Pursuit of Lower Critical Dimensional Uniformity in EUV Resists

James Thackeray, James Cameron, Vipul Jain, Paul LaBeaume, Suzanne Coley, Owendi Ongayi, Mike Wagner, Aaron Rachford and John Biafore*

The Dow Chemical Company, Dow Electronic Materials
455 Forest Street Marlboro, MA 01752
*KLA-Tencor Division
8843 N. Capital of Texas Highway, Austin, TX 78759

This paper describes Dow’s efforts toward improved Critical Dimensional Uniformity (CDU) in EUV resists. Many non-material related factors contribute to good CDU, such as aerial image quality. We have focused on fundamental resist properties like intrinsic dissolution contrast and we have found that the photo-decomposable base (PDB) concept can be successfully employed. With the use of a PDB, we can reduce CDU variation at lower exposure energies. For sensitivity, we have focused on more efficient EUV photon capture through increased EUV absorption, as well as more highly efficient PAGs for greater acid generating efficiency. The formulation concepts will be confirmed using Prolith stochastic resist modeling. For the 26nm hp contact holes, we observe excellent overall process window with over 280nm depth of focus for a 10% exposure latitude Process window. The 1σ CDU is 1.1 nm. We also obtain 20nm hp contact resolution in one of our new EUV resists.

Keywords: Photoresist, chemical amplification, polymer-bound PAG, acid diffusion, photo-decomposable base.

1. Introduction

EUV resists designed for low diffusion and high sensitivity have dominated the highest performance materials for EUV lithography. In this paper, we focus primarily on contact hole performance. Specifically, this paper will focus on critical dimension uniformity (CDU), a better measure of the roughness of contact holes. Aerial image quality at the wafer plane and intrinsic resist contrast are the key factors in good CDU performance. Smith et al. have pointed out that CDU can be a direct consequence of the photon shot noise in EUV lithography [1]. So it has been shown that CDU increases nonlinearly as the sensitivity is decreased. With the onerous sensitivity targets required with the current low power sources, it is very difficult to overcome the photon shot noise effect[2]. One goal is to make an EUV CH resist that minimizes CDU as low as possible. With higher power sources, the shot noise problem would be reduced, because you could produce the same number of wafers at a higher dose [3].

Nonetheless, the resist community has continued to come up with performance advantages for EUV resists. The first innovation was to develop high contrast, low diffusion chemically amplified resists that could meet the onerous sensitivity targets whilst still achieving high resolution [4]. These materials include the polymer-bound PAG (PBP) concept [5]. With polymer-bound PAG, we have steadily lowered acid diffusion length to the 5nm range allowing sub-20 nm lithographic performance. We have also introduced novel PAGs which reduce the impact of out-of-band (OOB) radiation flare in these resists [6]. This paper will introduce some newer concepts which can also enhance EUV resist performance.

The first concept, introduced in KrF resists in the 1990s, is the concept of photodecomposable
base (PDB) [7]. Funato and Pawlowski first used PDBs in KrF chemically-amplified resists as latent image stabilizers. In the continuum, the conversion of PDBs to neutral fragments is modeled as:

\[
\frac{\partial q}{\partial t} = -C_q I q
\]  

(1)

\[
q(t) = q_0 e^{-C_q t}
\]  

(2)

where \( q \) is the concentration of PDB, \( I \) is the intensity of light and \( C_q \) is the exposure rate constant of photo-decomposition. The rate of base decomposition, \( C_q \), by the direct photolytic mechanism (ArF, KrF) can be expressed

\[
C_q = \phi_{photodecomp} \frac{\varepsilon_q \ln 10 \lambda}{N_A h c}
\]  

(3)

where \( \phi_{photodecomp} \) is the quantum efficiency of the decomposition process and \( \varepsilon_q \) is the PDB molar absorbance coefficient. When irradiated in EUV, PDB conversion is assumed to behave similarly to PAG conversion. PDBs are designed to act as acid quenchers in unexposed areas, yet decompose into neutral fragments in exposed areas as shown in Figure 1.

![Figure 1](image1.png)

Figure 1. 1D continuum models of generated acid, conventional quencher and photo-decomposable quencher in model resist, post-exposure.

The reduction of the acid neutralization rate in the exposed area, produced by PDB exposure, increases the extent of deprotection and the chemical contrast of the resist at the mask edge (see Figure 2) leading to enhanced sensitivity and critical dimension uniformity (CDU). We will show that we are able to design specific PDBs that work well in EUV.

![Figure 2](image2.png)

Figure 2. Stochastic simulation of blocked polymer concentration after PEB for 27 nm hp lines.

The second concept we utilized is the development of more EUV efficient PAGs. Given the limited photons available in EUV, it is important that we harvest the maximum number of photons, and secondary electrons, to give the highest acid yield possible [8]. It is known that the PAGs in EUV work by an ionization mechanism, as shown in Figure 3 [9]. By virtue of this mechanism, it becomes clear that PAGs which are more easily reduced would be potentially more sensitive to EUV exposure and the subsequent secondary electron cascade. The mechanism also points out that the resist matrix plays a key role in secondary electron generation after the absorption of the EUV photon. Accordingly, we have strategically and systematically designed, and developed novel PAGs capable of being more easily, irreversibly reduced.

![Figure 3](image3.png)

Figure 3. Mechanism of EUV acid generation.

This paper will discuss the resist performance enhancements for a PBP-based system utilizing more EUV efficient PAGs as well as photodecomposable bases.
2. Experimental

2.1 Resist formulations

Various polymers were formulated for positive tone EUV lithographic evaluation at AMET Albany, LBNL BMET, IMEC NXE3100 or NXE3300 exposure tools. The resist materials were all based on PBP lithographic polymers.

2.2 Resist Processing

Resist formulations were spun cast to a resist thickness of 60nm on 200mm Si wafers coated with 25nm of underlayer. For high resolution tests, the resists were coated to 35nm film thickness. The films were post-apply baked at 110°C or 130°C for 90 seconds and exposed to EUV light source (NA=0.30; Quad; 0.22Å 0.68Å Mask) using both an open frame array in order to obtain a contrast curve and through a binary mask containing dark field line/space patterns or contact hole patterns. The exposed wafers were postexposure baked at 100 °C for 60 seconds and then developed with 0.26N tetramethylammonium hydroxide solution for 30 seconds. Annular exposure conditions were done typically, with dipole exposure done for ultimate resolution. At LBNL, a pseudo PSM was used for high resolution testing.

2.3 Determination of PAG Reduction Potentials

Reduction potentials reported here in are cathodic peak potentials of irreversible voltammograms obtained in cyclic voltammetric (CV) experiments. All CVs were collected in a one compartment cell with a Pt working electrode (BASI, MF-2013) Pt wire auxiliary electrode (BASI, MW-4130), and Ag/AgCl reference electrode (BASI, MF-2052). Hence, all values are relative to the Ag/AgCl redox couple. A 0.1 M solution of tetrabutyl ammonium perchlorate (>99%, Sigma-Aldrich) dissolved into acetonitrile (HPLC grade, Sigma-Aldrich) was used as the electrolyte solution for all electrochemical experiments. Caution! Perchlorate salts are potentially explosive and should be handled with care.

Prior to each experiment, the Pt working electrode was thoroughly cleaned and polished with a polishing alumina slurry, rinsed with distilled water and dried. The electrolyte solution was checked for contamination of electrochemically active species by conducting a cyclic voltammetry experiment prior to addition of the PAG analyte, sweeping across an electrochemical potential window of 0 to -2.0 V vs. Ag/AgCl. Upon confirming a clean electrolyte solution, the selected PAG was dissolved into the electrolyte solution (~10^-3 M concentration for PAG) followed by N2 purging of the resulting solution for 5-10 minutes prior to electrochemical measurement. Three successive cyclic voltammograms were collected on each PAG for determination of cathodic peak potentials. The scan rate for potential sweep was 0.1 V/s with a step size of 0.01 V. No iR-compensation was applied.

3. Results

3.1 Diffusion length improvement

Many authors have pointed out the importance of lowering acid diffusion length in order to improve ultimate resolution and exposure latitude [4,6]. In KrF, typical KrF acid diffusion length is 20-50 nm. In ArF, typical ArF acid diffusion length is 10-20nm. Finally for EUV resists, the acid diffusion length is further reduced to 5-10nm. We have benchmarked one of our PBP-based resists which also has standard quencher. Figure 4 illustrates the large process window for 26nm hp CH on an NXE3100 exposure tool, with DOF 280nm over a 10% EL range. By fitting the CD data using Prolith 4.1.4 SRM, we obtain an acid diffusion length for this resist of 4.9nm. The resist model is very accurate for predicting measured CDU, as shown in Figure 5. The experimental CDU measured was extremely low at 1.1nm, 1sigma. This excellent performance illustrates that standard quencher-based resists are quite good. Finally, Figure 6 illustrates the excellent overall performance for 24nm hp CHs exposed on an ASM-L NXE3300 EUV scanner. LCDU of 2.8nm 3sigma was obtained for the CH resist developed at DOW.

Figure 4. 26nm hp contact hole process window on NXE3100 [Courtesy IMEC]
Figure 5. The experimental CH CD data vs ProLth 4.1.4 SRM modeled data exhibits a very good fit for both 56nm and 52nm pitch. On the bottom of the figure, we show strong model prediction of the LCDU experimentally measured.

Figure 6. 24nm hp CH performance on the NXE 3300 B EUV scanner.

3.2 PDB concept
The PDB concept has been exploited for dark field applications in ArF lithography [10]. The addition of PDB to the resist formulation improves the photoacid gradient at the image line edge leading to higher contrast resist material. With the combination of low acid diffusion coupled with higher contrast, large improvement in resolution, LWR and contact hole CDU can be seen. Figure 7 shows the LWR for a standard quencher formulation vs. a PDB-containing formulation at 28 nm hp. The LWR improves by 1.0 nm (~20%) in the PDB-containing resist. Figure 8 shows the excellent resolution capability of a PDB-containing resist with a good process window achieved for 20nm hp contacts exposed at the LBNL BMET exposure tool. Although CDU and sensitivity need improvement the outstanding resolution is impressive.

Figure 7. Standard quencher formulation (A) vs Photodecomposable Base (B)

Figure 8. 20nm hp contact hole process window at LBNL using PDB-based formulation. Dose to size 60mj at LBNL; predicted Dose to size of 30mj on NXE3100.

3.3 Efficient PAG concept
As EUV lithography matures, the design of customized materials specifically for the EUV wavelength must be employed. In our earlier work we described photoacid generators [PAG] with reduced sensitivity to out-of-band radiation. Added to that work, is the necessity for PAGs that are more responsive to the EUV wavelength of 13.4 nm. It is our objective to maximize the PAG sensitivity to EUV wavelength whilst minimizing the PAG sensitivity to the longer wavelength OOB flare in the scanner. Our attention has been focused on improving the ionization pathway of the PAG to increase the yield of EUV acids generated in the PAG. The ionization pathway for the PAG means that electron transfer is the
mechanism of acid generation in EUV exposure. If PAGs are designed to be more sensitive to electrons then acid yield for the PAG should be improved. Thermodynamically, the reduction potential of the PAG may be a strong lever for reducing sensitivity while maintaining good CDU. Figure 9 illustrates a direct correlation between the reduction potential of the PAG and the EUV sensitivity. Compared to TPS (Reduction Potential -1.6 V vs Ag/Ag+) [11], these new PAGs are more easily reduced by over 1.0 volt.

Figure 9. Reduction potential of PAGs in acetonitrile vs. EUV photospeed

4. Discussion

We have successfully shown that small molecule design can enhance EUV resist performance. We have demonstrated that the PDB concept can be successfully applied to EUV resists leading to improved CDU and faster photospeed with better CDU performance as our earlier resist with standard Q. The PDB concept can also be applied to opening smaller contact holes down to 20nm hp. We have also shown the capability of more efficient PAGs that maximize EUV sensitivity. In this way, we can move the RLS triangle to maintaining LWR and CDU while reducing sizing energy. Figure 10 shows the asymptotic plot of Local CDU vs. Sensitivity based on NXE3100 data and also modeled formulations. This plot shows that the PDB concept and the efficient PAG concept can both be utilized to decrease sizing dose while maintaining CDU. Based on NXE data, the brick wall on sensitivity is 22mj. Whether this brick wall is due mainly to photon shot noise or further resist improvements needed will be the subject of our future work. The CDU floor of 0.9 nm (1σ) is a function of the aerial image, the quality of the EUV mask, photon shot noise, and the quality of the resist.

Figure 10. CDU vs resist sensitivity trade off curve.

Acknowledgments

The authors would like to thank IMEC, LBNL, Sematech and ASM-L for lithographic support.

References


All four of these factors will be optimized over the coming years. However, photon shot noise can only be improved by stronger power sources, allowing more relaxed resist sensitivity targets.


