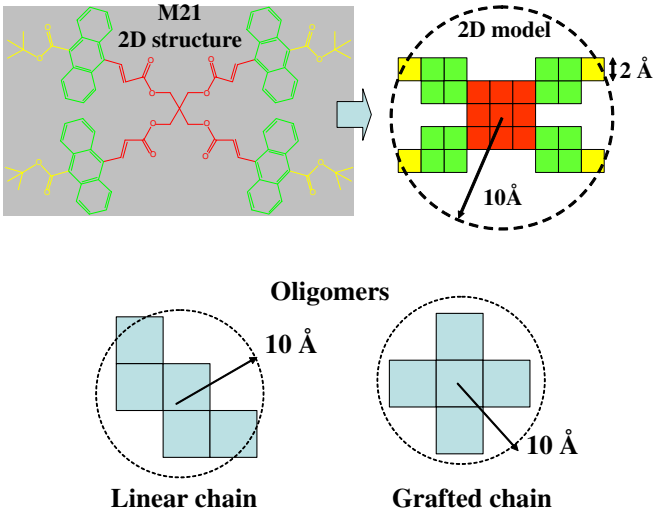

Fig. 2. (a) 2D model of M21. Taking into account the sizes of its descriptive units, the whole molecule has diameter R_g ~1 nm. (b) Oligomers of five monomers per chain and the same diameter of the linear or grafted architecture were also simulated under the same conditions.

and resist films made of oligomers with the same molecular diameter will be presented.

2. Model description

In order to examine the LER behavior under similar lithographic conditions, between the molecular resist architecture and oligomer chains with approximately equal size (in terms of estimated molecular diameter, R_g), the following modeling methodology was followed.

As shown in Fig. 2a, the two-dimensional (2D) structure of M21 is converted in a 2D model taking into account the sizes of its composing molecular units.

The corresponding 2D model of oligomers is also shown in Fig. 2b. In the current work linear and grafted oligomers with diameter equal to the one of M21 molecule resist were considered.

One other area of comparison between the molecular and oligomer resist films, that had to be adjusted, was that of free volume. Free volume in polymeric resist films is assumed to be around 10%. The same value was used for the oligomer resist film in this work.

However, in the case of M21, due to the 2D representation and the limitations in conformations in the lattice (only two orientations are allowed, the one shown in Fig. 2a, and the one rotated by 90°), the corresponding resist films simulations could not result in free volume less than 28%. However, if the free volume size distribution is plotted for the two resist lattices as shown in Fig. 3, it is observed that M21 film's free volume is composed overall from tiny pieces due to its molecular structure. On the other hand, the same picture for the oligomer chains results in greater size of free volume pieces. So this fact is encouraging for comparing these two resist film cases under limited free volume conditions.

The whole process of stochastic lithography simulation has been described in detail in [3–6]. The physics and chemistry of dissolution was performed in terms of the critical ionization model with critical ionization fraction $F_C = 0.2$, which translates to at least one of the five monomers in the oligomer and one of the four ionizable groups in M21, being ionized by the developer in order for the chain or M21 to dissolve and be removed from the lattice.

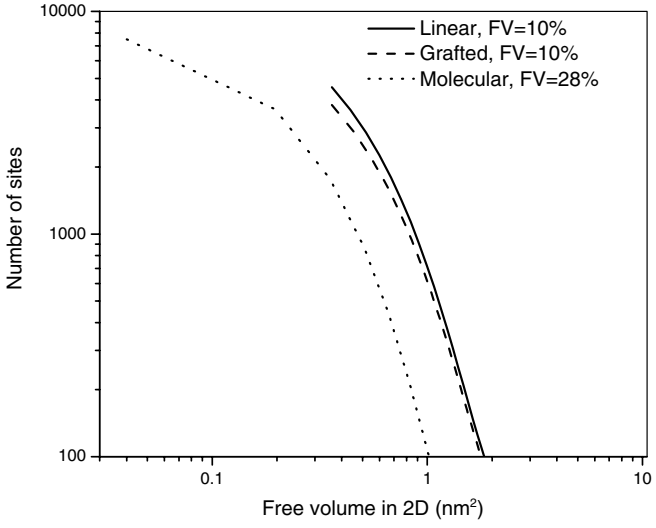

Fig. 3. Distribution of free volume in 2D in molecular and oligomer films. While molecular resist free volume is 28% and the corresponding oligomers have 10%, the area of the molecular resist free volume is distributed into much smaller pieces. M21's 28% free volume size distribution is still under the corresponding curves of oligomer with free volume around 5%.

A top–down snap-shot view of a region of the developed resist film is shown in Fig. 4. Nominal width of the developed space is 45 nm.

3. Results

Several runs were performed and the LER vs. edge length of either M21 or the oligomer chains was averaged. Simulations consider first the case of conventional resist chemistry, i.e. without acid diffusion present and deprotection fraction DF = 1, in the exposure region (i.e. the space to be developed). The second case is that of chemically amplified resist chemistry with photoacid generator concentration $C_{PAG} = 10\%$ and acid diffusion range suitably chosen in order to give DF = 0.8 in the exposed region.

The results from all such simulations are shown in Fig. 5. It is clear that acid diffusion is responsible for a high increase in LER in such low size molecules. Molecular resist shows improved LER compared with the oligomer based, especially when acid diffusion is present. This can be explained also by the size of the free volume distribution. In the molecular resist the size of free volume areas is small and this prevents long-range acid diffusion and therefore the distortion of edge linearity. Simulations with oligomers and free volume even below 10% (e.g. even down to 1–2%) have shown that although LER decreases, it is still larger than the corresponding LER of the 28% free volumer molecular resist.

Linear and grafted oligomers show approximately the same LER behavior. This is expected and has to do with their small size. However, previous simulation work had shown that in higher degrees of polymerization (over 20 monomers per chain), grafted chains have less LER than the linear under conventional chemistry conditions, but they result in more LER than the linear under chemical amplification conditions [5].

Fig. 6 shows the CD distribution of the developed structure in the resist film, shown in Fig. 4, both for the oligomer chains and for the molecular resist. A Gaussian profile is observed as is expected from experimental findings of image analysis of top–down edges obtained from scanning electron microscopy images of resist lines/spaces. It is also clear that when no acid diffusion is the case, all distributions are close, but when acid diffusion is present, the oligomer chains suffer a severe degradation both in LER and average CD, while the molecular resist distribution is less affected.

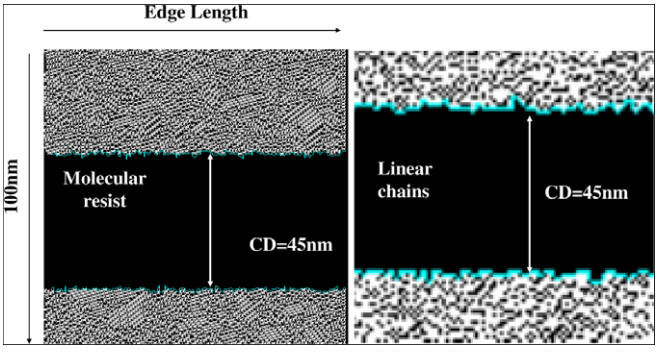

Fig. 4. Top–down snap-shot of the 2D simulation lattice after dissolution. Nominal space dimension was 45 nm in both cases. LER is determined vs. edge length for the left and right edge of the space and the two values are averaged. Five runs per case where averaged. Black spots correspond to free volume sites.

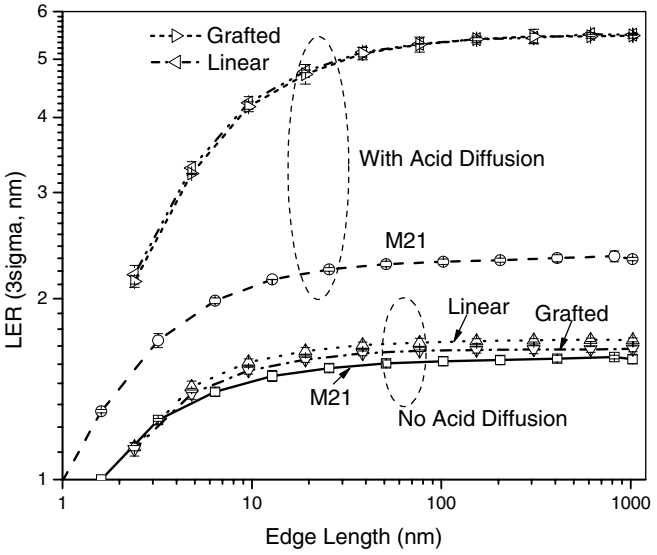

Fig. 5. LER vs. edge length for M21 and linear chains for conventional chemistry (no acid diffusion) and chemically amplified one (with acid diffusion).

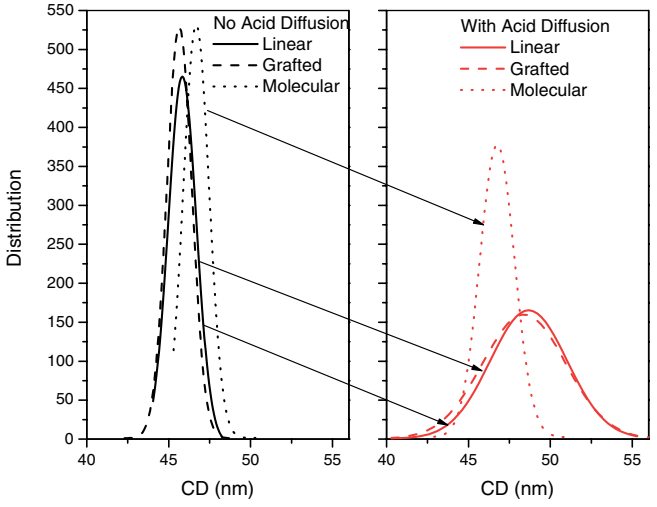

Fig. 6. Width distributions of the structures shown in Fig. 4, for linear oligomer and molecular resist film without and with acid diffusion. Molecular resist's distribution is less affected by acid diffusion.

4. Conclusions

Two-dimensional simulations with a stochastic lithography simulator aimed at comparisons of the LER between films of a molecular resist model and resist films made of oligomers with the same molecular size or radius of gyration. The results showed that molecular resists have much lower LER. This was true both under no acid diffusion and with acid diffusion. This behavior is attributed, apart from the small and more compact size of the molecular resist, also to the distribution of the free volume in the films made from such materials, because, in their case, free volume size distribution is shifted in very small areas and mainly inter-molecularly, prohibiting easy acid diffusion.

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