A Resolution Enhancement Material for 193-nm Lithography Comprising 2-Hydroxybenzyl Alcohol and Poly(vinyl alcohol) with Uniform Resist Pattern Shrinkage

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A series of resolution enhancement materials (REMs) for 193-nm resist employing poly(vinyl alcohol), 2-hydroxybenzyl alcohol (2HBA), and a non-ionic surfactant have been prepared and evaluated. The resolution enhancement has been achieved by resist pattern thickening (pattern space shrinkage) that is caused by the interaction between REMs and 193-nm resists. The key component, 2HBA, demonstrated the capability of shrinkage of the printed spaces or holes on 193-nm resists without a cross-linking reaction. This system expanded the process margin and minimized the dependence of resist pattern sizes, pitches, and shapes in the shrinkage reaction that had been one of the critical issues in the cross-linking-type chemically shrinking materials. The optimized REM afforded about 10 to 15-nm shrinkage for hole, trench, and lines and spaces (L/S) patterns with various pitches that was suitable for advanced Logic LSI application.

**Keywords:** resolution enhancement material, 193-nm resist, 2-hydroxybenzyl alcohol, poly(vinyl alcohol)

1. Introduction

With the increase in demand for microfabrication in the manufacture of small-dimension large-scale integrated circuits (LSIs), optical lithography using 193-nm light (ArF, argon fluoride excimer laser) has been widely adapted for manufacturing from 90 to 2x nm node LSIs. With advancement of each LSI generation, a higher resolution has been needed at the same exposure wavelength. To improve the resolution, there have been popular optical solutions such as off-axis illumination [1], phase-shifting masks [2,3], and optical proximity correction [4] in combination with high-NA exposure tools. Although these technologies offer a superior resolution, they do not show enough lithographic margins such as depth of focus, particularly for high-NA exposure tools. Additionally, resist patterns obtained in an extended resolution region by such optical techniques often suffer from pattern deformation and line width roughness.

On the other hand, some techniques used in lithographic processes to produce smaller resist pattern spaces or holes with adequate lithographic margin, such as thermal flow [5-9], gas-phase fluorination [10], and chemically shrinking materials [11-15], have been reported. These processes are mainly devoted to fabricate small contact holes in memory devices because they need optically disadvantageous dark field masks used for fabrication of resist patterns. Among these processes, chemically shrinking materials are the
most popular solution for resolution enhancement techniques because they are easy to apply for the lithographic process. However, there are few cases of adapting such shrinking materials to trenches, L/S patterns, and other shapes. In addition, the degree of shrinkage of the pattern spaces or holes generally depends on the pattern size and pitch. Moreover, current chemically shrinking materials often suffer from defects caused by acid-catalyzed cross-linking reactions at resist pattern surfaces. Therefore, they are difficult to apply for mass production of logic LSIs that have various pattern pitches and shapes in the same layer.

We previously reported chemically shrinking materials [16] having enhanced affinity for 193-nm alicyclic acrylate resists for resist pattern thickening to produce smaller resist pattern spaces or holes. In a typical formulation of the material, poly(vinyl acetal) and tetramethoxymethyl glycoluril were used as a base polymer and a cross-linker, respectively. Although the materials had shrinking capability for spaces or holes printed on commercially available 193-nm alicyclic acrylate resists, they were sensitive to the post-apply baking temperature. We assumed that the above-mentioned shrinking dependence was caused by the cross-linking reaction between the shrinking material and resist on the side walls of the patterns. The cross-linking reaction started over 90 °C and completed over 110 °C to produce a water-insoluble gel layer over the resist pattern. Therefore, the material had a small process margin by such reaction behavior.

In our previous study, we found that the addition of some phenol glycosides to the chemically shrinking material, particularly salicin or arbutin, effectively reduced the above-mentioned issues [17]. We assumed that highly hydrophilic phenol glycosides afforded water solubility in the weak cross-linked region, so that the strong cross-linked region selectively remained on the resist patterns. Hence, the above-mentioned shrinking behavior and insoluble layer formation over 110 °C baking was drastically improved. The addition of phenol glycosides, however, deteriorated the storage stability of the material. The reason is that a mold grows easily in solutions including glycosides. Based on the observation, we focused on the benzyl alcohol structure of salicin, and evaluated some benzyl alcohol derivatives for non-cross-linking-type resist pattern (holes or spaces) shrinking reactions.

In this paper, we describe a new REM for 193-nm resists for logic LSI applications, which is less sensitive to critical dimensions (CDs), pitches, and resist pattern shapes.

2. Experimental
2.1 Materials
Poly(vinyl alcohol) (PVA-205C; Kuraray Co., Ltd.), poly(vinyl acetal) (KW-3; Sekisui Chemical Co., Ltd.), alcohol ethoxylate non-ionic surfactant (TN-80; ADEKA Corporation), silicone surfactant (KP-341; Shin-Etsu Chemical Co., Ltd.), triphenyl sulphonium nonafluorobutane sulfonate (TPS-109; Midori Kagaku), 2-hydroxybenzyl alcohol (Sigma-Aldrich Co.), and tetramethoxymethyl glycoluril (Sanwa Chemical Co., Ltd.) were used without further purification. Both commercially available alicyclic acrylate-based Resists A and B were supplied by resist vendors. Deionized water (DIW) was used as a solvent.

2.2 Formulation of the REMs
The preparation of the PVA solution was as follows. To 100 g of cold water being stirred with a magnetic stir bar in a 200-ml recovery flask was slowly added 4 g of PVA-205C and immersed in a 92 °C oil bath with stirring. After 4 h, the solution was allowed to cool to room temperature. The solution was filtered through a 0.2-µm cellulose acetate membrane filter to give the mother liquor (REM-1).

Using the mother liquor, we prepared four solutions for the preliminary study (Table 1). A typical cross-linking-type REM-5 was also prepared as a comparative material, and the composition was as follows: DIW/2-propanol/KW-3/tetramethoxymethyl glycoluril/TN-80 = 99.6/0.4/16/1.35/0.25 (g).

<table>
<thead>
<tr>
<th>Sample</th>
<th>DIW (g)</th>
<th>PVA (g)</th>
<th>2HBA (g)</th>
<th>TN-80 (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REM-1</td>
<td>100</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>REM-2</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>0.12</td>
</tr>
<tr>
<td>REM-3</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>-</td>
</tr>
<tr>
<td>REM-4</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 1 Composition of resolution enhancement materials.
2.3 Evaluation conditions

2.3.1 Resist patterns

Resist A or B coated wafers were exposed using 193-nm excimer laser exposure systems (Canon NA = 0.85; Nikon NA = 0.92) for the pattern thickening (hole or space size shrinkage) evaluation. The exposed resist patterns used for the shrinking evaluation were dense contact hole and isolated trench (single space) patterns with different CDs. The dense hole patterns were exposed with four different CD (mask size)/pitch (nm) for Resist A: 130/200, 142/260, 156/300, and 196/400, and for Resist B: 138/200, 158/260, 170/300, and 210/400. The isolated trench patterns were printed with five different CDs (mask size, nm): 100, 170, 240, 320, and 500. The L/S patterns of exposed CD (mask size)/pitch (nm) used for evaluation were 100/200 for Resist A and 106/220 for Resist B. The typical REM treatment conditions are as follows: spin coat/3500 rpm for 40 s, baking/110 °C for 60 s, and rinse/DIW 30 s in the dip mode.

2.3.2 Shrinkage inspection and dry etching

The shrinkage of hole or space size of the REM-treated resist patterns were examined with scanning electron microscopes (SEMs), Hitachi S-6100 and S-9200. The shrinkage amount of hole or space size (ΔCD) was calculated by the difference between the mean initial values (five points) and the mean post-treatment measured values (five points). Dry etching was carried out using a magnetron plasma reactive ion etcher. Using a CF₄/CHF₃ mixed gas, the films with or without shrinkage were etched under the conditions common for etching SiO₂ films.

2.3.3 TOF-SIMS measurements

Positive mass spectra of TOF-SIMS (time-of-flight secondary ion mass spectrometer) were obtained on a TRIFT V nanoTOF (ULVAC-PHI) spectrometer in the mass range 0–3000 m/z. A Bi³⁺-source was used at a beam energy of 30 keV and 0.5 nA current with a 500-μm raster size.

3. Results and Discussion

3.1 Evaluation of benzyl alcohols

We focused on the benzyl alcohol structure in phenol aglycone of salicin. This is because benzyl alcohol is easily dehydrated to produce a stable benzyl cation. We expected that the utilization of the reactivity of the benzyl cation is one of the promising pathways for non-cross-linking-type shrinkage reactions. Benzyl alcohol (BnOH), 2HBA (phenol aglycone of salicin), 4-hydroxybenzyl alcohol (4HBA), 2-aminobenzyl alcohol (2ABA), and 4-aminobenzyl alcohol (4ABA) were selected as representative compounds and evaluated in terms of commercial availability and water solubility (Fig. 1). The effect of benzyl alcohols for the shrinkage of hole diameter on printed hole patterns upon using Resist A are summarized in Fig. 2. The incorporation of benzyl alcohols was 1 g in 104 g of REM-1 for each solution. All benzyl alcohols successfully shrunk the hole patterns. The obtained ΔCD range from about 10 to 40 nm; however, they showed clear CD/pitch dependence except 2HBA. In addition, 4HBA and 2ABA exhibited limited solubility in the mother liquor (REM-1), indicating that they had narrow margins in the preparation of REMs. On the other hand, 2HBA showed moderate shrinkage and weak CD/pitch dependence as well as good solubility in REM-1. Based on these observations, 2HBA was found to be the most promising reagent for REMs.

![Figure 1. Chemical structure of benzyl alcohols.](image)

3.2 Effect of 2HBA

The effect of 2HBA with or without TN-80 for the shrinkage of hole diameter was investigated using Resist B. Figure 3 shows the preliminary results for the effect of the solutes using REM-1 to REM-4. REM-1 (poly(vinyl alcohol) aqueous solution) was proved to have little effect for shrinkage.
However, the addition of TN-80 and 2HBA, especially, REM-4 showed moderate shrinkage (10 to 15 nm in hole diameter) in each CD/pitch pattern, suggesting that the shrinkage reaction does not depend on the pattern sizes and pitches. The shrinkage behavior in Resists A and B is also demonstrated in Fig. 4. Since the obtained ∆CD range from about 10 to 20 nm in holes, L/S, and trench patterns of both resists, and the shrinkage behavior was quite similar, the new system was found to have small dependence for 193-nm resist materials.

Figure 5 compares the post-apply baking temperature dependence of REM-4 and 5 using the same hole patterns. ∆CD obtained by REM-4 treatment gradually increased with increasing the baking temperature. Applying REM-4, obtained maximum ∆CD was 7.4 nm for the 158/260 nm pattern, and minimum ∆CD was 5.8 nm for the 138/200 nm pattern with the elevation of the baking temperature from 90 °C to 150 °C. The calculated shrinkage amount difference between maximum and minimum ∆CDs was 1.6 nm for the series of CD/pitch patterns. REM-5, however, exhibited a drastic shrinkage behavior. When REM-5 was applied, obtained maximum ∆CD was 39.0 nm for the 210/400 nm pattern, and minimum ∆CD was 13.0 nm for the 138/200 nm pattern with baking temperature elevation from 90 °C to 110 °C. The shrinkage amount difference between maximum and minimum ∆CDs was 26.0 nm. Thus, the difference obtained for REM-5 was 16 times bigger than that for REM-4. Moreover, the shrinkage amount was quite different between 138/200 and 210/400 patterns after REM-5 treatment. ∆CD for the 210/400 nm pattern was three times bigger than that for the 138/200 nm pattern with 20 °C difference in the baking temperature. This behavior means that REM-5 has both

![Figure 2. Comparison of shrinkage of hole patterns printed on Resist A treated by a series of benzyl alcohol including aqueous PVA solutions. Each sample was baked at 110 °C for 60 s followed by DIW rinse for 30 s.](image1.png)

![Figure 3. Comparison of shrinkage of hole patterns printed on Resist B treated by REM-1–REM-4. Each sample was baked at 110 °C for 60 s followed by DIW rinse for 30 s.](image2.png)

![Figure 4. Top-down SEM images of shrinking behavior of hole, L/S, and trench patterns printed on Resist A treated by REM-4 after baking at 110 °C for 60 s followed by DIW rinse for 30 s. The measured CDs of the holes or spaces are given in parentheses.](image3.png)
strong CD/pitch and baking temperature dependence on the pattern thickening reaction. Furthermore, as mentioned above, REM-5 was fully cross-linked on the resist patterns over 110 °C baking and unable to obtain any resist patterns after DIW rinse.

On the other hand, REM-4 did not show such kind of behavior up to 150 °C. Figure 6 compares the SEM pictures before and after REM treatment for the 138/200 hole patterns. REM-4 showed moderate shrinkage and gave 10.0 nm of ΔCD at 110 °C and 16.4 nm at 150 °C baking, while REM-5 (cross-linking type) afforded 25.6 nm of ΔCD even at 110 °C and fully cross-linked over 110 °C baking (no SEM image). This mild shrinking behavior suggests that a rapid reaction like cross-linking in REM-5 does not occur in REM-4. From the process margin point of view, we preferred a mild condition. Consequently, the baking condition for REMs was set at 110 °C for 60 s for further investigation.

3.3 Impact of 2HBA loading amount

The impact of 2HBA was investigated using REM-1 as a base solution. REM-1, REM-3 (including 1 g of 2HBA in 104 g of REM-1), and two sample solutions were additionally prepared by mixing with 2 and 3 g of 2HBA in 104 g of REM-1. We also used the same dense hole patterns in section 3.2 and isolated trench patterns (mask size: 100, 170, 240, 320, 500 nm) printed on Resist B. Figures 7 (a) and (b) show that 1 g of 2HBA addition gave favorable ΔCD (~10 nm) for both hole and isolated trench patterns. When over 2 g of 2HBA loading was applied, hole or space size dependence on shrinkage appeared clearly in either hole or trench pattern.

In particular, the dependence was extremely strong for the trench patterns in the case of 3 g addition of 2HBA. It is evident that 2HBA promotes resist pattern shrinking from the results. However, a high concentration of 2HBA caused strong hole or space size dependence on shrinkage, implying that the amount of 2HBA in the REM-penetrated patterns affects the dependence. Therefore, to minimize the dependence with moderate shrinkage, we chose 1 g addition of 2HBA in 104 g of REM-1.

3.4 Optimization of REM solution

REM-4 and two sample solutions were additionally prepared by the addition of TN-80 (0.06 and 0.25 g) in 105 g of REM-3. We also used the same dense hole and the isolated trench patterns in section 3.3 printed on Resist B. Figures 8 (a) and (b) demonstrate that the shrinkage amount of the trench patterns was sensitive to the concentration of TN-80, as compared to that of the hole patterns. As TN-80 addition increases, the shrinkage of the trench width increases larger than that of the hole diameter. This tendency indicates that the concentration of the surfactant is significant for the resist pattern shrinking reaction. The observed behavior corresponds with the results.
Figure 7. Effect of 2HBA loading for (a) hole diameter shrinkage and (b) isolated trench width shrinkage on Resist B. Each given weight (g) of 2HBA was dissolved in 104 g of REM-1. The baking condition was 110 °C for 60 s followed by DIW rinse for 30 s.

Figure 8. Effect of TN-80 loading for (a) hole diameter shrinkage and (b) isolated trench width shrinkage on Resist B. Each given weight (g) of TN-80 was dissolved in 105 g of REM-3. The baking condition was 110 °C for 60 s followed by DIW rinse for 30 s.

in our previous study demonstrated that the amounts of some non-ionic surfactants play an important role for controlling the resist pattern shrinkage amount. When a large amount of TN-80 is incorporated with an REM, the affinity between the resist patterns and REM is considered to be increased. In addition, the infiltration of the REM in the resist patterns also becomes easier with increasing TN-80 loading. Consequently, these results suggest that the penetration of an REM in trench patterns is easier than that in the hole patterns. To minimize the shrinkage bias between the trench and hole patterns, the TN-80 concentration should be carefully settled. Thus, we have determined 0.06 g of TN-80 loading in 105 g of REM-3 for suppressing the trench-hole bias with an adequate shrinkage amount. Based on the evaluation, the optimized composition (hereinafter referred to as REM-opt) was determined as follows: DIW/PVA-205C/2HBA/TN-80 = 100/4/1/0.06 (g).

Figure 9 shows the shrinkage results for printed dense hole and trench patterns on Resist B using REM-opt. REM-opt afforded moderate shrinkage amount in both hole and trench patterns, indicating that the pattern shape and size dependence on shrinkage was successfully suppressed. Using REM-opt, we also examined that pattern pitch dependence on shrinkage targeted 70-nm hole patterns on...
Resist B (Fig. 10). Since the bias obtained in through-pitch $\Delta CD$s fluctuated within 6 nm, the reaction system proved to have uniform reactivity for various pitches. Terai et al. [18] reported the cross-linking-type chemically shrinking material (ArF RELACS, Resolution Enhancement Lithography Assisted by Chemical Shrink) that had good through-pitch bias (~10 nm). Although the evaluation conditions and the resist material are quite different in the report, our results seem to demonstrate the advantage of the reaction system employed in REM-opt. REM-opt exhibited superior shrinkage performance in not only hole patterns but also trench and L/S patterns. Moreover, more complicated pattern shapes were shrunk uniformly by REM-opt. Figure 11 displays the uniform shrinkage in various pattern shapes, suggesting that our system has advantages for the logic LSI application.

3.5 Dry etching
The dry etching of the underlying SiO$_2$ films was examined using with or without REM-opt treatment printed on Resist B. The initial hole diameters were set to 72.4 nm for the resist and 81.6 nm for REM-opt treatment. After REM-opt treatment, 70.6 nm of diameter was obtained in the latter patterns. Figure 12 demonstrates that the resist and shrunk patterns allow the etching of the SiO$_2$ films during maintaining the CD. This result indicates that the shrunk region is estimated to have the same etching resistance as the resist itself. Therefore, REM-opt enables us to use for LSI fabrication.

3.6 Surface analysis
TOF-SIMS analysis was performed using Resist B and its post-REM-opt-treated and DIW-rinsed samples. Table 2 compares the peak intensities normalized by the total ion counts of C$_2$H$_3$O ($m/z = 43$) fragment peak associated with the acetate group in the PVA
In the sample of post-REM-opt treatment followed by DIW rinse, we observed the C$_2$H$_3$O peak with enough high intensities when it was compared to Resist B. The result shows that the PVA exists in the thickened region on the resist surface even after DIW rinse. Therefore, it is obvious that the thickened region is not formed by resist swelling but by the REM treatment. Further analytical investigation of the reaction mechanism is undergoing.

4. Conclusions

New resolution enhancement materials using a PVA and 2HBA system have been described. The system worked quite efficiently to thicken resist patterns to produce smaller hole or space patterns printed on alicyclic methacrylate 193-nm resists. The combination of 2HBA and an alcohol-ethoxylate surfactant (TN-80) successfully fabricated the shrunk patterns with small CDs, pitches, and pattern shapes dependence on shrinkage. The dry etching of the underlying SiO$_2$ films was successfully performed using the shrunk resist patterns, indicating that they had the same etching resistance as the resist itself. This REM system can be used to shrink 193-nm resist patterns for fabricating not only memory devices but also logic devices. Application of the REM system can be extended to an acrylate platform using EUV (extreme ultraviolet) resist materials for smaller dimensions. Since the reaction mechanism of the REM system had not been clarified yet, the investigation of the reaction mechanism is undergoing.

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