A New Type of Binder Resins Used in PS Plate and Positive Photoresists: Resorcin—Divinyl Benzene Resins

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The Friedel—Crafts reaction between divinyl benzene (DVB) and resorcin produced a new type of photopolymer. When resorcin—DVB resins used in negative photoresists, 2um resolution can be reached [1]. When resorcin—DVB resins used as binder resins of PS plate and positive photoresists, they can fit with many kinds of photoactive compounds (PAC). The resolution of the positive resists can be lower than 0.95 um. The exposure and developing rates of the positive photoresists are fast and they have good alkali resistance. Resorcin—DVB resins can be used as the ballast resins of diazonaphthoquinone (DNQ) group to synthesize DNQ—PAC. The positive photoresists whose PAC are resorcin—DVB diazonaphthoquinone have high resolution and the forming image has high contrast. During research, we also found that the alkali resistance of binder resin is closely relevant to the M/A value of the resin and the alkali resistance of PAC is closely relevant to the M/A value of the ballast resin.

Keywords: resorcin—DVB resin, binder resin, ballast resin

1. Introduction

The binder resins widely used in integrated circuit and PS plate are still the lined novolac resins showed as the formula (1), which are condensed by cresol and formadehyde.

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{C}_6\text{H}_2 & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2
\end{align*}
\]

where \(n:m=(5\sim10):(5\sim0)\), mostly \(n:m=(6\sim7):(4\sim3)\).

However, a lot of studies and facts show that there are many problems existing in cresol—formadehyde resins. For example, first, it is difficult to control molecular weight and molecular weight distribution in the synthesis of cresol—formadehyde resins. Second, strong acid is not proper used as catalyst of the synthesis. Third, the control of micro-structure of the resins is difficult, but the micro-structure has large effects on the properties of the resins. Fouth, the M/A value, the ratio of the total mass of phenol resin (M) to the total mass of the hydroxy group (A), is almost constant, about 7.0. Then, difficulty may exist in controlling resist sensitivity, alkali resistance and film retention. Their correlation to the M/A value is discussed later in this paper.

This paper introduces a new series—Resorcin—Divinyl Benzene Resins. The resins have special virtues when used as binder resins of positive photoresists. Moreover, they can be used as ballast resins of DNQ group.

2. Experimental

2.1. Synthesis of resorcin—DVB resins (A series resins)

Into a 100 ml four—necked round bottom flask equipped with stirrer, a reflux condenser,
a 200°C thermometer and a dropping funnel, 22.0g (0.20mol) resorcin and 0.20g (0.0033mol) oxalic acid were charged with stirring. The flask was heated till resorcin completely melted, then divinyl benzene was dropped from the dropping funnel. Keep the dropping rate at one drop per second to one drop per two second. After dropping, keep the reaction at 120~140°C for 4 hours, then rise up the reaction temperature slowly to 180°C and keep at the temperature for 1 hour. Finally, distillate the small molecular material and unreacted monomer at reduced pressure.

2.2. Differential thermal analysis of resorcin-DVB resins

 Carry differential thermal analysis on A series resins with BIOF differential thermal analysis instrument.

2.3. Synthesis of the DNQ—PACs whose ballasts are resorcin—DVB resins

B series DNQ—PACs was synthesized by the introduction of DNQ group to resorcin—DVB resins [2].

2.4. Preparation and characteristics of positive photoresists

2.4.1. A typical photoresist is made up of three parts as follows.

(1) Binder resin, Resorcin—DVB resin 10g
(2) PAC, Diazonaphthoquinone 1 Og
(3) Solvent, Monoethyl ether glycol 90g

2.4.2. Characteristics of C series positive photoresists

C series positive photoresists are made up of A—4 resin (binder resin) and B series PACs according to different B/P value which means the ratio of the mass of binder resin to the mass of PAC. The characteristics of C series positive photoresists are performed by using RCE—mode vacuum exposure machine, 1500W metal halid light with 1.4mW/cm² of light strength.

2.4.3. Characteristics of D series positive photoresists

D series positive photoresists are made up of A—4 resin (binder resin) and polyhydroxy benzophenone diazophthoquinone such as NT—123, 4NT—250 and 4NT—300.

2.4.4. Alkali and solvent resistance and ink receptivity of the positive photoresists

Testing alkali and solvent resistance: Let PS plate whose coating quantity is 2g/cm² be soaked into five percent sodium silicate aqueous or xylene for five minutes to test the film retention.

Testing ink receptivity: After soaked into water, the PS plate with image was coated with dried skimmed cotton absorbed ink till the blackness of the image didn’t change. The times of coating are the measurement of ink receptivity of resists.

3. Results and discussion

3.1. Synthesis condition of resorcin—DVB resins

Table 1 lists different effects of different molar ratios of reactants on the properties of products.

Table 1 shows that with the increasing ratio of DVB in reactants, the softening points of the resins are increased, but the solubility in alkali aqueous is decreased.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molar ratio</th>
<th>Color of the resin</th>
<th>Softening Point(°C)</th>
<th>Solubility Alcohol</th>
<th>Solubility Acetone</th>
<th>Solubility Ethyl celloosolve</th>
<th>Solubility NaOH—H₂O(1%)</th>
<th>M/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>1.00 0.75</td>
<td>light yellow</td>
<td>74</td>
<td>easily soluble</td>
<td>easily soluble</td>
<td>easily soluble</td>
<td>easily soluble</td>
<td>6.10</td>
</tr>
<tr>
<td>A-2</td>
<td>1.00 0.80</td>
<td>light yellow</td>
<td>82</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>6.29</td>
</tr>
<tr>
<td>A-3</td>
<td>1.00 1.00</td>
<td>light yellow</td>
<td>90</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>7.06</td>
</tr>
<tr>
<td>A-4</td>
<td>1.00 1.25</td>
<td>light yellow</td>
<td>113</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>8.10</td>
</tr>
<tr>
<td>A-5</td>
<td>1.00 1.40</td>
<td>light yellow</td>
<td>120</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>soluble</td>
<td>8.59</td>
</tr>
</tbody>
</table>
Only on homogenous condition, at the range of 120–140°C, using oxalic acid as catalyst, we can succeedly synthesize resorcin—DVB resin with high softening point, good solvent solubility, light color and transparency [3].

In the synthesis of novolac resins, mid—strong or strong acid is often used as catalyst. Because of the exits of the acid, the properties of the positive photoresists whose binder resins are novolac resins would be affected. So the synthesized novolac resins must be watered to purify. To resorcin—DVB resins, oxalic acid was used as catalyst, then, at the end of reaction, make the reaction temperature up to 180°C to let oxalic acid decompose. After that, oxalic acid can not have effects on the positive photoresists and it is unnecessary to water the resins.

3.2. The differential thermal analysis of resorcin—DVB resins

Figure 1 is the differential thermal analysis figure of A—3 resin. Table 2 shows the results of differential thermal analysis of resorcin—DVB resins.

![Differential thermal analysis figure of A—3 resin](image)

Table 2. The results of differential thermal analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>Te' (°C)</th>
<th>Tm' (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A—1</td>
<td>63</td>
<td>71</td>
</tr>
<tr>
<td>A—2</td>
<td>71</td>
<td>82</td>
</tr>
<tr>
<td>A—3</td>
<td>80</td>
<td>90</td>
</tr>
</tbody>
</table>

*Te represents the temperature of heat—absorbing, Tm represents the temperature of melting.

The thermal properties of polymer differ greatly with that of small molecular compounds. Only highly crystalizing polymer can have very seemly melting point, but partly crystalizing polymer and amorphous polymer can be soften at a broad range of temperature, which have not melting point but glass transition temperature. From the differential thermal analysis figures of A—1, A—2 and A—3 resins, we can see that they all have melting points. These state that resorcin—DVB resins are highly crystalizing. Because of being highly crystalizing, after a long period of time, resorcin—DVB resins would not creep, and they have good start temperature of heating deformation (STHD). While the novolac resins used widely in PS plate and positive photoresists as binder resins almost have creep phenomena which can not be conquered, so run length of PS plate and STHD of positive photoresists are decreased. Usually, highly crystalizing resins are all difficultly soluble in alkali aqueous. For example, highly crystalizing p— cresol formadehyde resins can not be singly used as binder resins of PS plate and positive photoresists because of their difficult solubility in alkali aqueous. The synthesized resorcin—DVB resins are not only crystalizing, conquering creep and have good STHD, but also soluble in alkali aqueous. Hence, use them as binder resins, run length and STHD can be increased effectably.

3.3. The synthesis of B series PACs

Table 3 shows different results of synthesized PACs by different ballast resins

Table 3. The synthesis of B series PACs

<table>
<thead>
<tr>
<th>PAC</th>
<th>Ballast</th>
<th>Introduction ratio(%)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B—1</td>
<td>A—1</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>B—2</td>
<td>A—2</td>
<td>46</td>
<td>84</td>
</tr>
<tr>
<td>B—3</td>
<td>A—3</td>
<td>46</td>
<td>56</td>
</tr>
<tr>
<td>B—4</td>
<td>A—4</td>
<td>48</td>
<td>82</td>
</tr>
</tbody>
</table>

It is proved by solvent experiments that B series PACs have good solubility in alcohol, acetone, ester and ether, which makes it possible to use them as PACs of positive photoresists.

3.4. Resorcin—DVB resins used as ballast
resins and binder resins of positive photoresists

3.4.1. Resorcin - DVB resins used as ballast resins

The photosensitivities of C series positive photoresists made up of B series PACs and A-4 binder resin are given in table 4. In table 4, the developer is 5% aqueous solution of Na2Si03, and developing temperature is 20°C. 2-4 represents that the Kodak photographic step tablet has four steps changing color and two steps being cleared, and 2-98 represents that 2% dots of 150 line are not lost and 98% dots of 150 line is clear in the net-dot ruler. Imaging result of manufacturing plate net ruler being good means that 250 line is clear and continued in the ruler. These all demonstrate that the resolution of C series positive photoresists is high and the obtained images have high contrast.

3.4.2. Resorcin - DVB resins used as binder resins

The photosensitivities of D series positive photoresists are given in table 5. In D series positive photoresists, A-4 resin used as binder resin can fit with many kinds of PACs, such as NT-123, 4NT-250 and 4NT-300, according to different B/P value, and the formed positive photoresists have high photosensitivities.

Usually, applied binder resin can fit with NT-123 then can't fit with 4NT-300; can fit with 4NT-300 then can't fit with NT-123. Therefore, the application field of resorcin - DVB resins are wide when used as binder resin.

Table 6 gives photosensitivity results on silicon wafer of the positive photoresists made up of A-4 resin and DNQ-PAC. No. 1 is one of the C series resists which is composed of A-4 resin and B-4(PAC). Its B/P value is 4. No. 2 is the resist which is composed of A-4 resin and 3NT-160(PAC). Its B/P value is 3. Both No. 1 and No. 2 are dissolved in monoethyl ether glycol at 15% concentration.

### Table 4. The photosensitivities of C series resists

<table>
<thead>
<tr>
<th>Resist</th>
<th>PAC</th>
<th>B/P</th>
<th>Exposure (min)</th>
<th>Developing (S)</th>
<th>Step tablet (Kodak No. 2)</th>
<th>Net-dot ruler (150 line)</th>
<th>Manufacturing plate net ruler (250 line)</th>
<th>Imaging result</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>B-1</td>
<td>4</td>
<td>4</td>
<td>40</td>
<td>2-4</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-1'</td>
<td></td>
<td>2</td>
<td>2</td>
<td>25</td>
<td>2-5</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-2</td>
<td>B-2</td>
<td>3</td>
<td>4</td>
<td>40</td>
<td>3-5</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-2'</td>
<td></td>
<td>4</td>
<td>2</td>
<td>25</td>
<td>2-5</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-3</td>
<td>B-3</td>
<td>3</td>
<td>4</td>
<td>40</td>
<td>2-5</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-3'</td>
<td></td>
<td>4</td>
<td>2</td>
<td>25</td>
<td>2-4</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-4</td>
<td>B-4</td>
<td>3</td>
<td>4</td>
<td>40</td>
<td>2-4</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C-4'</td>
<td></td>
<td>4</td>
<td>2</td>
<td>25</td>
<td>2-4</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5. The photosensitivities of D series resists

<table>
<thead>
<tr>
<th>Resist</th>
<th>PAC</th>
<th>B/P</th>
<th>Exposure (S)</th>
<th>Developing (S)</th>
<th>Step tablet (Kodak No. 2)</th>
<th>Net-dot ruler (150 line)</th>
<th>Manufacturing plate net ruler (250 line)</th>
<th>Imaging result</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>NT-123</td>
<td>2</td>
<td>120</td>
<td>10</td>
<td>3-8</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>D-2</td>
<td>4NT-250</td>
<td>3</td>
<td>60</td>
<td>15</td>
<td>3-8</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>D-3</td>
<td>4NT-300</td>
<td>4</td>
<td>150</td>
<td>60</td>
<td>3-8</td>
<td>2-98</td>
<td>good</td>
<td></td>
</tr>
</tbody>
</table>
Table 6 shows that the exposure and developing rates of positive photoresists No. 1 and No. 2 are more fast than normal applied positive photoresists, whose exposure time is about 45 seconds, developer is 5% sodium hydroxide and developing time is one minute. Moreover, the exposure and developing rates of positive photoresist No. 2 are very fast. The resolutions of positive photoresists No. 1 and No. 2 are high and they both have good alkali resistance. These results state that using resorcin–DVB resin as binder resin fitting with DNQ–PAC to form the positive photoresist has great application value.

Table 7 gives the results of alkali and solvent resistance and ink receptivity of C and D series positive photoresists.

Table 7 shows that C and D series positive photoresists have good alkali and solvent resistance and ink receptivity. When binder resins are same, alkali resistance is mainly based on the quantity of PAC and alkali resistance of the PAC. The more the quantity of PAC, the stronger alkali resistance of photoresists. When the quantity of PAC is same, the difference of alkali resistance of resists is because of the difference of alkali resistance of PACs. When the backbone of ballast resins are same, the difference of alkali resistance of PACs is because of the difference of the ballast resins. Alkali resistance of resist C–1’, C–2’, C–3’ and C–4’ is different, they have same quantity of PAC, but the PACs are different. The difference of the PACs because of the difference of their ballast resins. So the M/A value of the ballast resins has effect on alkali resistance of PAC, for M/A value is closely relevant to alkali resistance of the ballast resins [3].

In table 1, we compared the M/A value of A series resins. From table 1, we can know that from A–1 resin to A–5 resin, the M/A value increases. Use A series resins as ballast resins, with the M/A value increasing, alkali resistance of the ballast resin increases, and alkali resistance of PAC increases. Alkali resistance of positive photoresists is not only relevant to alkali resistance of PAC, but also has a key factor—alkali resistance of binder resin. In research, we found that alkali resistance of binder resin is closely relevant to the M/A value of the resin. When A–3 resin is used as binder resin, alkali resistance of the positive photoresist is poor. While alkali resistance of the positive photoresist whose binder resin is A–5 is too strong and only alkali resistance of the positive photoresist whose binder resin is A–4 performs well. We found that the M/A value of binder resin with
good alkali resistance would be controlled in the range of 7.5~8.0. Therefore, if PAC with good alkali resistance is expected, the M/A value of the ballast resin should be about 8.5.

4. Conclusion
(1) The synthesis method of resorcin-DVB resins is simple and it is unnecessary to water the resins to exclude acid catalyst.
(2) Resorcin-DVB resins are highly crystalline and have crystal melting point, then conquer creep phenomena.
(3) Use resorcin-DVB resins as ballast resins to synthesize PACs. When the PACs used in positive photoresists, then the positive photoresists have high resolution and the forming images have high contrast.

(4) Resorcin-DVB resin used as binder resin of positive photoresists, can fit with many kinds of PACs and can be used in wide application fields.
(5) Alkali resistance of binder resin is closely relevant to the M/A value of the resin. Alkali resistance of the PAC is closely relevant to the M/A value of the ballast resin.

5. Reference