Improving the Process Capability of SU-8, Part III

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SU-8 Resists are used widely in the development and fabrication of MEMS devices [1-4]. The resist's images are the product of photochemical and thermal cationic processes and result in vertical sidewalls and high aspect ratio features. These are among SU-8's most desirable attributes. As applications using SU-8 move into production, reproducibility and purity of the materials becomes of major importance. In most resist systems the resin is the major cause of batch to batch inconsistency. In SU-8, the photoacid generator has been the primary reason for the resist variation. The PAG used in the standard formulation is a sulfonium salt widely used in industrial applications. However, it is a multi component mixture and the composition varies widely from batch to batch. Metal ion contamination is also a concern as the PAG contains a metal ion which could be deleterious to semiconductor devices.

This work allowed us to identify single component PAG structures having acceptable lithographic performance compared to standard SU-8 resist. All PAGs identified show lower sensitivity compared to the mixed triarylsulfonium salt currently used. No usable metal ion free PAGs were found, however.

Keywords: SU-8 resist, photoacid generators, epoxy resist reproducibility

1. Introduction

The molecular engineering of SU-8 negative resist is such that it produces thick uniform coatings which are essential to the development and fabrication of MEMS devices [1-4]. SU-8 resin is a highly functional, fully epoxidized bisphenol-A/formaldehyde novolac polymer. Combined with the appropriate photogacid generator (PAG), it forms a thick film negative resist capable of producing high aspect ratio features with vertical profiles. Cationic photoacid generation is responsible for initiating image formation. Further, SU-8 formulations are stable for long time periods at room temperature. It is the effectiveness and uniformity of the photoinitiated cross-linking reaction that generates the desirable high contrast features. As applications using SU-8 move into production, reproducibility and purity of the materials becomes of major importance. In most resist systems the resin is the major cause of batch to batch inconsistency. However, in SU-8 it has been the photoacid generator that is the reason for most of the resist variation. The PAG used in the standard formulation is a mixed sulfonium salt widely used in industrial applications. However, it is a multi component mixture and the composition varies widely from batch to batch, thus leading to significant lot to lot variability of the resulting resist. Metal ion contamination is also a concern as the PAG contains a metal ion which could be deleterious to semiconductor devices.

Work reported previously [5] showed compositions containing a hexafluorophosphate PAG having some beneficial properties, but at a lower sensitivity. However, it is also a multicomponent PAG and not really suitable for improving the uniformity of the resist. Work at IBM [6] has shown that use of sensitizers or polyaromatic containing hexafluoroantimonate PAGs have much increased sensitivity, but they also have excessive absorption at the exposing wavelength which limits their use in thick resist
films. In this paper we present our results of studies directed toward the selection of PAG materials compatible with SU-8, which will not degrade the lithographic performance, are single component materials, have good solubility, do not have excessive absorption at 365nm, generate a very strong acid, and preferably do not contain a heavy metal ion.

In our study of these SU-8 PAG modifications we closely monitored the solubility, PAG purity, absorbance, photosensitivity, and lithographic performance: The objective was to compare in a screening program the sensitivity of various experimental PAGs formulated into SU-8 resist solutions to the sensitivity and performance of SU-8 2025 formulated with the standard PAG, Cyracure UVI-6976, which is a 50% solution of a mixed triarylsulfonium SbF6⁻ salt in propylene carbonate, Figure 1. HPLC analysis of the Cyracure demonstrated three major components whereas two alternative PAGs show single peaks, Figure 2. In fact, high resolution HPLC analysis shows more than 20 components to this mixture. Further, the analysis of a number of lots shows a widely varying ratio of the components. This has led to manufacturing and performance problems.

**Figure 1.**

**UVI-6976**

![HPLC Chromatograms of Various PAGs](image)

**2. Experimental**

The following PAGs were evaluated in this screening:

1. CD1012: di-(2-hydroxydecyloxyphenyl) iodonium SbF₆⁻
2. 479-2092C (OPPI-SbF₆): (4-octyloxyphenyl)phenyliodonium SbF₆⁻
3. DTBPI-PFBS: di-(t-butylphenyl)iodonium perfluorobutanesulfonate
4. OcOPP-PFBS: (4-octyloxyphenyl)-phenyliodonium perfluorobutanesulfonate
5. TTBPS-PFBS: tri-(t-butylphenyl)sulfonium perfluorobutanesulfonate
6. OcOPDPS-PFBS: (4-octyloxyphenyl)diphenylsulfonium perfluorobutanesulfonate
7. TTBPS-PFBzS: tri-(t-butylphenyl)sulfonium perfluorobenzensulfonate
8. TBPDPS-PFBzS: (t-butylphenyl)diphenylsulfonium perfluorobenzensulfonate
9. PI 2074: tolylcumyliodonium tetrakis(pentafluorophenyl)borate
10. Cyracure UVI-6990: 50% mixed triarylsulfonium PF₆⁻ in propylene carbonate
11. Cyracure UVI-6976: 50% mixed triarylsulfonium SbF₆⁻ in propylene carbonate (CONTROL)

CD1012 was an experimental product obtained from Sartomer Company. A sample of 479-2092C was obtained from GE Silicone Products. PI 2074 was obtained from Rhodia.
Performance Coatings. Cyracure UVI-6990 and 6976 were purchased from Dow Chemical. The remaining sulfonic acid PAGs were obtained from Toyo Gosei Kogyo. All PAGs were formulated into pre-made 71.5% solutions of SU-8 resin in cyclopentanone solvent. The ratio of PAG to SU-8 resin was 5% in all cases. These solutions were rolled for a total of 8hrs with gentle heat (50 °C), then filtered at 4.5 um.

Coating and Soft bake

The solutions were coated onto 100 mm Si wafers using a Brewer CEE 100CB coater with the following program:
- Static dispense
- Spread cycle: 500 rpm
- Acceleration: 100 rpm/sec
- Time: 5 sec
- Spin Cycle: 3000 rpm
- Acceleration: 300 rpm/sec
- Time: 30 sec

The coated wafers were soft baked on a Brewer Vacuum Contact Hotplate at 65 °C for 2 min followed by 95 °C for 10 min. The thickness for all coatings obtained at 21.3 °C and 40.35% RH was approximately 35 µm.

Exposure

The coatings were exposed using a broadband i-line AB-M vacuum contact short arc Hg exposure source through a chrome/quartz mask with line/space patterns from 2 to 50 µm held under −15 in Hg pressure. A 320 nm cut off filter was placed on top of the mask. An exposure matrix was performed for each PAG/resin coating with exposure doses of 315 mJ/cm2, 475 mJ/cm2, and 600 mJ/cm2.

Post Exposure Bake (PEB)

The exposed substrates were PEB at 65 °C for 2 min followed by 95 °C for 10 min, then allowed a 5 min relaxation cooling on a non-conductive surface to room temperature.

Development

The wafers were immersed in SU-8 Developer for 3 min with mild agitation in the form of swirling during the last minute. The imaged wafers were immediately spray rinsed using a squirt bottle of SU-8 Developer and then IPA. The wafers were dried with a pressurized air gun.

3. Results and Discussion

Two PAGs, TTBPS-PFBS and TTBPS-PFBSzS, were insoluble in the cyclopentanone resist solution at the desired concentrations. Sample solutions of 479-2092C, OcOPDPS-PFBS, and DTBPI-PFBS were readily soluble. The rest of the PAGs displayed solubility issues when spin coated and/or soft baked. These formulations were remade with the PAGs being dissolved into a 50% solution of cyclopentanone first, and then added to the resin solution. Surfactant was also added to these solutions to minimize any striations that might form. The solubility of CD1012 increased sufficiently enough that a sample could be formulated and a good coating achieved. The UV spectra of a number of these PAGs at 30 mg/l in γ-butyrolactone were run and compared, Figure 3. From these spectra it would be surprising if any of the new PAGs showed any sensitivity, since they have virtually no absorbance at 365 nm.

Nominal 35 µm films of those experimental PAG solutions which were soluble were then evaluated lithographically by comparing the resolution capability of 2 to 7 µm line/space patterns as shown in Figures 4-7. No attempt was made to optimize any of these formulations and all were made to contain the same wt % PAG on resin.
All samples were processed in the same manner and the image results evaluated under the microscope and by using digital images.

Surprisingly, there were three PAGs that showed a good deal of promise, 479-2029C, octyloxyphenyl-phenyliodonium-SbF6, CD1012, di(hydroxydecyl-oxyphenyl)iodonium SbF6, and PI 2074, tolyl-cumyliodonium tetra(pentafluorophenyl)borate. All three are single component PAGs rather than a mixture as found with the Cyracure (See Figure 2). SU-8 formulations containing a single component PAG should alleviate photosensitivity variability currently found using different lots of Cyracure. However, both PAGs 479-2029C and CD1012 required more exposure energy than standard SU-8 to give equivalent images, approximately 515 mJ/cm² for each compared to approximately 215 mJ/cm² when using Cyracure. This offset is much larger than our historical data indicates as recent lots of Cyracure have been approximately 25-30% faster. Interestingly, samples formulated with both 479-2029C and CD1012 displayed less mask bias than Cyracure. This may be due to the higher transparency of these two materials at the exposing wavelength. The optimal ratio of PAG to SU-8 resin has not yet been evaluated yet; although it was found that 2% and 5% loadings worked very well when the exposure dose was varied to compensate for the different loadings. The borate salt showed some very promising images and a good sensitivity, but was plagued with scum in the unexposed areas after exposure. Unfortunately the only workable images were obtained with the SbF6 salts; thus we are not able to eliminate the metal ion contamination issue.

Figure 4 indicates that the SU-8 solution with OcOPPI-PFBS was able to achieve a latent image in the film but the entire film dissolved once immersed in developer, even at a 900 mJ/cm² exposure dose. It is anticipated that higher doses and higher PEB temperatures would lead to reasonable images. The other sulfonate PAGs did not show any detectable activity under these conditions. This demonstrates the importance generating a sufficiently strong superacid such as with PAGs containing SbF6 salts.

A more complete description of each of the groups follows:

**Cyracure 6990, 50% Triarylsulfonium PF6**

The resolution characteristics of the resist containing the mixed triarylsulfonium hexafluorophosphate PAG, Figure 5, show that it requires significantly more energy, 600 mJ/cm² to achieve the same resolution as the control sample containing the hexafluoroantimonate, which needed approximately 235 mJ/cm². The UV-vis absorbance spectra for these PAGs overlap, demonstrating that the strength of the superacid generated is important in achieving the higher rate of crosslinking. Not surprisingly, both PAGs demonstrated a very similar mask bias in the line and space structures.

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**Figure 4. Lithographic results of sulfonate PAGs**

<table>
<thead>
<tr>
<th>PAG</th>
<th>Exposure Dose</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPPI-PFBS 5%</td>
<td>600</td>
<td>Latent Image after PEB, Dissolves during development</td>
</tr>
<tr>
<td>OPPI-PFBS 5%</td>
<td>900</td>
<td>Latent Image after PEB, Dissolves during development</td>
</tr>
<tr>
<td>OcOPDPS-PFBS 5%</td>
<td>600</td>
<td>No Image</td>
</tr>
<tr>
<td>DTBPI-PFBS 5%</td>
<td>600</td>
<td>No Image</td>
</tr>
<tr>
<td>TBPDS-PFBSzS 5%</td>
<td>600</td>
<td>No Image</td>
</tr>
</tbody>
</table>
Figure 5. Lithographic results of Cyracure UVI 6990

<table>
<thead>
<tr>
<th>PAG</th>
<th>Exposure dose, mJ/cm²</th>
<th>Line Resolution, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyracure PF₆⁻ 5%</td>
<td>315</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>4, 5, 6, 7</td>
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</tbody>
</table>

Figure 6. Lithographic results of tetrakis(pentafluorophenyl)borate PAG

<table>
<thead>
<tr>
<th>PAG</th>
<th>Exposure dose, mJ/cm²</th>
<th>Line Resolution, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2074 1%</td>
<td>475</td>
<td>2</td>
</tr>
<tr>
<td>2074 2%</td>
<td>475</td>
<td>3</td>
</tr>
<tr>
<td>2074 5%</td>
<td>315</td>
<td>4, 5, 6, 7</td>
</tr>
<tr>
<td>Exposure</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
<tr>
<td>----------</td>
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</tr>
<tr>
<td>7</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
<tr>
<td>6</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
<tr>
<td>5</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
<tr>
<td>4</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
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<tr>
<td>3</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
<tr>
<td>2</td>
<td>2% OPP1-8BpF</td>
<td>479-2029C</td>
</tr>
</tbody>
</table>

FIGURE 7. Lithographic results of alkoxyarylhydroquinone PACs.
PI 2074, diaryliodonium tetra(perfluorophenyl)borate

This PAG displayed approximately the same relative sensitivity as standard SU-8, Figure 6. Unfortunately, there was a large amount of cross-linked scum between the exposed images after development. Scum was still prevalent even when the PAG content was lowered to 2%. It has been theorized that this scum is due to residual acid in the PAG sample. However, experiments have not been able to verify this. A matrix was performed in which we looked at lower PEB temperatures as well as no PEB. In all cases, the imaged wafer produced scum when heated, even at 65 °C. No PEB produced no image and no scum – note that the film was baked using the standard 65/95 °C process after coating. An analysis for residual acid was also performed and did not indicate any detectable acid. Because of the high molecular weight of the anion portion of the salt, the gram absorbance of this material is actually quite low and may require higher loadings to work appropriately. Additional work is underway to determine the cause of the scum as well as investigating the effect of purification of the commercial material.

479-2029C, alkoxyphe nylphenylidonium SbF6
CD1012, di(hydroxyalkoxyphenyl)iodonium SbF6

The chemistries of 479-2029C and CD1012 are very similar in that they are both diaryliodonium SbF6 PAGs containing long chain alkoxy substituents. The main distinction between them is that 479-2029C contains a branched alkoxy group and CD1012 has a linear alkoxy with 2-hydroxyl substitution. The hydroxyl group is expected to lead to higher sensitivity by accelerating the reaction of the epoxy. It is surprising, therefore, that both materials give almost identical lithographic performance, Figure 7. Perhaps the lower solubility of the CD1012 has limited its reactivity. Not only do both have similar sensitivities, they both show the same high resolution and wall profiles with a noticeably lower mask bias than SU-8 2025. The 479-2029C is commercially available from several sources and is therefore an attractive replacement PAG. It is a single component material of 100% purity with a melting point range of 57-58 °C. Its high solubility is also advantageous.

4. Conclusions

In conclusion, this data shows that long chain alkoxyaryl PAGs are sufficiently soluble at high concentrations to meet the needs of these high solids systems. As expected, the unconjugated triaryl sulfonium PAGs are unresponsive as they have virtually no absorption above 320 nm. However, the iodonium PAGs have a sufficient tail absorption above 350 nm that leads to only a somewhat reduced response. The sulfonate PAGs are insufficiently responsive to have utility with the process conditions currently used, i.e. PEB temperature less than 100°C. The borate salt shows considerable interest in that it has high sensitivity and does not contain a heavy metal ion. However, there is some question whether the borate will affect the parasitic parameters of the device. Yet to be determined is whether the scumming issue can be overcome. It appears that the soluble, single component iodonium SbF6 PAGs are all effective. They do show lower sensitivity because of their higher transparency at 350-400 nm. PF6 is less effective than SbF6 because of its lower acid strength. It also contains the same mixed triarylsulfonium moiety deemed unacceptable for the current SbF6 salt.

In general, it appears that the strength of the acid generated and the absorbance of the PAG at the exposing wavelength are the most important factors in determining if the PAG is suitable for formulating with SU-8. The solubility of the commercially available PAGs seems adequate. Future work will include the testing of an anthracene based PAG, expanding the formulation range and optimizing the processing of the OPPi-SbF6 and CD1012 PAGs. Additional work will be conducted to determine if a workable metal free material can be found.

Therefore, this work has allowed us to identify single component PAG structures having equivalent lithographic performance when compared to the standard SU-8 resist. All PAGs identified as acceptable show lower sensitivity compared to the mixed triarylsulfonium salt currently used. These PAGs also provide significant improvements in batch to batch uniformity. However, to date no usable metal ion free PAGs were found.
Acknowledgements
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References