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ArF Single Layer Resist Composed of Alicyclic Main Chain Containing Maleic Anhydride

Jae-Chang Jung, Cheol-Kyu Bok and Ki-Ho Baik

Memory R&D division, Hyundai Electronics Industries Co., Ltd., San 136-1, Ami-ri, bubal-eub, Ichon-si, Kyongki-do, 467-701, Korea

ArF excimer laser (λ = 193nm) lithography is emerging following KrF DUV lithography (λ = 248nm). 193nm lithography has proven its potential for feature sizes down to 0.15µm lines/spaces patterns using high NA (0.6) because of resolution improvement. However, in practical use of ArF technology, there are problems involved in the properties of photosist. To solve these problems, we synthesized ArF polymer resin, poly(2-(2-hydroxyethyl)carboxylate-5-norbornene / 2-t-butylcarboxylate-5-norbornene / 2-carboxylic acid-5-norbornene / Maleic anhydride), all of the main chains are composed of alicyclic unit. 2-(2-Hydroxyethyl) carboxylate-5-norbornene was found as a very suitable adhesion promoter. Using this resist, 0.15 µm L/S pattern was obtained at 14mJ/cm² doses, using an ArF stepper on the developer, 2.38wt% tetramethyl ammonium hydroxide aqueous solution.

Keywords: ArF resist, 2-(2-Hydroxyethyl) carboxylate-5-norbornene, 2-t-butyl carboxylate-5-norbornene

1. Introduction

ArF excimer laser (λ = 193nm) lithography is a potentially applicable technology for sub 0.15µm design rule. However, in practical use of ArF technology, there are many problems involved in the properties of photosist such as light transparency for 193nm, dry etching resistance, adhesion, sensitivity and use of 2.38wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution as a developer. A lot of research efforts have been focused on solving these problems. To increase the dry etch resistance, alicyclic unit was introduced as a pendant group [1-8]. Recently it has been reported that an alternating copolymer of norbornene and maleic anhydride is a new matrix resin for ArF resist polymer[9]. To work out these problems, we synthesized ArF polymer resin, poly(2-(2-hydroxyethyl)carboxylate-5-norbornene / 2-t-butylcarboxylate-5-norbornene / 2-carboxylic acid-5-norbornene / Maleic anhydride; HN / BN / AN / MA), all of the main chains are composed of alicyclic unit. In this paper, we will describe the introduction of HN unit and the lithographic performance results will be demonstrated.

2. Method

2.1 Preparation of monomer

2-(2-hydroxyethyl)carboxylate-5-norbornene (HN) was prepared by Diels-Alder reaction between cyclopentadiene and 2-hydroxyethyl acrylate. The reaction product was purified by vacuum distillation.

2-t-butylcarboxylate-5-norbornene (BN) was prepared by Diels-Alder reaction between cyclopentadiene and t-butylacrylate. The reaction product was purified by vacuum distillation.

2-carboxylic acid-5-norbornene (AN) was prepared by Diels-Alder reaction between cyclopentadiene and acrylic acid. The reaction product was purified by vacuum distillation.

2-methand-5-norbornene (MN) and maleic anhydride was purchased from Aldrich and used without further purification.

2.2 Polymerization

All the polymers were synthesized by radical polymerization. Monomers (MN, HN, AN, BN and MA) were dissolved in tetrahydrofuran (THF)
solution and N,N'-azobis(isobutyronitrile)(AIBN) was added to this mixture solution as a radical initiator. After the reaction, the reaction mixture was diluted by the addition of TIC. Then the polymer solution was precipitated in an ethyl ether solution and purified. The synthetic scheme is showed in Fig. 1.

2.3 Measurements
All monomers and polymers were characterized by Bruker DPX 300MHz spectrometer and the exposure was performed in an ArF stepper.

3. Results and discussion
3.1 Characterization of resist polymer
The lithographic properties of synthesized polymers are summarized in Table 1. We used BN monomer as a dissolution inhibitor and two MN and HN monomers as a adhesion promoter. But comparing the solubility of two polymers in Table 1, poly2 and poly5, we observe that MN unit gives a very soluble properties to the resist polymer. The NMR spectra explain this phenomena. Fig. 2(a) shows the NMR spectra of poly(BN/MA). There is no peak at 3.5 ~ 4.5ppm. But methylene proton peaks of -CH2-OH(MN) and -CO-CH2-CH2-OH(HN) appear at this region. If we assume that maleic anhydride is incorporated alternatively in polymer and hydroxy group is not considered in calculation, we can easily obtain actually incorporated monomer ratio in polymer by comparing of integral values. These data are shown in Table 2. As MN and HN are smaller molecule than BN, they easily incorporate in polymer than...
Fig. 2. NMR spectra of (a) BN/MA=1:1, (b) poly2, (d) poly5, (d) poly7

Table 1. Lithographic properties of polymers

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Mole ratio in feed (MN/AN/BN/MA)</th>
<th>*Solubility in 2.38% TMAH</th>
<th>Sensitivity (0.20 µm L/S pattern)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly1</td>
<td>(0.50/0.00/0.00/0.50/1.00)</td>
<td>very soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly2</td>
<td>(0.35/0.00/0.00/0.65/1.00)</td>
<td>very soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly3</td>
<td>(0.00/0.60/0.00/0.40/1.00)</td>
<td>slightly soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly4</td>
<td>(0.00/0.50/0.00/0.50/1.00)</td>
<td>slightly soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly5</td>
<td>(0.00/0.40/0.00/0.60/1.00)</td>
<td>slightly soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly6</td>
<td>(0.00/0.20/0.00/0.80/1.00)</td>
<td>insoluble</td>
<td>44mJ</td>
</tr>
<tr>
<td>poly7</td>
<td>(0.00/0.15/0.05/0.80/1.00)</td>
<td>insoluble</td>
<td>78mJ</td>
</tr>
<tr>
<td>poly8</td>
<td>(0.00/0.15/0.08/0.77/1.00)</td>
<td>soluble</td>
<td>14mJ</td>
</tr>
<tr>
<td>poly9</td>
<td>(0.00/0.20/0.05/0.75/1.00)</td>
<td>slightly soluble</td>
<td>—</td>
</tr>
<tr>
<td>poly10</td>
<td>(0.25/0.25/0.00/0.50/1.00)</td>
<td>very soluble</td>
<td>—</td>
</tr>
</tbody>
</table>

*All the solubility data was obtained after developing in 2.38 wt% TMAH solution for 40 second.

Table 2. Mole ratio of monomer in polymer

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Mole ratio in feed (MN/BN/MA)</th>
<th>*Actual mole ratio of monomer in polymer (MN/BN/MA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly2</td>
<td>(0.35/0.65/1)</td>
<td>(0.87/0.13/1)</td>
</tr>
<tr>
<td>poly5</td>
<td>(0.40/0.60/1)</td>
<td>(0.52/0.47/1)</td>
</tr>
<tr>
<td>poly6</td>
<td>(0.20/0.80/1)</td>
<td>(0.37/0.63/1)</td>
</tr>
</tbody>
</table>

*It was derived by NMR spectra on the assumption that maleic anhydride is incorporated alternatively in polymer and hydroxy group is not considered in calculation.

BN. Especially the smallest molecular MN unit incorporates readily in polymer. Considering the polymerization yield and composition control, the small MN unit is not suitable to the bulky BN blocking unit as a component of adhesion promoter.

3.2 Lithographic performance

Polymer and photo acid generator(PAG) were dissolved in methyl-3-methoxypropionate(MMP). The solution was filtered through 0.2 µm membrane filter.

Evaluation was performed on poly5, poly6, poly7. Poly5, and poly6 (44 and 78mJ/cm² for 0.20 µm L/S) was not sensitive but poly7 was comparatively sensitive (14mJ/cm² for 0.15 µm L/S). Carboxylic acid group in poly7 affects the sensitivity of resist polymer. The SEM micrographs of poly7 are shown in Fig. 3. 0.15 and 0.16 µm L/S pattern are well defined at 14 mJ/cm², with rounding profile.

4. Conclusion

We have synthesized the ArF resist polymers composed of alicyclic main chain. Using this resist, 0.15 µm L/S pattern was obtained at 14mJ/cm² exposure by ArF stepper on the conventional 2.38w% TMAH solution. In this study, we can find out that monomer molecular size plays a key role in the design of resist, especially, in the case of alicyclic main chain. If all components have similar size, it will give better yield and suitable composition control. Our adhesion promoter, HN, is very suitable to the bulky blocking unit.

References
Fig. 3. SEM Micrographs of poly (HN/BN/AN/MA=0.15/0.80/0.05/1.00) photoresist pattern
(ArF, 0.60NA, 14mJ/cm², 2.38wt% TMAH)