Design Considerations for EUV Resist Materials

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This paper discusses the relative merits of traditional PAG blend resist approach vs a novel Polymer-bound PAG resist approach. In looking at EUV exposures it is shown that the Polymer-bound PAG approach possesses advantages in LWR and Resolution over a PAG blend resist approach. The Polymer-bound PAG approach achieves 25nm half pitch resolution with an LWR of 3.8nm and a photospeed of 10mJ. The Polymeric PAG approach also possesses higher exposure latitude vs a PAG blend resist. Although still maturing, it is felt that polymer-bound PAG-based resists will become quite useful at the 22nm node and below.

Keyword EUV, PAG, polymer bound PAG, 22nm node

1. Introduction:

There are many unique resist design considerations when building EUV resist materials. The ionizing radiation of EUV photons at 13.4nm provides a high energy photon (~92eV) which quickly generates secondary electrons which is captured by the photoacid generator.\textsuperscript{1,2} One must consider absorption and density of the resist material to EUV energies.\textsuperscript{3,4,5} Also, one must consider the PAG selection and the activation energy of the protecting group. In this paper we will primarily focus on a comparison of the traditional PAG blend resist approach vs. the innovative polymer-bound PAG resist approach, as outlined in Scheme I.\textsuperscript{7,8} Whether or not the resist is a traditional PAG blend or a polymer-bound PAG, the following properties are important considerations in EUV resist design.

1.1 A. EUV Photoacid Generation Mechanism

One must consider the efficiency at which the resist material generates secondary electrons. Tagawa et al have shown that the acid generation mechanism during EUV exposure is caused by ionization of polymer not excitation of the PAG as in longer wavelengths.\textsuperscript{1,2} This difference in acid generation mechanism could lead to improved acid generation efficiency leading

\begin{align*}
\text{Scheme I. a.) Traditional PAG blend Resist vs. b.) Covalently attached acid anion- based resist}
\end{align*}

to higher photospeed. Tagawa proposes that the predominant mechanism, as shown in Figure 1, begins with the ionization of the
base polymer, which then undergoes deprotonation ("ionization channel") vs the direct excitation of the PAG seen with longer wavelength exposures ("excitation channel"). The acid generation mechanism change for EUV lithography means that the base polymer will play an important role in acid generation. This has been confirmed in subsequent work showing the utility of 4-hydroxy styrene units in a lithographic polymer. Also, Yamamoto et al have shown that ethyl adamantyl leaving groups improve acid generation efficiency. This area of research is critical to improve the photospeed of EUV resist systems. As shown in Scheme I, we have designed our resist polymers to contain an EUV sensitization monomer (ESM1) which facilitates the facile generation of secondary electrons.

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\begin{align*}
\text{Step (1) Base Polymer} + \text{hv (13.4nm)} & \rightarrow \text{Base Polymer}^+ + e^- \\
\text{Step (2) Base Polymer}^+ & \rightarrow \text{deprotonation (H')} \\
\text{Step (3) e'} + \text{AG} & \rightarrow \text{Fragment + Counter anion} \\
\text{Step (4) H'} + \text{Counter anion} & \rightarrow \text{Acid}
\end{align*}
\]

Figure 1. EUV acid generation mechanism as described by Tagawa and Kozawa. Note direct excitation of base polymer is the primary means of EUV energy absorption. Acid is generated in secondary low energy electron reactions.\(^1\)\(^2\)

1.2 EUV Absorption and Density

Other workers have published the relative absorption of the elements in EUV exposure.\(^3\)\(^4\)\(^5\) [see Figure 2] Due to the thin layers (<50nm) expected for 22nm lithography, it is not expected that EUV absorption will be an issue with respect to resist sidewall angle. Resist B-values at 5/micron or less should not seriously affect resist side wall angles. Our attention rather has been to focus on selectively adding absorptive atoms to the resist to increase the EUV absorption cross-section. In this work, we have primarily used aromatic monomers as well as fluorinated monomers to increase the EUV absorption cross-section, thereby increasing the secondary electron yield upon EUV exposure. Through such optimization we expect to increase the EUV quantum yield for acid generation. Higher density of the resist would also increase the EUV quantum yield.

![Figure 2. EUV Absorption cross-section for first- and second- row elements of the periodic table. [after Ober Ref. 4(c)]](image)

1.3 Acid Diffusion Length and PAG Distribution

Acid diffusion length has been strongly correlated with resolution, mask error enhancement factor, and resist exposure latitude.\(^6\) In this paper, we will discuss the use of a traditional blended photoacid generator versus a covalently attached photoacid generator. In this manner, we can compare a resist with a photoacid that can diffuse freely in the resist matrix, versus a covalently attached acid to the resist polymer which has limited diffusion capability [Scheme I].

1.4 Activation Energy of Deprotection

The resist chemist has the opportunity to design resist polymers with varying acid deprotection rates as a function of PEB temperature.\(^9\) There are a host of acid-cleavable leaving groups available to the resist chemist. We have actively
investigated acetal (low activation), and tertiary carbon esters (low, medium and high activation). Another important consideration is whether or not the deprotected group remains in the resist film during resist processing. If the groups are too volatile they will outgas in the exposure equipment and cause possible optic damage. If the groups are not volatile, one must worry about back reactions and plasticization of the resist film. For this study, we used methyl-2-adamantyl-methacrylate (MadMA) as the protecting group.

2. Experimental

2.1 Resist materials

All new materials were formulated in 80/20 blend of ethyl lactate (EL) and propylene glycol monomethyl ether acetate (PGMEA). We formulated resists with EUV sensitive base polymer. The resists were called traditional PAG blend Resist A vs Polymer-bound PAG Resist B.

2.2 Phase AFM measurements

The Dimension 5000 was used for all AFM data collection. Tapping Mode AFM and Phase Imaging were employed to obtain images of the films. Using a scan area of 5x5 microns, 512 scan lines, aspect ratio of 1:1 and scan rate of 0.5Hz, roughness statistics were derived from the surfaces of the entire captured area. Using height and phase data the value reported is the root-mean-square (RMS). Two channels were enabled during image capture to optimize data comparison. Channel 1 collected Tapping Mode height data. Channel 2 collected Phase data. Tapping Mode topography and Phase images were viewed side-by-side in real time. Tip-surface interaction was closely monitored using feedback electronics. Between wafer samples the tool was calibrated and the cantilever was tuned.

In our report two positions on each of the partially exposed 10x10 matrix areas proved optimal. These two areas surveyed showed height and phase topography indicative of the RMS. Both positions on the wafer were compared for roughness and phase. The features in Figure 3 are represented as electronic Tapping Mode height images and display topography corresponded to the surface.

2.3 Resist Processing

The formulated resists were spin coated onto 25 nm AR107 BARC coated silicon wafer. The latter undercoat was used for the sole purpose of promoting adhesion. The resist film thickness was 50 nm. All resists were soft baked at 130 °C for 60 seconds. The post exposure bake (PEB) was varied from 110 °C to 130 °C. The resists were initially screened for clearing dose (E0), thinning and contrast curves using ArF exposure at Rohm and Hass FAB facilities in Marlborough. Some of the EUV exposures were conducted at Lawrence Berkeley National Laboratory (LBNL) on MET ALS EUV tool. The Berkeley MET EUV tool possesses an NA of 0.30 and was operated on Y monopole. Some of the work was also performed at the Paul Scherrer Institute in Geneva, Switzerland. The PSI tool is an EUV interferometer with potential to reach sub-25nm half-pitch resolution.

3. Results

3.1 Phase AFM

We have undertaken to study the difference between attached polymer-bound PAG vs the traditional PAG blend approach used in chemically amplified resist design. The most common formulation method involves the use of a lithographic polymer with a protecting group on a hidden developer-soluble group, along with a typical photoacid generator such as triphenylsulfonium triflate, with the addition of a conventional quencher, which is usually an amine or ammonium salt. We also have purposefully copolymerized the photoacid anion on the lithographic polymer thereby incorporating a polymeric PAG concept in EUV resist as shown in Scheme I. There are advantages and disadvantages to the two approaches outlined. For traditional PAG blend approach, the advantage of formulation simplicity is an overwhelming advantage.
Also, there are many designer PAGs readily available to test and optimize with a lithographic polymer. The disadvantage of the traditional PAG blend approach is the fact that the PAG can phase separate from the lithographic polymer during the coating process, contributing to the possibility of intrinsic line width roughness (LWR) and the creation of PAG aggregation. The other disadvantage is that a non-polymeric acid can diffuse easily in the resist film during PEB leading to potential acid diffusion and image blur. In fact workers at IBM have claimed that image blur due to acid diffusion makes the use of Chemically amplified resist problematic for patterns below 30nm.\textsuperscript{10}

Copolymerization of the PAG with the lithographic polymer is an elegant means to overcome PAG aggregation and acid diffusion. Of course the copolymerization process requires the synthesis of PAG monomers which by now is becoming more readily available. The resist photospeed control and PAG concentration control is now more difficult to do, but in practice can be controlled by making high and low PAG-bound polymers. The quencher used to control photospeed is also still available for product control.

We have undertaken to study the optimization of polymer-bound PAGs in a number of lithographic materials. We have found that polymer-bound PAG works well in methacrylate-type polymers and can be used with high and low activation leaving groups. Figure 3 shows the Phase AFM for Traditional Blend PAG Resist A vs Polymer-bound PAG Resist B. We immediately see that the RMS roughness for a partially exposed resist film is far worse for the conventional Blend PAG Resist A. The RMS roughness for the conventional Blend PAG resist A is nearly 20nm! For the polymer-bound PAG resist B the RMS roughness is down to 1.1nm.

3.2 Lithographic Results

The true question of the utility of a polymer-bound PAG approach is whether or not it provides a substantial advantage over PAG blend formulations in terms of Resolution, Sensitivity, LWR tradeoffs. To study this, we did lithographic evaluation of blend PAG formulation vs polymer-bound PAG formulations. For this work, we used equivalent molar quantity of PAGs in both systems. For the blend PAG formulation we used TPS’Cy6’ as the PAG of choice in a high activation methacrylate polymer. For the polymer-bound PAG, we used the same comonomers as in the blend resist but we attached the acid anion to the polymer chain through copolymerization.

The lithographic results for 30 nm and 25 nm half-pitch is shown in figure 4 and 5 respectively. In comparing the Blend formulation to the Polymer-bound PAG formulation it is evident that both resists are capable of resolving 30 nm lines and spaces. However, the Blend PAG resist is 40% faster...
than the Polymer-bound PAG resist, but the polymer-bound PAG resist is 50% better in LWR! It is interpreted that the Blend PAG formulation has evidence of PAG aggregation leading to uneven deprotection of polymer in the exposed line edge.

PAG Blend Resist A:
30nm 1/2pitch: LWR = 6.0nm
Dose to size: 6mJ

Polymeric PAG Resist B:
30nm 1/2pitch: LWR = 3.1nm
Dose-to-size: 10mJ

Figure 4. Resolution comparison of PAG Blend Resist A vs Polymeric PAG Resist B.

At 25nm half pitch, the Blend PAG resist is no longer able to resolve the features and apparent bridging is evident. The polymer-bound PAG is now showing better resolution than the Blend PAG resist. The question remains as to how low in resolution the polymeric PAG resist can go? Figure 6 shows resolved 20nm halfpitch lines with some evidence of pattern collapse and swelling.

PAG Blend Resist A:
25nm 1/2pitch: LWR = 8.0nm

Polymeric PAG Resist B:
25nm 1/2pitch: LWR = 3.8nm

Figure 5. Resolution comparison of PAG Blend Resist A vs Polymeric PAG Resist B.

Polymeric PAG Resist B:
20nm ½ pitch
Figure 6. Ultimate Resolution with Polymeric PAG Resist B.
4. Summary

The important advantages to the polymer process that the results above show that covalent attachment of a PAG on a lithographic polymer can show big advantage in terms of LWR and resolution of an EUV photoresist material. The polymer-bound PAG approach improves the overall PAG homogeneity in the resist film as well as reduces the potential acid diffusion length. There other PAG approach: we also see improved exposure latitude and high intrinsic PAG solubility can be built into the lithographic polymer. We expect that through judicious use of PAG monomer precursors that many types of lithographic polymers can be designed and optimized for EUV and potentially 193nm resist use.

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