Study of advanced 193nm resists: Material properties and lithographic performance

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193nm lithography requires new resist formulations to achieve transparency requirements for single layer resist. In this paper, the properties of two 193nm chemically amplified resists, one based on the methacrylate chemistry and the other on the alicyclic platform have been investigated as a function of process conditions. Experiments have been focused on the different behaviors of these two resist platforms during the Soft Bake (recompaction rates) and the Post Exposure Bake (prominant mechanisms in the exposed resist areas: reaction or diffusion controlled phenomena).

The lithographic performance of the methacrylate based resist has been extensively evaluated for various bake processes, and additional formulation effects have been pointed out.

Keywords: 193nm single layer resists, chemical amplification, methacrylate based resist, alicyclic based resist, diffusion contrast.

1. Introduction:

In the quest to achieve greater packing densities for the next device generations (below 0.15 μm), 193nm lithography is being introduced as the new extension of optical lithography, after i-line (365 nm) and DUV (248 nm).

This change in the exposure wavelength has also led to the need of specially designed photosensitive materials, as novolak and PHS based resists used at 365 and 248 nm are too opaque at 193nm (strong absorption of their aromatic ring).

Consequently, in order to fulfill the transparency requirement for a 193nm single layer resist, the first formulations have been methacrylate based [1]. However, the very low etch resistance of all these acrylate resists avoid their use in an industrial process [2]. Improved formulations have then been developed with higher dry etch resistance through the incorporation of pendant alicyclic groups, highly transparent at 193nm, such as IsoBornyl or Adamantyl groups, in methacrylate based resists [3-4].

A different chemical platform for 193 nm single layer resists has been introduced by Pfr Willson’s group, based on various alicyclic polymers. These new resists show promising etch resistance properties equivalent to those of 248 nm t-BOC resists [5], and lithographic performance, comparable to 193 nm methacrylate based resists for the best formulations [6].

Presently, different experimental 193 nm resists are available, belonging to both methacrylate based or alicyclic based platforms, with very similar lithographic performance. As 193nm lithography starts to be introduced in the industry, the choice of a reliable resist will become an important issue. Consequently, specific properties, advantages, limitations and differences in the behavior of these two chemistries, have to be investigated.

In this paper, two 193nm chemically amplified resists belonging to two different platforms were studied. The resists investigated were the
methacrylate based Sumitomo PAR101-A4 and the alicyclic based JSR ArF AT-43. As bakes are important process steps, the thermal properties of both resists were determined (glass transition temperature, thermal deprotection) and the resist behaviors were investigated as a function of the process conditions (densification of the resist film versus Soft Bake (SB) conditions, film recompaction during Pos Exposure Bake (PEB) in the exposed and unexposed areas). Special attention has been focused on the acid catalysed deprotection in the exposed areas of these 193nm resists during PEB. The different mechanisms involved in the deprotection of the resist matrix have been pointed out for each formulation.

Finally, an evaluation of the lithographic capabilities has been conducted for the 193 nm methacrylate based resist, and additional formulation effects have been demonstrated, that prevent the use of this resist under annealing conditions.

2. Experimental:

The thermal properties of the resists have been determined using a TA Instruments 2920 Modulated-Temperature DSC (MT-DSC) system (heating ramp : 5°C/min, +/-0.8°C/60s), a 2950 ThermoGravimetry Analysis (TGA) system (heating ramp : 10°C/min) and a 2970 DiElectric Analysis (DEA) system. (Heating ramp : 3°C/min).

An in-house built He/Ne (623.8 nm) ellipsometer, mounted over a hot-plate, has been used to monitor film thickness variations during the bake steps.

The lithographic evaluations at 193nm have been performed on a ASML PAS5500/900 scanner.

3. Results and discussions:

Chemically Amplified (CA) resists have to achieve various targets in terms of resolution, dimension control, depth of focus, reduced iso-dense bias and limited edge roughness. These requirements imply the diffusion control of both the latent image in the resist film after exposure and the deprotection reaction during PEB.

Two characteristics are of key importance for controlling CA resist performance:

- A high diffusion contrast between exposed and unexposed areas. This contrast is due to the difference in diffusion coefficients created by the additional free volume which was generated in the exposure areas during the deprotection reaction (or diffusion well effect [7]). However, this contrast can be reduced by the recompaction phenomena occurring during the PEB step. This behavior is dependent on the PEB conditions (temperature and time) related to the glass transition temperature Tg of both parts of the film.

- The stability to environment and delay time of the resist film. This property is better achieved with annealing type resists [8].

3.1. Determination of the Non annealing or Annealing type for the two resists under study and consequences:

Because of the reduced delay time and contaminant sensitivity of annealing systems, 193nm CA resists belonging to the annealing type are more attractive. However, such resist formulations, with a glass transition temperature inferior to the onset temperature of the thermal deprotection are not so easy to make with both methacrylate based or alicyclic chemistries.

As an example, Fig. 1 and 2 present the Modulated-DSC thermograms of the two resists under study [9].

Fig. 1. MT-DSC thermograms of the methacrylate based resist (Dashed line : Reversing heat flow, solid line : total heat flow)

Fig. 1 corresponds to the methacrylate based resist. The glass transition temperature is clearly observed on the Reversing Heat Flow signal as well as on the Total Heat Flow signal at about 160°C. As the onset of thermal deprotection is measured around 185°C, this methacrylate based resist can be considered to be an annealing type resist, with the possibility of a quite large bake range above Tg (160 to 180°C).
On the contrary, the glass transition of the alicyclic resist is hidden on the total heat flow signal because of the onset of thermal deprotection (Fig. 2). However, taking advantage of the deconvolution treatment offered by the Modulated-Temperature DSC technique, it is possible to measure small changes in heat capacity related to the glass transition on the Reversing Heat Flow signal.

Fig. 2. MT-DSC thermograms of the alicyclic based resist (Dashed line: Reversing heat flow, solid line: total heat flow)

Tg is observed just before the onset of thermal deprotection, at about 152°C. As a result, this alicyclic resist has to be considered to be a non-annealing type resist.

In order to investigate the influence of the non-annealing or annealing property on the film densification, actual thickness variations have been monitored during the SB step, using an in-situ Ellipsometer (623.8 nm He/Ne laser) [10] for both resists.

Film variations of the methacrylate based resist are presented in Fig. 3 as a function of time for various SB temperatures. As it can be observed, the film thickness variations fit a logarithmic law, indicating a relaxation process. This effect corresponds to the elimination of the free volume generated in the resist film during the spin coating process (time/temperature equivalency WLF laws). This resist also exhibits a behavior typical of methacrylate polymers, with rather long relaxation times (superior to 60s below and around Tg) [11].

As a consequence of these long relaxation times, no plateau region corresponding to the complete densification of the resist is reached for the recommended process conditions (130°C/60s), set below the Tg value. It should be noticed that this resist is used under non-annealing conditions (Tg = 161°C), leading to delay time problems (T-top profile) in an unfiltered environment.

Fig. 3. Thickness variations of the methacrylate based resist as a function of time for various Soft Bake temperatures

An unexpected behavior, i.e. an unusually reduced influence of the bake temperature on the final resist thickness is also observed for Soft Bake temperatures between 120 to 140°C. This effect is explained in section 3.3.

Considering the second resist sample (Fig. 4), which belongs to the alicyclic platform, a different compaction behavior can be noticed when compared to the methacrylate based resist. Indeed, in this case, the film recompaction is also controlled by relaxation laws, but shorter relaxation times are observed. As an example, for a Soft Bake temperature of 140°C (recommended process condition), i.e. 10°C below Tg (150°C) the film is stabilized after about 30s bake time, as opposed to several minutes for methacrylate polymers.

This behavior can appear to be paradoxical as alicyclic polymers are very rigid structures, and long relaxation time should have been expected. This fast relaxation mechanism during the soft bake step can be explained by the low molecular weight and the absence of entanglements of the alicyclic matrix.
As a result, the alicyclic resist presents the interesting property of being annealed by baking the film at relatively low temperatures (even 10°C below its Tg) for conventional bake time (60-90s). Well densified resist films are obtained under the recommended Soft Bake conditions (140°C/90s), leading to physically more stable films compared to the methacrylate based formulation.

3.2. Investigations of the deprotection reactions for the two resists under study:

Both resists have been exposed at 193nm in order to investigate the acid catalysed deprotection mechanisms.

After exposure and during PEB, the photogenerated acid deprotects the acid labile goups grafted on the resist polymer. This chemical change in the exposed film leads to a change in the film glass transition temperature. The behaviors of two different areas (exposed and unexposed), with two different Tg values, have to be considered during the PEB step. The Tg value of the unexposed areas remains stable around the value measured after SB. Conversely, the Tg of the exposed areas largely varies during the PEB step due to various effects: chemical changes due to deprotection, plasticizing effect of the generated free volume and recompaction of the deprotected film. Only the Tg value after completion of the PEB step, can generally be measured.

Considering only chemicals changes, Tg can only increase in the exposed areas due to the creation of carboxylic acid groups and subsequent hydrogen bondings [12]. The Tg of the deprotected methacrylate based resist has been measured at 166°C (compared to 160°C for the unexposed resist). In the case of the alicyclic based resist, the Tg of the exposed resist has been measured equal to 188°C (compared to 151°C for the unexposed resist). However, for this alicyclic resist, the glass transition temperature of 188°C measured after PEB is not so high as it could have been expected from data on pure alicyclic polymers (Tg >200°C) [13].

This increase in the Tg value of the exposed resist is favorable to maintaining a diffusion contrast, as the PEB temperature is well below the final Tg. However, the plasticizing effect of the additional free volume generated during deprotection also appears to be of paramount importance, as demonstrated by the following experiments which investigate film thickness variations during PEB by in-situ ellipsometry.

Fig. 5 presents the thickness variations of the methacrylate based resist film as a function of time during SB and PEB at the recommended process conditions (SB 130°C/60s, PEB 130°C/60s) as a function of time.

As previously mentioned, the film which has not been annealed during the SB step, continues to densify in the unexposed areas during PEB, following the same compaction rate than during the SB step.
On the other hand, an important film shrinkage is observed during PEB in the exposed areas, corresponding to the recompaction of the deprotected film.

Fig. 6 presents the thickness variations of the alicyclic based resist film during SB and PEB at the recommended process conditions (SB 140°C/90s, PEB 140°C/90s) as a function of time.

As opposed to the methacrylate based resist, the unexposed resist film is stable during PEB, indicating an already well densified film after SB (close to annealing conditions).

In the exposed areas, despite the rigidity of the alicyclic polymers, a shrinkage of the film occurs, as for the methacrylate based resist. This recompaction reduces the diffusion contrast between exposed and unexposed areas of the resist.

However, both resists do not present similar recompaction behaviors, and thus the mechanisms involved during the deprotection reaction can be different (Fig. 7).

Two steps in the recompaction effect of the exposed methacrylate film can be observed. During the first seconds of the PEB step, the resist thickness is stable, keeping favorable conditions to maintaining a high diffusion contrast [6]. Then, a fast recompaction occurs.

On the contrary, the exposed alicyclic based resist film starts immediately to recompact, following a slower relaxation process than that presented by the methacrylate based resist.

These behaviors may appear paradoxical for two reasons. Both resists are processed at PEB temperatures well below their final Tg values after deprotection and PEB (at least a 30°C difference) and should therefore not recompact quickly. Moreover, the alicyclic based film, shown to recompact fastly during the SB step, exhibits a slower recompaction rate than the methacrylate based resist during the PEB step.

In order to further investigate these phenomena, the mechanisms controlling both resist deprotections during PEB have been investigated using the DiElectric Analysis technique. This technique [14], is used to measure the electrical properties of the resists, such as the ionic conductivity, as a function of temperature and for frequencies varying from 1Hz to 10 kHz. Comparisons of the ionic conductivity variations between unexposed and exposed films allow to better define the mechanisms controlling the resist deprotection.

Fig. 8 presents the signature of the unexposed methacrylate and alicyclic based resists (193 nm flood exposure at 40 mJ/cm²) as a function of time during the Post Exposure bake.
polymer chains is enhanced and conductivity is increased. Above 190°C, thermal deprotection of the resist is reached, as indicated by dTGA and DSC thermograms. Ionic conductivity is further increased and the frequency curves merge, corresponding to the liquid state of the resist (thermal flow).

This results explains the fast recompaction rate of the exposed resist film observed after a few seconds of PEB (Fig.7). Indeed, as the methacrylate based resist has a slow relaxation rate, fast recompaction of the film can only occur when a large quantity of free volume has been generated. In the case of the reaction controlled methacrylate based resist, few seconds are necessary to sufficiently deprotect the resist and then induce recompaction. During these first seconds, the diffusion contrast is preserved in the resist film.

After exposure (Fig. 11), the ionic conductivity signal of the alicyclic resist does not present a peak in the ionic conductivity signal is clearly observed around 100°C, which perfectly corresponds to the acid catalysed deprotection reaction indicated by DSC and TGA thermograms. These conductivity variations in the exposed film occur within a limited temperature range (peak) for which no change in the matrix mobility is observed (glassy state). The resist can therefore be considered to be reaction-controlled.

The DEA signature of the alicyclic resist is strongly different from that of the methacrylate based resist: the frequency curves never merge. This behavior points out the highly rigid structure of alicyclic polymers which always remain in the glassy state. In addition, an important diffusion is observed around Tg. As the resist is not exposed, no acid has been generated in the film and this increase in the ionic conductivity can be attributed to the diffusion of additives.

After exposure (Fig. 11), the ionic conductivity signal of the alicyclic resist does not present a
peak at the temperature of the acid catalysed deprotection (116°C, as indicated by DSC and dTGA thermograms). This behavior is very different from that previously recorded for the methacrylate formulation. According to the conductivity variations, the deprotection reaction occurs without a sharp increase in the film mobility but rather follows the polymer mobility changes with temperature. The resist behavior can, thus, be described as diffusion-controlled. In order to reach a sufficient deprotection level with this type of resist, it is therefore necessary to boost the diffusion contribution by using PEB temperatures higher than those defined for reaction controlled formulations[14].

Consequently, as the alicyclic resist has a fast relaxation rate, the slow recompaction observed for the exposed resist film during PEB (Fig. 7) is indicative of a slow deprotection reaction of the resist matrix (and thus a slow generation of free volume), due to the limited diffusion of the photogenerated acid. This result underlines the limitation of this type of diffusion-controlled behaviors. Indeed, the acid diffusion coefficients can be increased by baking the resist at higher PEB temperatures. But in the same time, this high PEB temperatures decrease the diffusion contrast in the resist by accelerating the film recompaction (as PEB is performed at a temperature closer to its Tg value).

As a conclusion, maintaining a high diffusion contrast in 193nm chemically amplified resists is not obvious. The alicyclic resist seems to present better properties during the SB step, as the diffusion in the unexposed areas is minimized by the annealing of the film, even for SB temperatures below Tg. During the PEB step, diffusion contrast is reduced by the film recompaction in exposed areas for both resists. The fast relaxation rate of the alicyclic based resists can be detrimental to the preservation of the diffusion contrast during PEB. On the contrary, the slower relaxation rate of the methacrylate based resist allows a delay before the onset of the film recompaction and is favorable during this short period to the preservation of a high diffusion contrast between exposed and unexposed areas.

3.3. Lithographic evaluation of the methacrylate based resist: Additional formulation effects

Under the recommended process conditions (SB130°C/PEB130°C), the methacrylate based resist demonstrates good performance at 0.15 um (DOF around 0.65 um and EL around 12% for dense and isolated features, Fig. 12 and 13). However, this resist is not used as an annealing type resist, although DSC measurements (Fig. 1) demonstrate its potential capabilities to work as an annealing resist between 160 and 180°C (Tg = 161°C). Lithographic experiments have been performed to test this resist under various SB temperatures keeping constant the PEB conditions (PEB = 130°C/60s).

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The results obtained are presented in Table 1 for 0.15 um isolated line and dense 1/1 Lines and Spaces (L/S). A fast degradation of the resist performance is observed above 140°C (very sloped profiles), with an important resist top loss.

This unexpected behavior is confirmed by the variations in the resist sensitivity versus the SB temperature. If the resist was fully annealed, the diffusion should be reduced into the film and therefore sensitivity should decrease as the bake temperature is increased. Actually, a slight increase in sensitivity is observed for SB conditions around 140°C (Fig. 14), corresponding to a decrease in the dose to clear Eo of the resist.

This effect can be correlated with the degradation and/or evaporation of an additive, as it can be observed using thermal analysis measurements.

Fig. 15 presents the dTGA thermograms of the methacrylate based resist for two soft bake conditions: 130°C for 60s and 160°C for 60s. When the methacrylate based resist is baked at 130°C for 60s during the SB step, a small weight loss, compared to that corresponding to the thermal deprotection of the resist is observed around 130°C. On the contrary, when the resist is baked at a higher temperature during SB (160°C for 60s), the measured weight loss around 130°C is reduced.

Table 1. Performance of the methacrylate based resist for 0.15 um dimensions as a function of SB temperature (PEB = 130°C/60s).

<table>
<thead>
<tr>
<th>SB conditions</th>
<th>0.15 um Isolated line</th>
<th>0.15 um Dense L/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C/60s</td>
<td>DOF ~ 1 um</td>
<td>DOF ~ 1 um</td>
</tr>
<tr>
<td></td>
<td>EL ~ 15.8 %</td>
<td>EL ~ 13.5 %</td>
</tr>
<tr>
<td>130°C/60s (Reference)</td>
<td>DOF ~ 0.65 um</td>
<td>DOF ~ 0.70 um</td>
</tr>
<tr>
<td></td>
<td>EL ~ 12.4 %</td>
<td>EL ~ 12 %</td>
</tr>
<tr>
<td>140, 150, 160 and 170°C/60s</td>
<td>Resist top loss, Degradation of the profiles with SB temperature</td>
<td>Resist top loss, Degradation of the profiles with SB temperature</td>
</tr>
</tbody>
</table>

Fig.13. Bossung plots for 0.15 um Isolated line. Methacrylated based resist, recommended process conditions (SB 130°C/60s; PEB 130°C/60s).

Fig. 14. Dose to clear (Eo) of the methacrylate based resist on silicon versus Soft Bake temperature (SB time: 60s, PEB conditions: 130°C/60s).

Fig.15. Overlay of the dTGA thermograms of the methacrylate based resist after a SB of 130°C/60s (solid line) or 160°C/60s (dashed line).
This result confirms that a small quantity of material has been removed from the resist film during the high SB. Thus, because some of its additives are not stable above 140°C, this methacrylate based resist cannot be used under annealing conditions.

Finally, various PEB temperatures have also been screened (keeping constant SB conditions, i.e. 130°C/60s) to confirm that, in correlation with thermal analysis measurements (Fig. 5 and 8), lower PEB temperatures improve the diffusion contrast and consequently the resist performance. Table 2 illustrates the resist performance for various PEB temperatures.

<table>
<thead>
<tr>
<th>PEB conditions</th>
<th>0.15 um Isolated line</th>
<th>0.15 um Dense L/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C/60s</td>
<td>Bad profiles</td>
<td>Bad profiles</td>
</tr>
<tr>
<td>115°C/60s</td>
<td>---</td>
<td>DOF ~ 0.65 um EL ~ 20 %</td>
</tr>
<tr>
<td>125°C/60s</td>
<td>DOF ~ 0.75 um EL ~ 19 %</td>
<td>DOF ~ 0.80 um EL ~ 18 %</td>
</tr>
<tr>
<td>130°C/60s (Reference)</td>
<td>DOF ~ 0.65 um EL ~ 12.4 %</td>
<td>DOF ~ 0.70 um EL ~ 12 %</td>
</tr>
<tr>
<td>135°C/60s</td>
<td>---</td>
<td>DOF ~ 0.90 um EL ~ 12 %</td>
</tr>
<tr>
<td>140°C and higher</td>
<td>Degradation of the profiles with the PEB temperature</td>
<td>Degradation of the profiles with the PEB temperature</td>
</tr>
</tbody>
</table>

Table 2. Performance of the methacrylate based resist for 0.15 um dimensions as a function of PEB temperature (SB = 130°C/60s).

From these data, it can be concluded that low PEB temperatures (100°C) do not allow sufficient deprotection of the exposed resist and leads to bad performance (maximum of the acid catalysed deprotection around 115°C). Optimum lithographic results have been obtained with a moderate PEB at 125°C (Fig. 16 and 17). Under these lower PEB conditions, better performance in depth of focus (DOF) and energy latitude (EL) are observed for both dense and isolated features compared to the reference process with a PEB temperature equal to 130°C (Fig. 12 and 13). For PEB temperatures above 140°C, profile degradation, similar to that observed with high SB temperatures is observed due to the degradation of the additive in the resist. These results emphasize the advantages of working with moderate PEB temperatures, i.e. under process conditions that preserve a diffusion contrast between exposed and unexposed areas.

4. Conclusions:

Two 193 nm chemically amplified resists, based on two different chemical platforms, methacrylate and alicyclic, have been investigated
in order to compare their behaviors and specificities.

The alicyclic based resist exhibit an unusual fast recompaction rate, compared to methacrylate based formulations, which is favorable to the complete annealing of the resist film during the Soft Bake.

Regarding the Post Exposure Bake step, the preservation of a high diffusion contrast between exposed and unexposed resist, as well as the prominent mechanisms controlling the deprotection reaction, have been studied using various characterization techniques such as in-situ ellipsometry and DiElectric Analysis (DEA).

From these experiments, it appears that recompaction of the exposed areas is observed during the PEB for both resist chemistries, but resist deprotection is controlled by different mechanisms (reaction control or diffusion control deprotection). As diffusion controlled resists require process conditions with high temperature PEB, this deprotection mechanism can be more detrimental to the preservation of a high diffusion contrast in the resist, compared to reaction controlled resists with low activation energy protecting groups.

The importance in the formulation of stable additives has also been demonstrated with the methacrylate based resist, as bake temperatures used for 193nm resist processes can be quite high.

These results point out the need to futher study and deconvolute the influence of the chemical platforms from that of the protecting groups, photoacid generators and additives.

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References