

Stochastic simulation studies of molecular resists

D. Drygiannakis^a, G.P. Patsis^{a,*}, I. Raptis^a, D. Niakoula^a, V. Vidali^b,
E. Couladouros^b, P. Argitis^a, E. Gogolides^a

^a Institute of Microelectronics (IMEL), NCSR “Demokritos”, 15310 Aghia Paraskevi, Attiki 15310, Greece

^b Institute of Physical-Chemistry (IPC), NCSR “Demokritos”, 15310 Aghia Paraskevi, Attiki 15310, Greece

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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.

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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 polycarbycycle 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 polycarbycycles 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

* Corresponding author.

E-mail address: gpatsis@imel.demokritos.gr (G.P. Patsis).

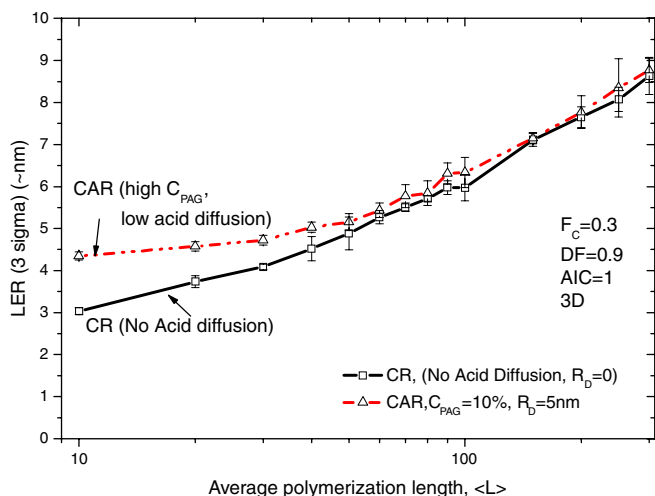


Fig. 1. Effect of average degree of polymerization on LER. One conventional resist (CR) and one chemically amplified (CAR) is shown. In all cases deprotection fraction is 0.9 in the exposure lattice. Critical ionization fraction for dissolution is 0.3. Results are from 3D simulations. RD is acid diffusion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

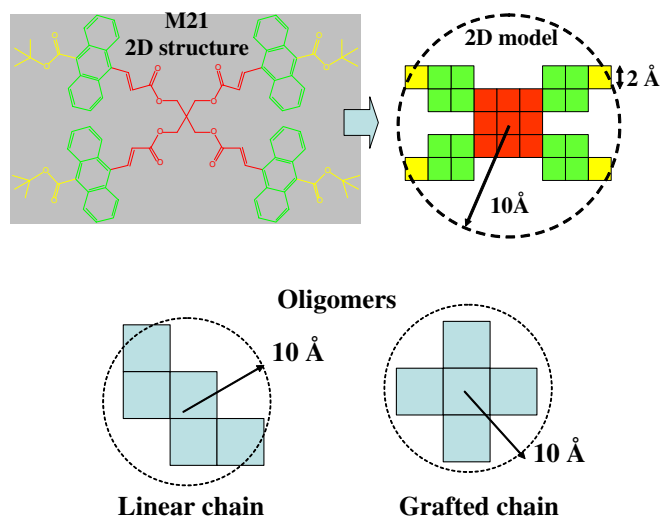


Fig. 2. (a) 2D model of M21. Taking into account the sizes of its descriptive units, the whole molecule has diameter $R_g \sim 1$ nm. (b) Oligomers of five monomers per chain and the same diameter of the linear or grafted architecture were also simulated under the same conditions.

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.

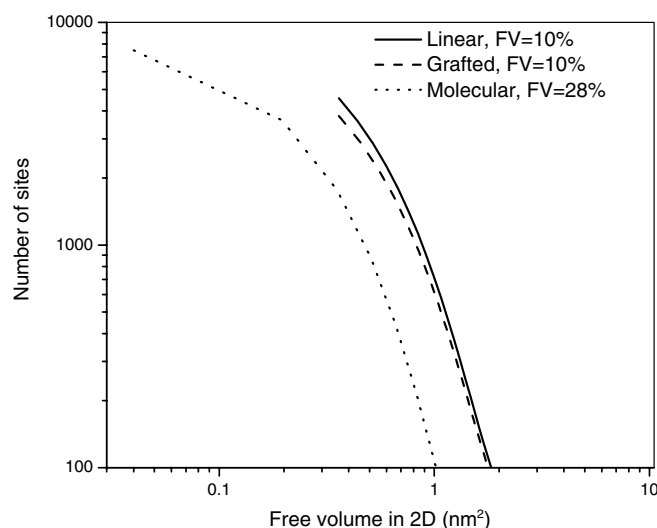


Fig. 3. Distribution of free volume in 2D in molecular and oligomer films. While molecular resist free volume is 28% and the corresponding oligomers have 10%, the area of the molecular resist free volume is distributed into much smaller pieces. M21's 28% free volume size distribution is still under the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

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