A DRM STUDY OF MICROPOSIT SAL603 RESIST 
IN DEVELOPERS OF DIFFERENT NORMALITY

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ABSTRACT
Microposit SAL603, a negative working chemically amplified electron beam resist, was studied for four developers of different normality: Microposit MF322 (0.268 N), MF321 (0.210 N), MF320 (0.255 N), or MF319 (0.237 N). Wafers were exposed to create eight regions, each with incrementally increasing exposure. Development in each of the eight zones was monitored simultaneously with a Perkin Elmer 5900 Development Rate Monitor (DRM). Increased developer normality was shown to increase development rate and photoresist contrast, but decreased sensitivity.

INTRODUCTION
Previously, commercially available negative e-beam resists (such as COP and EPB) exhibited sensitivities below 1uC/cm2, but suffered from swelling during development, which severely limited their resolution capabilities [1]. Recently developed, three component negative chemically amplified resists have shown sensitivities, (defined as the dose resulting in 90% thickness retention), as low as 1.5 uC/cm2 and contrast values as high as 7 or 8 [2,3,4]. In addition, these resists are developable in aqueous developers, and, therefore, do not suffer from swelling problems. Resolution capabilities of 0.1 um or less have been reported [2,4]. As device dimensions continue to shrink well into the submicron range, the ability to produce images with these characteristics is vital to the future progress of the semiconductor industry. Therefore it is critical to develop and characterize e-beam resists that can produce high quality, high resolution images.

Microposit SAL603 resist is a chemically amplified negative e-beam resist consisting of three components: a novolak resin, a melamine crosslinking agent, and a photoacid generator. In a conventional negative resist, one unit of exposure energy results immediately in one photochemical crosslinking reaction. When SAL603 is exposed to electron beam radiation, the photoacid generator absorbs the incident energy and undergoes a reaction which produces a small amount of a strong acid [4]. A post exposure bake (PEB) is required in order to induce crosslinking in the exposed regions. The PEB provides thermal energy for the
acid catalyzed bonding reaction between the crosslinking agent and the novolak resin, which thereby renders exposed regions insoluble in the developer. An acid catalyst molecule is released at the end of each crosslinking reaction, so each acid molecule is able to induce many crosslinking bonds. Thus, for chemically amplified resists, one unit of exposure energy leads to more than one crosslinking reaction. This type of reaction is shown in Figure 1 [5].

![Figure 1: Exposure chemistry of SAL603.](image)

In regions immediately surrounding highly crosslinked areas, or regions receiving low exposure dose, the resist will exhibit varying degrees of crosslinking. In the areas of partially crosslinked resist, the solubility in the developer is reduced, but not eliminated. This condition occurs because there is an insufficient amount of acid catalyst present to fully crosslink the resist. Depending on the development conditions, the final resist image can be altered considerably. If the developer is unable to dissolve the partially crosslinked material around the perimeter of highly crosslinked regions, line widths will be increased. Narrower linewidths will be produced when using a highly active developer, or when developing for a longer period of time. Either enhanced development method will result in the removal of some or all of the incompletely crosslinked resist.

The difference in the aggressiveness of developers is quantified in a factor called the normality, which indicates the relative alkalinity of the developer. The higher the normality, the more aggressive the developer is, and the higher the dissolution rate of the resist [6]. Quantitatively, normality is defined as follows [7]:

\[
\text{Normality} = \frac{\text{Number of available moles of OH}^-}{\text{liter of solution}}
\]  

(1)

Because the dissolution rate changes with developer normality, resist characteristics such as sensitivity and contrast will be altered as well. By monitoring the development of a partially crosslinked region caused by a low exposure dose, the development rate vs. remaining thickness can be determined for the exposure dose used in that region. From this data, changes in contrast and sensitivity can be determined.
This work examined Microposit SAL603 resist in aqueous developers of different normality. Relationships between normality and photoresist parameters including sensitivity and contrast were determined for Microposit MF322 (0.268 N), MF321 (0.210 N), MF320 (0.255 N), or MF319 (0.237 N) developers.

EXPERIMENT

The exposure tool available was a MEBES I with an accelerating potential of 10 keV. The recommended resist thickness for writing in these conditions was 0.5 μm. Prior to the developer normality study, thickness vs. spin speed data for SAL603 in 16% solid had to be determined. Four inch silicon wafers were hand coated on a spinner calibrated with a strobe light at speeds ranging from 1500 to 5000 rpm. Thickness measurements were made after a 1 minute 105°C prebake on a vacuum hotplate using an index of refraction for the resist of 1.66 determined by ellipsometry. The 0.5μm thickness was not obtainable, except at spin speeds less than 2000 rpm, which result in thickness nonuniformity across the wafer. Therefore, 3000 rpm was chosen because it provided a reasonably thick layer (0.4 μm) while still ensuring uniform coating thickness.

For the developer normality study, four inch silicon wafers with 8000A of oxide were prepared for exposure on the MEBES I. A Perkin Elmer 5900 Development Rate Monitor (DRM) was utilized for data collection and analysis. In order to obtain the data using the DRM, an exposure pattern of boxes receiving incrementally increasing exposure dose had to be produced horizontally across the center of the wafer (flat at the bottom). Perkin Elmer suggests the overall size of the exposure array be at least 5 cm long by 1 cm high. The array of eight 5mm x 20mm boxes shown in Figure 2 was used for the study. The exposures ranged from 0.5 μC/cm² in box 1 to 4.0 μC/cm² in box 8 in 0.5 μC/cm² steps. The wafers were developed in 1 of the 4 above mentioned normalities. Data analysis was performed with Dreams, the software system accompanying the DRM. Relationships between developer normality and parameters including contrast, sensitivity and development rate were determined.

RESULTS/DISCUSSION

The DRM uses interferometric analysis with a He-Ne laser (λ=6328 Å) to characterize the development. The data consisted of the reflected intensity as a function of time in the developer. Since the resist thickness is changing, a sinusoidal intensity signal results, corresponding to the constructive and destructive interference. For the 16% solids film, little thickness loss (<1000 Å) prevented the acquisition of analyzable data. Therefore, a 29% solids mixture of SAL603 was used for the rest of the study. The thickness vs. spin speed relationship was obtained for the 29% solids resist in the same manner as for the 16% solids, and both are shown in Figure 3.
Because a much thicker resist layer could be obtained with the 29% solids resist, a spin speed of 6000 RPM was chosen to provide a layer that would experience adequate thickness loss for analysis with the DRM, yet thin enough to allow exposure through the full layer of resist. No other wafer preparation processes were changed.

The relationship between developer normality and dissolution rate for a 0.68 μC/cm² exposure dose) after 15 min of development is shown in Figure 4. As expected, the developers showed the relationship of increasing development rate with increasing normality, with MF322 (0.268 N) clearly having a much higher development rate than the other developers. In fact, it was the only developer to completely clear. MF321 (0.210 N) has the lowest normality of those studied, and it only removed 32% of the initial resist thickness.
Developer normality also affects the contrast and sensitivity of SAL603. Figure 5 shows a comparison of the normalized thickness vs. log exposure curves for all four developers after four minutes of development. It is seen that increasing developer normality resulted in higher contrast (calculated by finding the slope of the curve at zero remaining thickness), and lower sensitivity (the dose required for 90% thickness retention). Sensitivity, contrast, and development rate values for each developer are summarized in Table 1.

Table 1: Tabulated results of contrast and sensitivity

<table>
<thead>
<tr>
<th>Normality</th>
<th>Developer</th>
<th>Contrast*</th>
<th>Sensitivity*</th>
<th>Dev Rate**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.210</td>
<td>MF321</td>
<td>1.83</td>
<td>0.86</td>
<td>6</td>
</tr>
<tr>
<td>0.237</td>
<td>MF319</td>
<td>2.86</td>
<td>1.14</td>
<td>12</td>
</tr>
<tr>
<td>0.255</td>
<td>MF320</td>
<td>3.43</td>
<td>1.68</td>
<td>22</td>
</tr>
<tr>
<td>0.268</td>
<td>MF322</td>
<td>4.19</td>
<td>1.74</td>
<td>48</td>
</tr>
</tbody>
</table>

* After four minutes of development.
** (A/sec) At 0.8 of normalized thickness remaining.

The sensitivity relationship supports the findings of Fedynshyn et al. in their work with SAL605 [4]. Higher contrast is achieved with higher normality resists because more of the partially crosslinked resist is removed during development with a higher normality developer, so that only the most highly crosslinked resist will remain after development.

Figure 6 shows the sensitivity curves of SAL603 resist after development in MF322 developer for 1, 2, 4, and 15 minutes. This curve shows that a longer development time results in decreased sensitivity and increased contrast. The difference 11 additional minutes of development causes between the sensitivity curves for the 4 and 15 minute development times is small compared to the change one minute creates in the curves for 1 and 2 minutes of development. This shows that there is wide process latitude available during development with SAL603 resist after 4 minutes.
CONCLUSIONS

The final image created with Microposit SAL603 resist was shown to be very sensitive to changes in development conditions. Sensitivity was shown to decrease from 0.86 uC/cm² to 1.74 uC/cm² with increasing developer normality. Contrast, however, increased with normality. The contrast value more than doubled from 1.83 to 4.19 for a change in developer normality from 0.210 N to 0.268 N. Development rate also increased with normality. Increasing development time was shown to have an identical effect on the development characteristics as increasing normality. SAL603 was also shown to allow wide process variation during development with only minimal changes in the characteristic curve after 4 minutes of development.

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REFERENCES