APPLICATION OF PHOTOSENSITIVE SILICONE—CONTAINING GRAFT POLYMERS SYNTHESIZED FROM MACROMONOMER TO MICRO LITHOGRAPHY

Yoshio TACHIBANA, Yasutaro YASUDA
Research Laboratory, Toagosei Chemical Industry Co., LTD.
Fumami-cho, Minato-ku, Nagoya-shi, Aichi 455

Ken-ichi KOSEKI, Tsuguo YAMAOKA
Faculty of Engineering, Chiba University
Yayoi-cho, Chiba-shi, Chiba 260

We synthesized photosensitive silicone-containing graft polymers from macromonomer to apply to micro lithography. In this paper, we describe the synthesis and the resist properties of the graft polymers.

The photosensitive silicone-containing graft polymers (Si-GP(AA), Si-GP(CA), Si-GP(N₃)) were obtained by the reaction of acrylic acid (AA), cinnamic acid (CA), and p-azidobenzoic acid (N₃) with glycidyl groups of silicone-containing graft polymer which was polymerized from silicone macromonomer (I) (Mn=1,000), glycidyl methacrylate and methyl methacrylate. Another silicone-containing graft polymer (GS-30) was polymerized from silicone macromonomer (II) (Mn=4,000) and methyl methacrylate. Fig. 1 shows the structures of photo-sensitive silicone-containing graft polymers. The silicon contents of these polymers were 8-10 wt%. The contents of monomer unit, having photosensitive group, in Si-GP(AA), Si-GP(CA) and Si-GP(N₃) were about 45 wt%. i-line (365nm) or deep UV light (254nm) exposure were used for lithographic printing.

Received April 12, 1988
Accepted May 14, 1988
characteristic evaluation.

Table 1. summarizes the molecular parameters of the silicone-containing graft polymers as well as their resist properties for 365nm or 254nm light. As CA and N₃ groups exhibit their absorption spectra in deep UV region, Si-GP(CA) and Si-GP(N₃), the sensitivity values(Dg°•5) of which were 13.5 mJ/cm² and 5.7 mJ/cm², respectively, had high sensitivities for deep UV light. The graft polymers showed a sensitivity only in deep UV region, while they have no sensitivity for i-line. However, by the addition of spectral sensitizer such as diazidochalcone and NDBE, the resists showed a high sensitivity (Dg°•5) of about 100 mJ/cm² for i-line exposure. The resists were spin-coated (0.2µ m in thickness) on a hard-baked phenol novolak resin (1.5µ m in thickness) and patterned by i-line or deep UV light and etched by O₂ RIE (O₂ flow: 30sccm, pressure: 2.3mTorr, power: 1,000W, time: 2min30sec). Fig.2. shows a SEM photograph of fine patterns by O₂ RIE process using GS-30/diazidochalcone(100/15) as a top resist. It is shown that the fine line pattern (0.5µ m) were transfered to phenol novolak resin by dry etching with O₂ RIE.

The photosensitive silicone-containing graft polymers have been studied as a top layer for a bilayer resist system. High sensitivity, high resolution and high resistance to O₂ RIE were obtained.

<table>
<thead>
<tr>
<th>Composition of Resist</th>
<th>Exposure</th>
<th>Molecular weight of polymer (Mn x 10²)</th>
<th>Dg°•5 (mJ/cm²)</th>
<th>Ph.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS-30/diazidochalcone</td>
<td>30sec</td>
<td>6.76</td>
<td>15.2</td>
<td>87</td>
</tr>
<tr>
<td>Si-GP(CA)/NDBE (100/15)</td>
<td>30sec</td>
<td>7.62</td>
<td>5.4</td>
<td>840</td>
</tr>
<tr>
<td>Si-GP(CA)</td>
<td>30sec</td>
<td>5.37</td>
<td>3.6</td>
<td>13.5</td>
</tr>
<tr>
<td>Si-GP(CA)/NDBE (100/15)</td>
<td>30sec</td>
<td>4.08</td>
<td>2.24</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*Fig. 1 Exposure 450
**NDBE :