Inhibition and Promotion Efficiency of Bis-phenol Type Dissolution Inhibitors During Development

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This paper focuses on the inhibition and the promotion efficiency of inhibitors in a novolac resin respecting dissolution rate into a developer. Several t-Boc derivatives of bis-phenols, which have different substituent groups on their methyl carbon, were synthesized as model compounds. Their properties were evaluated in the case of adding to a novolac resin. It was observed that the bulky substituent groups provided the inhibitors with a high inhibition efficiency, though polarity group such as esters, impaired inhibition efficiency. On the contrary, the decomposed form of inhibitor which containing ester group, promoted dissolution rate of resist efficiently. The authors have reported the high performance of the t-Boc derivative, named CP-Tboc which contained a lactone ring as a bulky substituent group. The decomposed form of CP-Tboc in the exposed area exhibits high promotion efficiency. To compare the promotion efficiency of CP-Tboc with an inhibitor having ethyl ester group, it was confirmed that the hydrolysis of lacton ring during the development increases the dissolution rate. This high promotion ability is advantages in that it avoids the influence of cross-linking of matrix polymer caused by EB exposure.

Keywords: resist, dissolution inhibitor, cresolphthalein, t-Boc

1. Introduction
To obtain high performance chemically amplified resists, a number of dissolution inhibitors containing substituted phenol moieties have been synthesized and investigated. The chemical structure of each inhibitor influences its inhibition-efficiency respecting the dissolution rate. Although there have been lots of reports on the dissolution behavior of novolac based resists containing diazonaphthoquinone (DNQ) esters [1,2], few studies have been carried on the inhibition ability of t-Boc derivative inhibitors [3-6]. Aoai et al. have studied the inhibition efficiency respecting several skeletons using inhibitors with 1 to 6 phenol units [4]. They have pointed out that the hydrophobicity, molecular size and dispersion ability of acid-decomposable groups respecting the inhibitors are influential parameters. However, the promotion effect of the generated form by thermal decomposition on dissolution rate is also a very important point in the design of an inhibitor.

The authors have reported a unique dissolution inhibitor named CP-Tboc which contains t-Boc group and lactone ring [7]. The design concept of CP-Tboc is shown in Fig. 1. To obtain a resist with high sensitivity and high contrast, only the dissolution inhibitor in the exposed area is required to be effectively decomposed. The resulting product is also required to increase its dissolution rate of the exposed resist film in the developer beyond the original dissolution rate of the matrix resin. In the development process, CP-Tboc exhibits high promotion efficiency in novolac resin at the exposed area. It is supposed that the high promotion efficiency of CP-Tboc is caused by the hydrolysis of lactone ring in an alkaline developer. This result indicates that the selection of substituent

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group of inhibitor has a significant influence on the performance of the inhibitor. Therefore, the authors investigated the inhibition and the promotion properties of inhibitors during development, using several bis-phenol derivatives as model compounds, each of which has different substituent groups.

In this paper, the authors report the effect of the substituent groups of the bis-phenol derivatives on the inhibition and promotion efficiency, before and after the release of t-Boc group. Through this investigation, the effect of substituent group of CP-Tboc on inhibition and promotion efficiency was clarified. In addition, using CP-Tboc, the utility of promotion efficiency in EB exposure was investigated.

2. Experimental

2.1. Preparation of materials

The novolac resins (NV-1, NV-2), a copolymer of p-cresol, m-cresol and 2,5-xylenol utilized in this work were purchased from commercial sources. The dissolution rates of NV-1 and NV-2 into 0.27N TMAH aqueous solution were 63 nm/sec. and 10 nm/sec., respectively. The acid-sensitive t-Boc derivatives of bis-phenols used in this experiment were synthesized as described in the literature [8]. Bis-phenols were obtained from Honshu Kagaku Co. Ltd. The chemical structures of these dissolution inhibitors are shown in Table 1 and Table 2. Triphenylsulfonium triflate (TPS-OTf) was utilized as an acid generator.

2.2. Resist composition and processing

![Fig. 1. Conceptual scheme for CP-Tboc](image)

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**Table 1** Performances of inhibitors regarding development

<table>
<thead>
<tr>
<th>Dissolution Inhibitor</th>
<th>Structure</th>
<th>Dissolution rate (nm/s)</th>
<th>Volume of R1 (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1: H</td>
<td>R2: H</td>
<td></td>
</tr>
<tr>
<td>F-Tboc</td>
<td></td>
<td>24</td>
<td>133</td>
</tr>
<tr>
<td>A-Tboc</td>
<td>CH₃</td>
<td>H</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106</td>
<td>40.1</td>
</tr>
<tr>
<td>D-Tboc</td>
<td>CH₃</td>
<td>H</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98</td>
<td>55.7</td>
</tr>
<tr>
<td>Z-Tboc</td>
<td></td>
<td>24</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td></td>
<td>68.3</td>
<td></td>
</tr>
<tr>
<td>E-Tboc</td>
<td>CH₃</td>
<td>CO₂H</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>163</td>
<td>75.8</td>
</tr>
<tr>
<td>AP-Tboc</td>
<td>CH₃</td>
<td>H</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>107</td>
<td>79.2</td>
</tr>
<tr>
<td>PP-Tboc</td>
<td></td>
<td>6.1</td>
<td>200</td>
</tr>
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</table>

**Table 2** Performances of inhibitors regarding development

<table>
<thead>
<tr>
<th>Dissolution Inhibitor</th>
<th>Structure</th>
<th>Dissolution rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R₁: R₂ : R₃</td>
<td></td>
</tr>
<tr>
<td>AC-Tboc</td>
<td>CH₃ CH₃ CH₃</td>
<td>4.4 90</td>
</tr>
<tr>
<td>ZC-Tboc</td>
<td>CH₃</td>
<td>1.1 86</td>
</tr>
<tr>
<td>CP-Tboc</td>
<td>CH₃</td>
<td>3.3 220</td>
</tr>
</tbody>
</table>

Inhibitor: R₃=t-Boc  
Original phenol: R₃=H
The novolac resins, acid generator, and inhibitors described above were dissolved in 1-acetoxy-2-ethoxyethane. After filtration with a 0.2 µm membrane filter, the resist solution was spin-coated onto silicon wafers and baked on a hot plate at 90 °C for 5 minutes. EB exposure was carried out by using JBX-5A (20 keV accelerating voltage, JEOL Ltd.). After the post-exposure-baking process (PEB: at 90 °C for 30 min.), the resist film was developed in an aqueous base developer (AD-10: 2.38% tetramethyl ammonium hydroxide aqueous solution obtained from Tama Chemical's Co., Ltd.).

2.3. Measurements

The IR absorption spectrum was measured using micro FTIR spectrometer JANSSEN (Japan Spectroscopic Co. Ltd.) The dissolution rate of the resist films into an alkaline developer was measured using 5900 Development Rate Monitor (Perkin-Elmer Co., Ltd.).

Samples for the UV-visible absorption measurements were prepared by the following process. Individual 1.0 cm² areas of the resist film on a silicon wafer were exposed to EB as dose regions from 2.25 to 18.0 µC/cm². The exposed silicon wafer was divided into individual exposed areas. After baking at 100 °C for 5 minutes, the exposed resist film on a piece of the divided silicon wafer was then dissolved in 10 ml of AD-10. UV-visible absorption spectra were taken on a UV-3101PC spectrometer (Shimadzu Corp.).

3. Results and discussion

3.1. Inhibition efficiency and structure of dissolution inhibitors

To investigate the effect of substituent groups on the inhibition efficiency, inhibitors with simple structures were prepared. Every compound was provided with two t-Boc substituted for the phenol moieties as shown in Table 1. The inhibition efficiency of the inhibitors was examined by adding 0.0004 mole of each inhibitor to 1.0 g NV-1. The dissolution rates of the prepared resists are shown in Table 1. In this experiment, the dissolution rates of the resist films in the alkaline developer were calculated from the difference of...
the resist thickness before and after dipping into the alkaline solution. The resist thickness was measured using a Talystep (Talor Hobson).

The volume of the substituent part, $R_1$, which was calculated using MOPAC is shown in Table 1. Figure 1 is the plot of the relationship between dissolution rate of the resists and the volume of $R_1$. As shown in Fig. 1, a bulky substituent group of $R_1$ decreases dissolution rate efficiently. However, E-Tboc and PP-Tboc deviate from the others' tendency. The points of E-Tboc and PP-Tboc which have an ester structure in $R_1$ in common are displayed in a circle in Fig. 2. It is supposed that the polarity groups such as esters impair the inhibition ability.

In Table 2, the properties of inhibitors which have methyl group at their $R_2$ position are also shown. These inhibitors show higher inhibition than the inhibitors without methyl group at $R_2$.

These results suggest that the bulky substituent groups work effectively to provide a high inhibition efficiency to t-Boc derivatives of bis-phenols skeletal substances. In addition, the bulky and less polar substituent group at $R_1$ reduces dissolution rate of the resist film efficiently.

PP-Tboc has bis-phenol skeleton and a $1$-$\text{(3H)}$-isobenzofuranone structure as $R_1$ part which is the combination of bulky benzene ring and ester structure. From these experiments, it is expected that the inhibition efficiency of PP-Tboc is furnished by the bulky benzene ring and that the lactone ring works impair inhibition efficiency in the novolac resin matrix. The authors supposes that the high inhibition efficiency of the CP-Tboc is attributable to both the bulky benzene ring and the methyl group at $R_2$ position.

3.2. Promotion efficiency and structure of dissolution inhibitors

The dissolution inhibitor’s other important property, which provides a high contrast to the resist is the promotion efficiency after elimination of $t$-Boc group by acid catalyzed thermal reaction.

Instead of the resist of exposed area, the resist samples containing the original phenol compound of each inhibitor were prepared. The dissolution rates of resist containing $0.0004$ mole of the original phenol compound in $1.0$ g of NV-1 are shown in Table 1. The original phenols have no $t$-Boc group on $R_2$.

Figure 3 is the plot of the relationship between dissolution rate of the resists shown in Table 1 and the volume of $R_1$. From the figure, it is recognized that each original phenol promotes the dissolution rate of matrix resin. However, the resists containing original phenols of E-Tboc and PP-Tboc exhibit high promotion ability, whereas the others remain at a lower level. This result is also assignable to the existence of an ester group at the $R_1$ position. It is supposed that the polar groups, such

![Fig. 4. IR spectra of CP-Tboc](image)

![Fig. 5. UV-visible spectral change of resist containing CP-Tboc dissolved in aqueous base](image)
as ester groups, provide a high promotion ability of dissolution to the deprotected form of the dissolution inhibitor.

3.3. The effects of the substituent groups of CP-Tboc in resist process

From the result, it is recognized that the lactone ring of PP-Tboc works as the promotion factor during development.

The authors have reported the reaction mechanism of CP-Tboc in the resist film during the resist process. The proposed scheme is explained in Scheme 1. The scheme was ascertained by the following experiment, using spectral analysis.

The survival of lactone ring of CP-Tboc through the resist film formation was examined using IR spectrum. The IR spectrum of CP-Tboc is shown in Fig 4. The sample for the IR spectrum measurement was prepared by casting CP-Tboc from a THF solution on a KBr plate. In the spectrum, no absorption band which was assigned to -OH vibration, was observed around 3000 cm⁻¹. This result indicates that the lactone ring of CP-Tboc survives resist film formation on a substrate.

The hydrolysis of decomposed form in the exposed area during development was investigated using UV spectrum. Figure 5 shows the UV-visible absorption change of the developer when the resist films containing CP-Tboc and an acid generator were exposed, where the exposure dose is a parameter. The UV-visible absorption of the solution containing an exposed resist exhibited an absorption maximum at 568.5 nm, which coincided with that of the o-cresolphthalein’s colored form (4) in alkaline developer.

Corroborated by these analytical proof, the experimental result that the promotion efficiency of PP-Tboc and CP-Tboc surpasses that of E-Tboc whose ester group is not hydrolyzed easily also supports the chemical sequence presented in Scheme 1.

3.4. Effect of promotion efficiency on resist properties

The promotion efficiency dose not work only to increase resist’s contrast.

To investigate the promotion efficiency using CP-Tboc, A-Tboc was employed as a reference substrate. In the experiment, the authors employed CP-Tboc because CP-Tboc is more soluble in organic solvent than PP-Tboc. The prepared resists, containing 0.00047 mol wt% of CP-Tboc and A-Tboc in novolac resin of NV-2, were named CP-NV and A-NV respectively. As an acid generator, 1 wt% of TPS-OTf was also added to the resists.

To compare the behaviors of the inhibitors in the exposed region, the relationship between the decomposition ratio of t-Boc group and the dissolution rate of the films were measured.

The decomposition ratio of t-Boc was calculated from absorption change of IR spectra. Figure 6 and Fig. 7 display the IR spectra of A-NV and CP-NV. Because CP-Tboc contains two carbonyl groups, it is difficult to calculate the decomposition ratio using absorption change of C=O vibration. Hence, the decomposition rate was calculated using C-O-C absorption change. The relationship between decomposition ratio of t-Boc group and exposure dose of A-NV and CP-NV is shown in Fig. 8. From this figure, it become obvious that the
concentration of decomposed A-Tboc is higher than that of CP-Tboc at the dose region lower than around 10 mC/cm².

In Fig. 9, the dissolution rate of these resists are shown. The curves in Fig. 9 follow the decomposition behaviors of CP-Tboc and A-Tboc. However, the highest dissolution rate of CP-NV is obtained at higher exposure dose than A-NV, and CP-NV shows higher dissolution rate in all the dose area.

Promotion efficiency respecting the resist performance is clarified in the exposure area. In Fig. 10, the characteristic curves of A-NV and CP-NV are shown. As shown in this figure, the negative tone property of A-NV is observed in the high dose region. For reference purposes, the case of NV-2 containing 1wt% TPS-OTf is added in Fig. 10. From these curves, it is expected that the cross-linking of matrix resin is responsible for limiting exposure dose margin. Though the sensitivity of A-NV and CP-NV are similar, CP-NV shows poor susceptibility to the influence of cross-linking of the matrix resin.

These experimental results indicate the promotion effect is advantageous in that it avoids the effect of cross-linking of matrix polymer in wide exposure region.

4. Conclusion

Several t-Boc derivatives of bis-phenols were synthesized and their properties were evaluated in novolac resin. It was observed that the bulky substituent groups worked effectively to provide a high inhibition efficiency to t-Boc derivatives of bis-phenols skeletal substances. Hence, the ester structure impaired inhibition ability of the dissolution inhibitor. On the contrary, the ester group of the inhibitor induced higher promotion efficiency to the exposed area of the resist. These results indicate that the substituent group which has a good combination of polarity and volume would bring about the high performance of the inhibitor.

Inhibitors which contain 1-(3H)-isobenzofuran-
furanone as a bulky substituent group exhibit high inhibition and promotion efficiency. The promotion ability of the inhibitors exceeds the promotion efficiency of the ethyl ester group. This result supports the hydrolysis process shown in Scheme 1, which was presented by authors.

It was proved that the high promotion property could successfully decrease the influence of cross-linking of matrix resin which impaired the exposure margin.

References