Dual-mode Behavior of Vinyl Ether Functionalized Photoresist

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1. Introduction

One of the targets in microresist researches is to design the photoresist that is able to produce quarter-micron patterns with high aspect ratio. The positive resist based on the photomodification of 1,2-naphthoquinone diazide 5-sulfonate (NQD) has been used for long years as a photoresist providing the highest resolution for g-line or i-line exposure. However, NQD resist seems not to be used for the excimer laser or deep UV lithographic process judging from the composition that it has a strong absorption in the deep UV wavelengths.

A series of dual-mode photoresists (VEC) based on the unique reactions of vinyl ether groups have been studied and found to provide the high resolution with the deep-UV exposure. The VEC resists behave as a dual-mode resist which works as a negative and a positive resist depending on the process after the exposure. The schematic expression of the reaction of the VEC resist is shown in Figure 1.

When the resist layer coated on a wafer is exposed to the light after prebaking at the temperature lower than 80°C, it works as a negative resist where the resist in exposed areas are insoluble to developer. On the other hand, if the prebake temperature is higher than 100°C, the whole layer on a wafer is completely insoluble in an aqueous base or common organic solvents, suggesting the resist polymers are crosslinked at this prebake temperature. Then, with the exposure, PAG existing in the layer generates the acid, which decrosslinks the polymer via an acidolytic reaction to recover the solubility of the resist polymer. Figure 2 demonstrates the solubility change of the VEC resist with respect to the patterning process together with those of conventional NQD positive resist.

Fig.1 Reaction scheme of dual-mode photoresist.

Fig.2 Comparison of solubility change of vinyl ether resist and NQD/novolak resist
2. Chemical reactions involved in VEC resist

While several reactions are possible to use for the dual-mode resist mentioned above, the reaction mode of vinyl ether compounds has been chosen for the present study. Vinyl ethers have been studied extensively as an alternatives of acrylate monomers. Vinyl ether groups with electron rich bonds produce the stable carbocations that initiate rapid cationic polymerization. The cationic polymerization of vinyl ethers offers highly sensitive photopolymers because of both their large kinetic chain length and their oxygen insensitivity. Vinyl ether functionalized monomers and prepolymers and polymers bearing vinyl ether groups in the side chain have been studied. Basic reaction mechanisms such as cationic polymerization and the acid-catalyzed hydrolysis of vinyl ethers have also been studied. However, the application of vinyl ethers to photosensitive materials has been focused on the oxygen insensitive polymerization and the use of the vinyl ether reactions in terms of acidolysis or addition reaction to hydroxyl groups has not been reported so far.

As is shown in Scheme 1, the vinyl ethers perform three different reactions depending on the ambient conditions. The vinyl ethers are converted very rapidly to carbocations in the presence of acidic species. The carbocations initiate the cationic polymerization of vinyl ether monomers to produce the corresponding polymers as far as the enough amount of vinyl ether monomers is present. However, if the vinyl ether monomers are not enough for the occurrence of the cationic polymerization, the carbocations perform a different reaction to produce aldehyde and alcoholic compounds with aid of a small amount of water in the ambient moisture. Further, the vinyl ether groups readily react with acidic compounds involving phenolic or carboxylic groups and produce acetal compounds. The acetal bonds are very sensitive to acid to undergo the acidolytic reactions. The combination of these reactions gives the VEC resist.

\[
\begin{align*}
\text{Scheme 1:} & \\
\text{Cationic Polymerization} & \\
\text{Acidolysis} & \\
\end{align*}
\]
3. Design of photosensitive polymer materials.

Based on the unique reactions of vinyl ether groups mentioned above, a series of photoresists have been synthesized. Table 1 summarizes the structures and some other properties for the VEC resist.

Table 1 Examples of vinyl ether functionalized photopolymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Crosslinkers</th>
<th>PAG's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cresol novolak resin</td>
<td>R-O-CH(_2)-O-CH(_2)-OH</td>
<td>ANS-DPI, MMA-methacrylate, BMAm-butylmethacrylate, AA-Acryl acid</td>
</tr>
<tr>
<td>Poly(p-hydroxystyrene)</td>
<td>R-O-CH(_2)-O-CH(_2)-OH</td>
<td>ANS-DPI</td>
</tr>
<tr>
<td>Poly(MMA-BMA-AA)</td>
<td>R(_1)-CH(_2)-O-CH(_2)-CH(_3)</td>
<td>Ph(_2)-CF(_3)-SO(_2)-</td>
</tr>
<tr>
<td>Poly(p-hydroxystyrene-co-p-vinloxy ethoxystyrene)</td>
<td>R(_2)-CH(_2)-O-CH(_2)-CH(_3)</td>
<td>ANS-DPI</td>
</tr>
</tbody>
</table>

4. Characteristics of VEC resists

Fig.3 demonstrates the characteristic curves of VEC-2 which were determined with the prebake condition that the crosslinks are not formed. The curves exhibit quite different behavior depending on the concentration of PAG. When the concentration of PAG is 5wt.%, the curve behaves like a negative resist. However, if 15wt.% PAG is present, the curve exhibits like a negative resist with the lower exposure energy, and then like a positive resist with the higher exposure energy. These curious behaviors of the VEC resist can be explained by considering the manifold reaction paths of the vinyl ether groups. With respect to the curve for 15wt.% PAG, the amount of photoacid generated by exposure is small in the low exposure energy region, and therefore the cationic polymerization occurs via the formation of carbocation to make the polymer insoluble. With the higher exposure energy, a large amount of acid is generated and most of the vinyl ether groups are converted to carboxations. And the concentration of the remaining vinyl ether monomers are too low to undergo the cationic polymerization. As the result, the decomposition of the vinyl ether monomers may be prior to the polymerization.

![Fig.3 Characteristic curves of VEC-2](image)

After the prebaking at 120°C for ten min, the layer is completely insoluble in organic solvent or an aqueous base developer. With imagewise exposure and the successive baking (PEB), the layer is again soluble in developer to give the positive patterns. The spectral sensitivity is governed by that of PAG from deep UV to visible light. As an example, a SEM picture of 0.3 μm L/S patterns are shown.

![Fig.4 Characteristic curves of three component resists](image)
In three component systems, an aqueous base soluble polymers containing phenolic or carboxyl groups, multifunctional vinyl ether monomers and PAG are the principal composition. The three component systems offer also the dual-mode to work as a negative or a positive resist depending on the process condition. Fig.4 shows the characteristic curves for negative and positive resist. The lithographic characteristics is variable depending on the structures of matrix polymer, functionality of vinyl ether monomer, PAG and on the process condition. In Table 2, examples of the lithographic characteristics of three component systems using three kinds of aqueous base soluble polymers. Detailed reaction mechanisms and resist characteristics will be discussed.

Reference:
5) F.A.M. Abdull-Rasoul, A. Ledwith, Y. Yagci, Polymer, 1978, 19, 1219