Structural Effect of Polymer and Inhibitor on Alkali Dissolution and Dissolution Inhibition Characteristics

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The relationship between the higher structure of resist polymers, such as novolak (NVK) and poly(hydroxystyrene) (PHS), and their alkali dissolution and dissolution inhibition characteristics were investigated. From the calculations of the polymers with molecular mechanics (MM) and molecular dynamics (MD), NVK exhibited the structure with intramolecular hydrogen bondings through ortho-ortho methylene bonds, while PHS formed them through the OH group on ortho position, thereby both giving oriented structures with OH groups in the molecular interior. The alkali dissolution of the polymers having such higher structures showed lower values, and these tendency corresponded to the interpretation of percolation mechanism with respect to the alkali dissolution of polymers. In order to estimate the higher structures of the polymers, the n values in the Henderson-Hasselbach equation were measured. The increase in the n values resulted in the decrease in the alkali dissolution of the polymers. Furthermore, the structural factors of dissolution inhibitors on chemical amplification resist were also studied for their inhibition characteristics. The acid decomposition of inhibitors were stepwise proceeded resulting in that the dissolution inhibitors significantly lost their inhibition ability at a certain step in decomposition. With selective use of this step, the dissolution discrimination of the resist could be improved.

Keywords: novolak, poly(hydroxystyrene), higher structure, Henderson-Hasselbach equation, dissolution inhibitor

1. Introduction

The integration level of semiconductor devices has increased 4-fold per 3 years, and currently semiconductors with 64 to 256 M bits (for design rules; 0.35-0.25 µm) are being produced. These developments are greatly indebted to the improvement in optical and processing technologies and also to the improvement in lithographic technology, especially in the performance of resist materials. This has resulted from the advance in the fundamental knowledge of the alkali dissolution and dissolution inhibition mechanism of resist films, and also from the scrupulous design of resist polymers and inhibitors based on such knowledge [1-5].

NVK and PHS, which are generally used as resist polymers, are similar amphiphilic resins having both hydrophilic part and hydrophobic part. However, the two differ significantly in the alkali dissolution rates [6,7]. P-PHS and o-PHS, which vary in the position of the OH group, also differ in the dissolution rates [8]. These are probably due to the differences between the secondary and tertiary structures of the polymers that are derived from the monomer structures and compositions. With respect to alkali dissolution and dissolution inhibition mechanism, Reiser et al. have proposed the percolation theory as the generic interpretation for resist polymers [9]. According to this theory, the developer base acts to diffuse through the hydrophilic channels formed in the resist film by the hydrophilic OH groups, by which the dissolution of the polymer is proceeded. Therefore the dissolution
rate corresponds to the density of the hydrophilic groups in the films, that is, the number of the hydrophilic channels. The alkali dissolution is inhibited by inhibitor compounds added to the film to shield the hydrophilic channels. These behaviors are basically considered the same in both diazo naphtho quinone (DNQ) resist and chemical amplification resist.

The purpose of this report is, therefore, to discuss the relationship between the higher structures (especially secondary and tertiary structures) of NVK and PHS, and the alkali dissolution. In addition, herein discussed is the structural effect of inhibitors that are used for dissolution inhibition of the polymers.

2. Experiments

2.1. Syntheses of Materials

[m/p-Cresol NVK]
An aqueous solution of 37 % formalin was added to the predetermined amounts of m- and p-cresol monomers, in molar ratio of 0.85-0.95 (formalin/monomer). Oxalic acid as a catalyst was added thereto and then reacted at 100°C for 15 hours. Next, the reaction mixture was further heated up to 200°C, and then gradually degassed to 5 mmHg. NVK resin was obtained by distillation of water, the non-reacted monomer and oxalic acid.

[o/p- or m/p-co-PBS]
The predetermined mixtures of o- and p-acetoxystyrene or m- and p-acetoxystyrene were dissolved in 1-methoxy-2-propanol at 30 wt% concentration, and 0.3 mol% (to the monomers) of azobis(isovaleronitrile) was added thereto and heated at 70°C in N2 flow for 2 hours with stirring. 0.3 mol% of azobis(isovaleronitrile) was further added and heated for 2 hours under the same condition as above. This procedure was repeated two times. Finally, these were heated at 90°C for 1 hour. The resulting reaction solutions were poured into de-ionized water, and the polymers thus precipitated were dried and then hydrolyzed with 25% tetramethylammonium hydroxide (TMAH) in methanol. After neutralization with hydrochloric acid co-polymers of o/p- or m/p-PHS were obtained.

[t-Butyl ester inhibitors]
Low molecular phenolic compounds with three to six OH groups were dissolved in N,N-dimethyl acetamide. 1.1 molar amount of K2CO3 and then 1.05 molar amount of t-butyl bromoacetate to the phenolic OHs were added to the solutions. After the reaction for 5 hours at 120°C with stirring, the solutions were poured into water and the products were extracted with ethyl acetate. The extracts were concentrated under reduced pressure, followed by purification in silica-gel column chromatography (eluent : hexane/ethyl acetate). Fully esterified products were obtained in 70-80 % yields.

[t-Butyl carbonate inhibitors]
The same phenolic compounds used above were dissolved in THF, and the equimolar amount of t-BuOK was added to the solutions. The 1.1 molar amount of di-t-butyl dicarbonate was added dropwise to the reaction mixtures with stirring. The stirring was continued for 3 hours at room temperature. Isolation and purification were carried out in a similar manner as above. The yields of fully substituted products by carbonate groups were 80-90 %.

2.2. Measurement of Dissolution Rate of Polymers
The polymers were dissolved in 2-ethoxyethyl acetate, and spin-coated onto a bare silicon wafer. The polymer films with 1.0 µm thickness were obtained after baking at 120°C for 60 seconds. The dissolution rates of the films were measured by using Perkin-Elmer’s DRM (dissolution rate monitor). An aqueous solution of 0.262 N TMAH was used for determining the dissolution rates.

2.3. Determination of Dissolution Inhibition
1.0 µm thickness films of a composition of 25 wt% inhibitor / 75 wt% polymer were obtained in the same manner as in the above. The dissolution rates (DR) of the films in 0.262 N TMAH were measured by using DRM. The values of dissolution inhibition were defined as follows.

Inhibition = DR of composition / DR of polymer

2.4. Molecular Mechanics (MM) and Molecular Dynamics (MD) of Polymers
Polygraph (KGT Inc.) was used for the calculation. In accordance with the monomers composition in the polymers, the primary structures of the polymers were formed. The stabilized structures were obtained through the calculation of MM and MD of the polymers. Dreiding-II force field parameter was used for MM calculation, and the quench method (quenched at 500K, quench step 50, total time 20 ps) in the canonical ensemble (isothermal) system was used for MD calculation. After two cycles of MM+MD calculation, the stabilized structures of the polymers were obtained through final MM calculation.

2.5. Evaluation of Interaction between Neighboring OHs on Alkali Dissociation
0.1 g of polymer was dissolved in 60 ml of 2-
methoxyethanol / de-ionized water (9/1), and titrated with 0.1 N NaOH. The pH at each titration value was recorded, and the polymer dissociation constant, \( \alpha \), was calculated from the amount of NaOH. These values were plotted for Henderson-Hasselbach equation (pH vs. \( \log(1- \alpha/ \alpha) \)). The 'n' value was obtained from the degree of slope in the linear part of the plot as a measure of the interaction strength between the dissociation groups.

2.6. Determination of Acid Decomposition Behavior of Dissolution Inhibitors

1.0 \( \mu \)m thickness films of a composition of 25 wt% inhibitor / 3 wt% photo-acid generator / 75 wt% m/p(4/6)-cresol NVK were obtained in the same manner as in the above. These were exposed at 254 nm with predetermined energy, and then heated at 90°C for 60 seconds. The films were dissolved with 2-ethoxyethyl acetate, the variation in the composition of acid-decomposed inhibitors was determined by HPLC.

2.7. Lithographic Patterning

The following compositions were tested for their lithographic performance by using KrF excimer laser stepper (NA=0.42, \( \sigma=0.50 \)). The resist films, 1.0 \( \mu \)m thickness, spin-coated on a bare silicon wafer were exposed, then immediately post exposure baked at 100°C for 60 seconds. The resist films were then developed with 0.262 N TMAH for 60 seconds.

3. Results and Discussion

3.1. Relationship between Higher Structures of Polymers and Their Alkali Dissolution

Fig.1 shows the structures of NVK and PHS that are typically used in resists, and their dissolution rates. In general the alkali dissociation is changed by the molecular weight of polymer. However, even for the polymers with similar molecular weights, there is found obvious difference in the dissolution rates between them having different structures. Although various interpretations for such differences have heretofore been made on the basis of the higher structures of polymers [10-12], there have not been enough. Since we have no means of directly measuring the higher structures of NVK and PHS, we carried out the simulations with MM and MD calculations for the structures of these polymers in this report to investigate the relationship between the structures and the alkali dissolution.
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After having understood the influences of these bonding modes on the secondary structures of NVK, we calculated the structures of actual cresol NVKs. First, we analyzed the bonding modes of NVK with $^{13}$C-NMR. $^{13}$C-NMR of p-cresol trimer, pentamer composed of the trimer and additional m-cresols added to its both sides, and resin obtained by further reacting m-cresol on the pentamer were measured, from which the chemical shifts of the methylene group in each bonding mode were assigned [13]. The chemical shifts of each methylene bond were 26.0 ppm, 29.7 ppm and 30.5 ppm for ortho-ortho bondings, 31.5 ppm and 32.2 ppm for ortho-para bondings, and 34.5 ppm for para-para bonding. Using these assignments, the contents of the bonding modes in m/p(6/4)-cresol NVK and m-cresol NVK synthesized by random condensation were measured (Table 1).

<table>
<thead>
<tr>
<th>NVK</th>
<th>Content of methylene bond (%)</th>
<th>Number of hydrogen bond</th>
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<tbody>
<tr>
<td>m/p(6/4)-NVK</td>
<td>67 23 10 8</td>
<td></td>
</tr>
<tr>
<td>m-NVK</td>
<td>31 47 22 5</td>
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</tbody>
</table>

Table 1. Content of methylene bond and hydrogen bond in 10 units of m/p(6/4)-cresol NVK, m-cresol NVK

The two NVKs differ significantly in the content of ortho-ortho bonding therein, 67 % in m/p(6/4)-NVK, while 31 % in m-NVK. The stable conformation on 10 units of NVK based on these data were calculated through MM and MD. Fig.5,6 show the results. In Fig.5,6, it is clear that m/p(6/4)-NVK has the tertiary structure in which most of OHs are oriented into the molecular interior by ortho-ortho bondings while the hydrophobic part face outward of the structure. Also in m-NVK, some part of OHs are oriented to the inside of the molecule, but the other OHs are distributed relatively throughout the whole molecular structure. The hydrogen bondings were formed in 8 OHs of m/p(6/4)-NVK and in 5 OHs of m-NVK. We may, therefore, reasonably conclude that the difference in the tertiary structures between them is related to the difference in the number of the intramolecular hydrogen bondings, that is, the ortho-ortho bondings. In addition, the tertiary structures corresponded to the difference in the alkali dissolution rates (Table 2). Although the reason for the relation may be considered because of the influence of intramolecular hydrogen bondings to suppress the dissociation of OHs [14] and of the influence on the conformation change in dissociation due to the electronic repulsion of phenolates [15], from the percolative viewpoint it is understood that the orientation of the hydrophilic OH groups into the molecular interior due to the intramolecular hydrogen bondings resulted in the decrease of the hydrophilic channels for base diffusion.
For the structure of PHS, some works have been published for MM calculation of PHS [11,12]. In this report, we combined MM and MD calculation of PHS and further investigated its stable structure. Fig.7, 8 show the results of the MM and MD calculations of 10 units of p-PHS and o-PHS. As in Fig.7, 8, hydrogen bondings are partly formed in p-PHS, while most of OHs are widely distributed throughout the whole molecule and oriented to the outside of molecule. On the other hand, in o-PHS, all OHs are arranged on the same side via hydrogen bondings, while the opposite side forms hydrophobic sites with benzene rings. One may say that, the great difference in the alkali dissolution between p-PHS and o-PHS (Table 3) is due to the difference in their higher structure, that is, the difference in the number of hydrophilic channels to be formed in the films. For o-PHS, it is also presumed that developer bases could suffer the steric hindrance of the main chain of the polymer in dissociation of the OHs.

It seems reasonable to conclude, from what has been mentioned above, that intramolecular hydrogen bondings form the polymer higher structure, which has hydrophilic sites in their molecular interior. As the result, the number of the hydrophilic channels in the polymer films are decreased, thereby resulting in the reduction of the alkali dissolution on the films. For these structures, dissolution inhibitors may effectively act to shield the hydrophilic channels and exhibit enough dissolution inhibition abilities.

3.2. Estimation of Higher Structures of Polymers Using Henderson-Hasselbach Plot

In order to understand the relationship between polymer structures and their alkali dissolution in detail, we have examined the determination of the higher structures of polymers using Henderson-Hasselbach equation (1).

\[ \text{pH} = \text{pKa} + n \log(\alpha/1-\alpha) \]  

(1)

The n value in the equation (1) is the constant that represent the interaction strength between the
dissociation groups in polymer electrolytes. If the adjacent groups in the polymers largely interact, the n value of the polymers shall increase. For example, the n value of methacrylic acid monomer is 1.0, while that of poly(methacrylic acid) is 2.3 [16]. In order to investigate the tendency on NVK and PHS, we synthesized some co-polymers (Table 2,3). These were plotted in accordance with the Henderson-Hasselbach equation, and the n values of the polymers were obtained from the slope of the linear part on the plots (Fig.9,10). The n values thus measured and the dissolution rates of the polymers are shown in Table 2,3.

For the m/p-cresol NVKs, the dissolution rates were lowered with the increase in the p-cresol content of the polymer, which forms the ortho-ortho bonding in the polymer, and the n values were increased thereby. For the PHSs, the similar tendency was observed with respect to o- and m-PHS contents. In particular, the tendency was remarkable when o-PHS content of the polymer, which forms the intramolecular hydrogen bonding in the polymer, was increased.

For all polymers, there was recognized the good relationship between the n value and the alkali dissolution rate, namely, with the increase in the n value, the alkali dissolution of the polymer was lowered (Fig.11,12). Judging from these data, the n value is an effective parameter for estimating the higher structures which affect on the alkali dissolution of the polymers. However, as shown in Fig.9, there was some deviation in the relationship for 2,3-dimethylphenol NVK, of which the alkali dissolution became lower than that to be estimated from the relationship. This is probably due to the hydrophobicity of two methyl substituents on the polymer. Comparing NVK and PHS, there was also found a difference in the degree of the relationship. Although the details of the reason are not fully understood, there may be the influence of hydrophobic site of the polymer similar to 2,3-dimethylphenol NVK. It will be necessary to

<table>
<thead>
<tr>
<th>Table 2. Properties of synthesized NVKs</th>
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<tr>
<td>Monomer</td>
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<tr>
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</tr>
<tr>
<td>p-Cr monomer</td>
</tr>
<tr>
<td>m-Cr</td>
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<tr>
<td>m/p-Cr</td>
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<td></td>
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<tr>
<td>p-Cr</td>
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<tr>
<td>o-Cr</td>
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<tr>
<td>2,3-DMP</td>
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Cr : Cresol 2,3-DMP : 2,3-Dimethylphenol

<table>
<thead>
<tr>
<th>Table 3. Properties of synthesized PHSs</th>
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<tr>
<td>Monomer</td>
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<tr>
<td>---------</td>
</tr>
<tr>
<td>p-HS</td>
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<tr>
<td>o-HS</td>
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<tr>
<td>m-HS</td>
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<td>p/o-HS</td>
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<td>p/m-HS</td>
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<tr>
<td>p-HS/St</td>
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HS : Hydroxystyrene St : Styrene

Fig.9 Henderson-Hasselbach plot of NVKs

Fig.10 Henderson-Hasselbach of PHSs
consider also the influence of hydrophobic factor in higher structures. In addition, the Tg values of the polymers decreased with the increase in the n value of the polymers, that is, with the increase in the number of intramolecular hydrogen bondings in the polymers.

In this report, we further examined the influence of acid decomposition stage of inhibitors. The details of acid decomposition on tri-functional inhibitor (a) was shown in Fig. 13, 14. The inhibitor (a) was stepwise decomposed with exposure into its di- and mono-functional form, finally, all the acid decomposable groups completely disappeared.

3.3. Structural Influence of Inhibitor on Dissolution Inhibition Characteristic

There have heretofore been made many studies to clarify the structural influences for DNQ compounds on the improvement of resist performance [3-5]. Furthermore the authors have reported the structural properties with respect to acid decomposable inhibitors [17]. That is, the increase in 1) hydrophobicity, 2) molecular size, 3) dispersivity of acid decomposable group are the important factors for the improvement of dissolution inhibition, namely dissolution discrimination. These structural factors of the inhibitors correspond to the interpretations of the percolation mechanism. It is shown that the inhibitor capable of efficiently shielding the hydrophilic channels in the polymers are effective for dissolution inhibition.
In order to clarify the dissolution inhibition behavior of the compounds formed in the individual steps, these functional compounds were separately prepared, and their inhibition magnitudes were measured (Fig. 15). In Fig. 15, it is known that there was a significant change in the inhibition between the di-functional and the mono-functional form, and the inhibition disappeared on the latter form. The inhibition behavior of the other inhibitor (b) having six acid decomposable groups was also investigated in the same manner (Fig. 16). Similar to the case on compound (a), the inhibition changed in the decomposition step of tetra-functional into tri-functional form.

It is believed that the same shall apply to the other inhibitors, and that on the process of stepwise decomposition the inhibitors significantly lose their inhibition ability at a certain step. If this step is selectively used in resist system, further improvement in the dissolution discrimination could be attained. Taking it into consideration, we compared the inhibitor (a) and its di-functional form (c) in resists. Fig. 17 shows the dissolution characteristics on the two resists through DRM. It is clear that the di-functional form (c) is more effective than the original inhibitor (a) in improving the dissolution discrimination of resist. Using this selective acid decomposition system, we carried out the lithographic evaluation by KrF excimer laser stepper (NA = 0.42). A 0.24 µm L/S image with vertical profile was obtainable.

4. Conclusions
The relationship between the structures of NVK and PHS obtained using MM/MD calculation and their alkali dissolution was investigated. It was found that NVK and o-PHS showed the structures such that OH groups oriented to the molecular interior through intramolecular hydrogen bondings. The alkali dissolution of the polymers having such higher structures became lower, which corresponded to the interpretation of the percolation mechanism on the alkali dissolution of the polymers. In order to determine the polymer higher structures, the n value of Henderson-Hasselbach equation were measured. The n values of the polymers well correlated to the
alkali dissolution, from which the $n$ value was regarded as effective parameter for determination of the higher structures of polymers. For inhibitors on chemical amplification resist, the process of their acid decomposition comprised a certain step that essentially participates in the dissolution inhibition, and the selective use of the step was effective in the improvement of the dissolution discrimination in the resist. The authors believe that these knowledge will greatly expand the technology window on achieving a more practical and better performing resist.

References