Novolak Structures Suitable for High Resolution Positive Photoresists and Application
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The mechanism of resolution improvement in novolak-based positive photoresists was investigated from the stand-point of the image formation process. The image formation process in the novolak-quinonediazide system involves the dissolution inhibition in unexposed parts and the dissolution promotion in exposed parts. The γ (gamma)-value, which is one of the indexes of resolution capabilities, depends greatly on the difference between the solubility of unexposed parts and that of exposed parts, i.e.- the lower dissolution rate in unexposed parts(R_o) and the higher one in exposed parts(R_p) are desirable to obtain high γ -values.

Dissolution rates(R_o , R_p) were measured on the positive photoresists containing various kinds of cresol-formaldehyde type novolak resins, and the influence of factors of novolak resins-such as molecular weight, isomeric structure of cresols, methylene bond position-on the dissolution rates was investigated.

The results indicates that there are two methods to raise γ -values; (1) to increase the ratio of para-cresol to meta-cresol (2) to raise S_4 value (which represents the ratio of "unsubstituted" carbon-4 atoms in benzene rings of cresols)- in other words, to make the novolak resin "high-ortho bonding" structure. (The ortho positions of cresols are highly used for methylene bondings.) In the case of (1), however, there was a trade-off relationship between γ -values and resist sensitivity because of the solubility decrease of the novolak resin itself. On the other hand, the method (2) was found to make it possible to raise γ -values without the decrease in the resist sensitivity.

These novolak designs make it possible to obtain fine pattern fabrications with line and spaces down to 0.4 μ m.

1. Introduction

As the density of VLSI increase, sub-micron level patterns has come to be demanded. Accordingly, there is an increasing need for photoresists having higher resolution capabilities.

The present work [1] examines the resolution improvement mechanism by considering the relationship between factors of novolak resins and the image formation process.

Fig.1 shows the image formation process in the novolak-quinonediazide systems. In exposed parts, quinonediazide are converted to indene-carboxylic acid and dissolve in alkaline developer with novolak resins. On the other hand, in unexposed parts, quinoediazides make novolak resins insoluble by acting as the dissolution inhibitor.

In order to improve the resolution capabilities, it is necessary to raise the dissolution rate of exposed parts(R_p)-dissolution promotion- and/or to lower that of unexposed parts(R_c)-dissolution inhibition. In other words, the γ (gamma)-value, which is one of the indexes of resolution capabilities, depends greatly on the ratio of R_p to R_o , that is, a higher R_p/R_o value corresponds to a higher γ -value.

Fig.2 shows three factors of novolak resins that can influence the material and lithographic properties. The first one is molecular weight. Novolak resins are synthesized by addition-condensation reaction of cresols with formaldehyde. In proportion to the degree of the reaction, novolak resins having various molecular weights are obtained. The second factor is the isomeric structure of cresols. There are three isomeric structures of cresols, i.e., o-cresol, m-cresol and p-cresol. The third factor is the methylene bond position. In the addition-condensation reaction, methylene bonds are formed between two cresol units. There are three positions for methylene bonding, i.e., two ortho positions and one para position. The methylene bond can only be formed at two of the three positions. Consequently, as shown in Fig.2, several kinds of methylene bonding structure exist.

In the present work, R_p and R_o were measured on positive photoresists containing various kinds of cresol-formaldehyde type novolak resins, and the influence of factors of novolak resins was investigated.

2. Experimental

2.1 Novolak resin preparation

Novolak resins were synthesized under various conditions in usual method [2,3]. The methylene bond positions were changed by using a variety of condensation catalysts such as hydrochloric acid, oxalic acid, organic salts of divalent metals including Ba, Mg, Mn, Zn, Cd and so on. Molecular weights were measured by gel permeation chromatography(GPC). The structure of novolak resins concerning the position of the methylene bond was measured by ^{13}C -NMR spectroscopy. In this measurement, the INEPT method introduced by Morris and Freeman[4] gave us useful information upon the aromatic carbon atoms. We paid attention to the ratio of "unsubstituted" carbon atom in benzene ring represented as S_n in Fig.3, which illustrates the example on m-cresol novolak resins.

Fig.4 shows the spectra of novolak resins having different bonding structures. With increasing S_4 , type(B) structure increases, namely, "high-ortho novolak resins", - the methylene bonds are highly formed at ortho positions of cresols.

2.2 Resist preparation

Resist solutions were prepared by mixing novolak resins with the fixed quinonediazide compound and solvent in the same ratio, and filtered through 0.2 μ m membrane filters.

2.3 Wafer processing condition

The wafer processing conditions used for lithographic evaluations are shown in Table 1.

2.4 Dissolution rate measurement

The following three rates were measured.

(1) R_n; dissolution rate of novolak resins

Novolak resin solutions without quinonediazide were spin-coated, prebaked, and the dissolution rate to developer was measured without irradiation.

(2) R_o; Dissolution rate of the unexposed part of resist (novolak + quinonediazide)

(3) R_p; Dissolution rate of the exposed part where exposure dose = 3 counts.

3. Results and Discussion

3.1 Relationship between factors of novolak resins and the dissolution rates

(1) Molecular weight

Fig.5 shows the relationship between dissolution rates and the exposure dose on resist containing novolak resins having different molecular weights. The curves are quite similar in shape, although R_n, R_o and R_p decrease proportionally to the increase of the molecular weight. Therefore, the R_p/R_o ratio is independent of the molecular weight.

(2) Isomeric structure of cresol

Fig.6 is the results when meta/para ratio was varied from 10/0 to 4/6 under the condition of the similar molecular weights. The synthetic conditions were held constant except m/p ratio.

The incorporation of para component has the effects of decreasing the dissolution rate of novolak resins(R_n) greatly, which causes the decrease of R_o and R_p. We believe that this large dependence of R_n on m/p ratio is attributed to the difference in polymer structures among polymers having different m/p ratios. With respect to R_o and R_p, R_o was found to vary by over the factor of 10³, compared to 10¹ of R_p variation when m/p ratio was varied from 10/0 to 4/6. Consequently, R_p/R_o ratio increase with increasing para ratio.

(3) Methlene bond position

Fig.7 shows the dependence of dissolution rates on S₄ value on m-cresol novolak resin systems. With increasing S₄, R_n decreases slightly, but R_o decreases greatly. This indicates that the dissolution of novolak resins is strongly inhibited in unexposed parts in high-ortho novolak resin systems. On the other hand, S₄ has little effects on R_p in exposed parts. As a result, R_p/R_o ratio increases with increasing S₄.

(4) Summary

Fig.8 illustrates the effects of m/p ratio and S₄ on dissolution rate vs. exposure dose curves.

Table 2 summarizes the effects of three factors of novolak resins on dissolution rate (R_o, R_p) and resist performance. (γ -values and sensitivity) It is obvious that the resist sensitivity generally corresponds to R_p .

The important information obtained from Fig.8 and Table 2 is as follows;

- (A) The molecular weight has no influence on γ -values, but the higher molecular weight reduces the sensitivity.
- (B) Two methods are probable to raise γ -values.
 - (a) to increase the ratio of para-cresol to meta-cresol.
 - (b) to raise S_+ , in other words, to make novolak resins "high-ortho bonding" structure.

It is noticeable that the reason for γ -value improvement in (a) and (b) are entirely different in nature. As discussed previously, method (a) reduces both R_o and R_p owing to the decrease of the solubility of novolak resins. However, the resulting R_p/R_o ratio increases, because the degree of the decrease of R_o is much larger than that of R_p . Of course, the decrease of R_p is undesirable in terms of the sensitivity. On the other hand, method (b) affects the dissolution inhibition particularly in unexposed parts, so there is little decrease in sensitivity.

3.2 Dissolution inhibition model

Why can high-ortho novolak resin systems selectively reduce the dissolution rate of unexposed parts? To answer this question, we must look into the dissolution inhibition mechanism which has not yet been completely solved.

One of the clues for this issue is the reactivity of dihydroxydiphenylmethane (DPM) with hexamethylene tritramine (HMTA) reported by Bender et al. [5,6] They found the unusually rapid cure rate of an o-o' materials compared to other isomeric DPM compounds. (Table 3) The accessibility of the "vacant para position" is regarded as enhancing cure rate owing to the high electron density. Keeping this fact in mind, we propose a new dissolution inhibition model in unexposed parts prominent particularly in high-ortho novolak resin systems, that is, dissolution inhibition due to "Azocoupling reaction between novolak resins and quinonediazide". (Fig.9)

The high-ortho novolak resins have a lot of vacant para positions that have high electron densities. Those positions can enhance the electrophilic azocoupling reaction, which inhibits the dissolution of novolak resins to the developer. Azocoupling reactions are usually catalyzed by base. In the image formation process, alkaline developer can catalyze the reaction.

3.3 High resolution positive photoresist PFX-15

The novolak design described above led us to develop several new resists having high resolution capability. One example of such resists is "Sumiresist[®] PFX-15".

Fig.10 represents scanning electron microscopy (SEM) micrographs of resist profiles of PFX-15 exposed by the wafer stepper with a lens of N.A.=0.54. Fine patterns with line and spaces down to 0.4 μ m having nearly vertical profiles are obtained without special technique like CEL or multilayer processes. The other characteristics and lithographic performance of PFX-15 will be presented elsewhere.

4. Conclusions

The high-ortho novolak resin systems allow improving γ -values without the decrease of resist sensitivity. That is explained by the enhanced insolubility in unexposed parts due to azocoupling reactions between novolak resins and quinonediazides.

These novolak designs make it possible to obtain fine patterns with line and spaces down to 0.4 μm .

Acknowledgements

The authors would like to acknowledge the support of many co-workers in Osaka Research Laboratory.

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Figure 1. Image formation process in the Novolak-quinonediazide systems.

Figure 2. Three factors of novolak resins.

Figure 3. ^{13}C -NMR spectrum measurement of novolak resins.

Figure 4. ^{13}C -NMR spectra of novolak resins having different bonding structures.

Wafer	: 3 or 4 inch Silicone Wafer
Coating	: 4000 rpm / 20 sec $\rightarrow$ Resist Thickness=1300 μm
Pretaking	: 90°C/20min in Convection Oven
Exposure	: Contact/Projection Aligner
	Canon-PLA 501F $\rightarrow$ Count (15 mJ/cm ² at 365nm)
	Step & Repeat Aligner
	Nikon NSR 1505G6E (NA=0.54)
Development	: Puddle or Dipping, 23°C, 60sec
	Developer: SOPD (Non-metal type)
Rinse	: Super pure water, 60sec
Film Thickness Measurements	: Rank Taylor Hobson, Talystep
Line width Measurements	: SEM

Table 1. Wafer processing conditions.

Figure 5. Influence of molecular weight on dissolution rates.

Figure 6. Influence of isomeric structure of cresol on dissolution rates.

Figure 8. Effects of m/p ratio and S_4 on dissolution rate vs. exposure dose curves

Structure	Gel time with 15% HMTA (sec)
<chem>Oc1ccc(cc1)Oc2ccc(O)cc2</chem>	60
<chem>Oc1ccc(cc1)Oc2ccc(O)cc2</chem>	240
<chem>Oc1ccc(cc1)Oc2ccc(O)cc2</chem>	175

DPM: dihydroxydiphenylmethane
HMTA: hexamethylenetetramine

Table 3. Reactivity of DPM with HMTA (Bender et al⁵)

Figure 7. Influence of methylene bond position on dissolution rates.

Factors of Novolak resin	Dissolution Rate		Resist Performance	
	unexposed parts (R_0)	exposed parts (R_p)	$\bar{r}$ -value = $\frac{R_p}{R_0}$	Sensitivity
Molecular Weight MW $\downarrow$	$\downarrow$ (+)	$\downarrow$ (+)	$\rightarrow$	$\downarrow$ (+)
Isomeric Structure of Cresol m/p ratio: $p \uparrow$	$\downarrow$ (+)	$\downarrow$ (+)	$\uparrow$ (+)	$\downarrow$ (+)
Methylene Bond Position $S_4 \downarrow$	$\downarrow$ (+)	$\rightarrow$	$\uparrow$ (+)	$\rightarrow$

Table 2. Effects of three factors of novolak resins on dissolution rates and resist performance

Dissolution Inhibition Model

Figure 9. Dissolution inhibition model

Figure 10. SEM micrographs of PFX-15 exposed by stepper with a lens of N.A.=0.54 (NSR-1505G6E)