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Insolubilization Mechanism of a Chemical Amplification Negative-Resist System Utilizing an Acid-Catalyzed Silanol Condensation Reaction

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A chemical amplification system for negative resists, utilizing a solubility-reversal mechanism, is described. The new system consists of a radiation-induced acid generator, a novolak matrix resin, and a silanol compound. Silanol compounds show chemical affinity to aqueous alkali solution and can act as dissolution promoters in aqueous alkali developers. In contrast, the condensation reaction products of silanol compounds, siloxanes, are typical hydrophobic materials and can therefore act as dissolution inhibitors in aqueous developers. The resist system resolves 0.3-μm line and space patterns by using electron-beam delineation (exposure dose 0.8 $\mu C/cm^2$ at 30 kV). The condensation reaction products of silanol compound in the exposed areas were detected by gel permeation chromatography. The insolubilizing mechanism of the new resist system is discussed.

Introduction

Electron-beam lithography is the most promising candidate among microfabrication techniques after advanced photolithography. There are several requirements in a practical resist process for direct electron-beam fabrication. High resolution, high sensitivity, and high dry etching durability are major requirements for electron-beam resists. It has been proposed that phenolic resin based resists should be used for a practical direct electron-beam fabrication.[1] Phenolic resin based resist systems, which can be developed in an aqueous alkali developer, have high-resolution capability because of their nonswelling dissolution characteristics during a development process. They also have high dry etching durability because of their high aromatic structure. The biggest problem with electron-beam lithography is its low throughput compared with that of conventional photolithography. To solve this problem, more sensitive electron-beam resists are required.

It has been shown that chemical amplification resist systems have a lot of useful capabilities for various microlithography techniques.[2] Recently, chemical amplification resists, which use a novolak matrix resin and can be developed in aqueous alkaline solutions, have been reported.[3-5] One of such resists is a negative electron-beam resist, which provides high sensitivity and high resolution, for aqueous alkaline developers.[4,6]

In a previous paper[7] we proposed a solubility reversal mechanism to enhance the performance of chemical amplification resists. This paper deals with another chemical amplification negative resist, which exhibited very high sensitivity to electron irradiation, with a solubility reversal mechanism.[8] The novel resist system consists of an acid generator, a novolak matrix resin, and a silanol compound. The same system showed a good lithographic performance as a deep-UV negative resist,[9] though the novolak resin matrix did not have good transparency to the KrF excimer laser exposure (248 nm). The system also exhibited high-resolution capability to i-line photolithography by using i-line-sensitive onium salt as the acid generator.[10]

Silanol compounds show chemical affinity to aqueous alkaline solution and can act as dissolution promoters in aqueous alkali development. In fact, one of the silanol compounds, *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane was found to be soluble in aqueous alkali developer.[11] On the other hand, the condensation reaction products of silanol compounds, polysiloxanes, are typical hydrophobic materials and therefore can act as dissolution inhibitors in aqueous alkaline developers. Exposure of the resist causes an acid to be generated from the acid generator. In a subsequent postexposure baking step, the acid catalyzes the condensation reaction of the silanol compound, and the condensation product acts as dissolution inhibitor in the exposed areas. In contrast, the silanol compound in the unexposed areas promotes aqueous alkaline solubility. Onium salts are well-known as effective acid generators in various chemical amplification resists,[2] and triphenylsulfonium triflate is used as the acid generator in this resist system. In this paper, we report on the insolubilization mechanism of the resist system.

Experimental Section

Materials. The novolak resin used here was a *m*/*p*-cresol–formaldehyde resin supplied by Hitachi Chemical Co. In addition, a commercially available poly(*p*-vinylphenol) obtained from Maruzen Petrochemical Co. under the trade name Lyncur M was used. A novolak resin from which oligomer had been removed was precipitated from methyl isobutyl ketone solution by dilution with chlorobenzene. Although chlorobenzene is known as a poor solvent of novolak resin, it can selectively extract oligomeric

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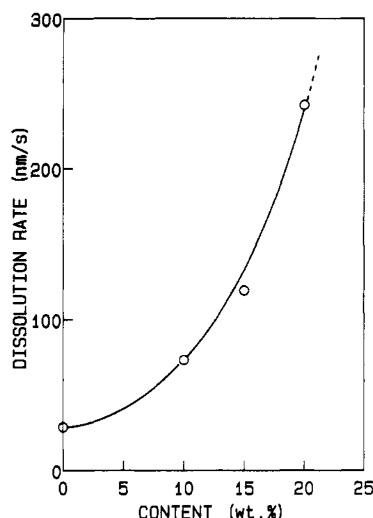

Figure 1. Dissolution rate of a novolak resin/diphenylsilanediol mixture film as a function of diphenylsilanediol content. Aqueous alkaline solution: tetramethylammonium hydroxide 2.38 wt % (0.261 N).

components of novolak.[12] Therefore, this precipitation method results in an oligomer-free novolak resin. Triphenylsulfonium triflate ($Ph_3S^+OTf^-$) was synthesized according to the literature.[13] Diphenylsilanediol (DPS) and triphenylsilanol (TPS) were obtained from Shin-etsu Chemical Co., and *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclosiloxane was synthesized by using a reported method.[14] Siloxane-oligomer samples were synthesized from diphenyldichlorosilane. As the synthesized samples contained some amount of DPS, they were washed with aqueous alkaline solutions to remove DPS. The coating solvent was 2-ethoxyethyl acetate. The aqueous alkali developers were an aqueous tetramethylammonium hydroxide (TMAH) solution (2.38 wt % 0.261 N) obtained from Tokyo Ohka Kogyo Co. under the trade name NMD-3 and the appropriately diluted developer solution.

Measurements. Dissolution rates of sample films were measured by laser interferometry.[15] A 5-mW He-Ne laser was used as the monitoring light source, and a silicon photodiode connected to a chart recorder was used as the signal detector. Electron-beam exposure characteristics were obtained with a modified Hitachi S-570 scanning electron microscope. Electron-beam-delineated patterns and the exposed samples were obtained with a prototype Hitachi HL-600 electron-beam lithography system. The acceleration voltage was 30 kV. Deep-UV exposure characteristics and the exposed samples were obtained by using a Hanovia 600-W Xe-Hg lamp (Conrad-Hanovia, Inc.) with an interference filter (250 nm) and a heat-minimizing filter. The light intensity was determined with a calorimetric flux detector thermopile (JASCO Inc). Sample films spin-coated on silicon wafers were baked at 80 °C for 10 min on a hot plate. Film thickness was determined by using a profilometer, Alpha-step 200 (Tencor Instrument Co.). Molecular weight distributions were measured by gel permeation chromatography (GPC) with a Hitachi L-6000 liquid chromatography system equipped with Gelpack A-150, A-140, and A-120 GPC columns (Hitachi Chemical Co.). The GPC solvent was tetrahydrofuran.

Results and Discussion

Dissolution Promoter in the Novolak Resin Matrix. In the resist system reported here, a metal-free onium salt, $Ph_3S^+OTf^-$, was used as the acid generator,[8] and such aryl onium salts were most effective among the various kinds

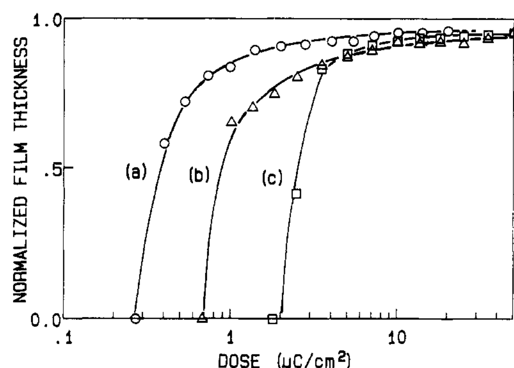

Figure 2. Electron-beam-exposure characteristics of triphenylsulfonium triflate/novolak resin/silanol compound systems using (a) diphenylsilanediol, (b) *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane, (c) triphenylsilanol. Acceleration voltage 30 kV.

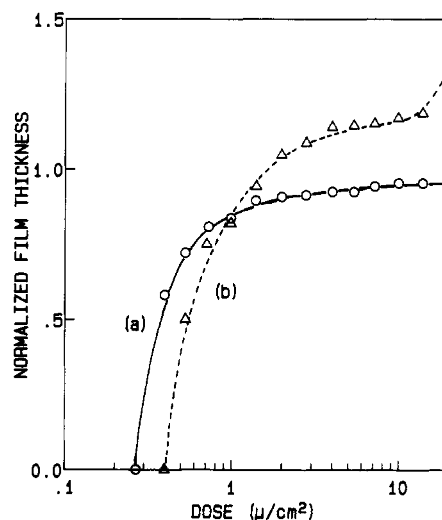

Figure 3. Postexposure baking temperature effect on electron-beam-exposure characteristics of triphenylsulfonium triflate/novolak resin/diphenylsilanediol. Baking temperature (a) 80 °C for 10 min, (b) 100 °C for 10 min.

of acid generators in this system.[9] However, aryl onium salts show a very strong dissolution inhibition effect in the resist for aqueous development.[16,17] On the other hand, silanol compounds can act as dissolution promoters in aqueous alkali development. Figure 1 shows the dissolution rate of DPS/novolak resin mixture films as a function of DPS content. As shown in the figure, DPS can act as a dissolution promoter. Therefore, silanol compounds in the system can compensate for the dissolution inhibition effect caused by the acid generator.

Exposure Characteristics and Lithographic Performance. Various silanol compounds were investigated in this study. The electron-beam exposure characteristics (at 30 kV) of the new resist systems using three kinds of silanol compounds are shown in Figure 2. DPS has two OH groups, TPS has one, and *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane has four. All of these are solid at room temperature and compatible with novolak resins. The composition of these resist systems is $Ph_3S^+OTf^-$/novolak resin/silanol compound = 3/80/20 (weight ratio). Postexposure baking (PEB) conditions were 80 °C for 10 min. The development was stopped at a time equal to about twice the immersion time to clear the

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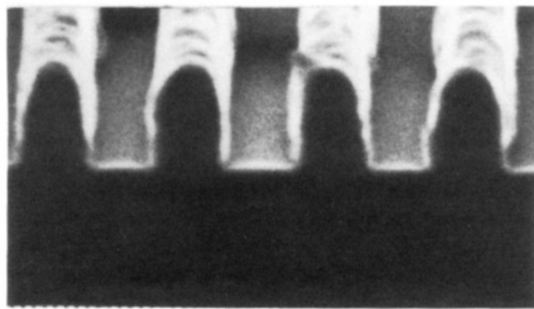

Figure 4. Scanning electron micrograph of 0.3-μm line and space patterns delineated by electron-beam exposure. Acceleration voltage 30 kV, exposure dose 0.8 $\mu C/cm^2$, initial film thickness 0.5 μm.

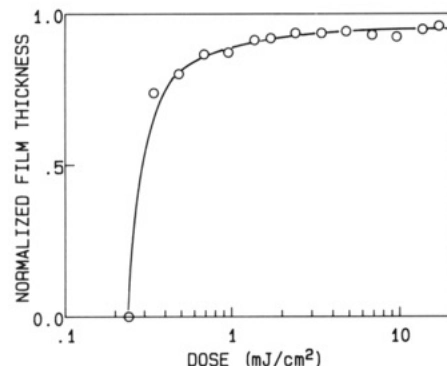

Figure 5. Deep-UV exposure characteristics of a triphenylsulfonium triflate/novolak resin/diphenylsilanediol system. Light source Xe–Hg lamp with interference filter (250 nm).

unexposed areas. As can be seen in Figure 2, the new resist using DPS had the highest sensitivity. The effect of PEB temperature on the resist using DPS is shown in Figure 3. As shown in this figure, the remaining film thickness became larger than the initial film thickness in the higher dose range. Moreover, some swelling-like patterns in electron-beam resist patterning were found. However, the film-thickness increase was found just after PEB even before the development. Therefore, the swelling occurs during PEB. And no such phenomenon was seen in the case where TPS or *cis*-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane was used. This suggests that DPS is very mobile in the novolak matrix and that the high sensitivity of the composition using DPS is caused by its high mobility in the matrix. A typical electron-beam-delineated pattern of the new resist is shown in Figure 4. The exposure dose was 0.8 $\mu C/cm^2$ at 30 kV. This resist system is also sensitive to deep-UV exposure.[9] Deep-UV exposure characteristics of the resist using DPS as the silanol component are shown in Figure 5. The KrF excimer laser lithographic performance of this system is reported elsewhere.[9]

Acid-Catalyzed Silanol-Condensation Reaction Products in the Phenolic Resin Matrix. To investigate the nature of radiation-induced acid-catalyzed silanol condensation in the novolak matrix, infrared spectra of samples before and after deep-UV exposure and PEB were measured. It was found that there is an absorption at 910 cm^{-1} due to silanol in an unexposed sample and that there appears an absorption at 1110 cm^{-1} due to the siloxane structure in a fully exposed and baked sample.[8,9] In the case of patterning dosage, however, these spectra changes were too small to be detected clearly, because the absorption bands of the novolak matrix resin spectra are superimposed on the signals. The most probable condensation reaction product of silanol compounds is their

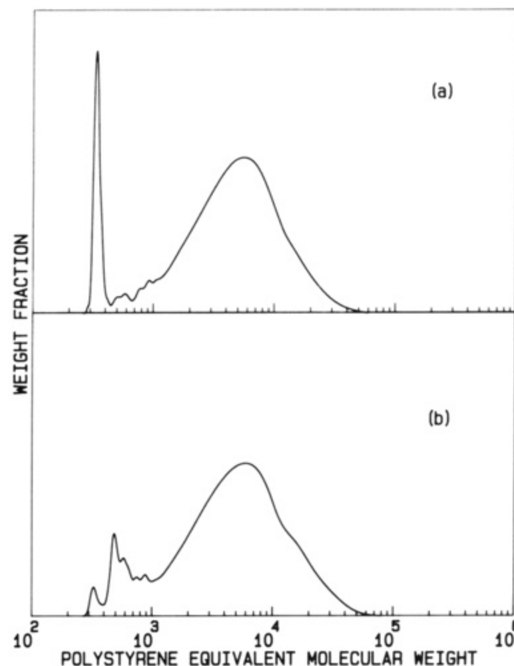

Figure 6. Molecular weight distributions of poly(*p*-vinylphenol)/diphenylsilanediol mixture (a) without *p*-toluenesulfonic acid, (b) with *p*-toluenesulfonic acid. Baking temperature 80 °C for 10 min.

dimer, and in such case, it is detectable by using gel permeation chromatography (GPC). To estimate the degree of silanol condensation in the resin matrix, model composition films were prepared and their molecular weight distributions were measured by GPC. Moreover, their dissolution rates in an aqueous alkali solution were measured. The model compositions were poly(*p*-vinylphenol)/DPS = 80/20 (weight ratio) mixtures with and without a trace amount of *p*-toluenesulfonic acid (about 0.1 wt %). The molecular weight distributions of these composition films are shown in Figure 6. The film baking conditions were 80 °C for 10 min, and the aqueous alkali solution was 1 wt % aqueous TMAH solution. The composition film without *p*-toluenesulfonic acid showed a large dissolution rate (70 nm/s). A sharp peak at a polystyrene equivalent molecular weight of 300 in Figure 6a is due to DPS. On the other hand, the film with *p*-toluenesulfonic acid showed a very small dissolution rate (1.9 nm/s), new peaks appeared in the oligomer region, and the sharp peak of DPS disappeared as can be seen in Figure 6b. These results suggest that acid-catalyzed silanol condensation products are oligomeric siloxanes in the phenolic resin matrix and that even the oligomeric siloxanes can act as dissolution inhibitors in aqueous alkali-solutions.

Direct Measurement of Radiation-Induced Acid-Catalyzed Silanol Condensation Products Utilizing Oligomer-Free Novolak Resin Matrix. Conventional novolak resins contain a lot of oligomer components and unfortunately the dimer or trimer peaks of the resin coincide with DPS and its oligomeric condensation products in the gel permeation chromatogram. To clarify oligomer region changes, we performed a model experiment using a novolak matrix resin in which the oligomer components had been removed. Figure 7 shows the molecular weight distributions of the model composition films before and after electron-beam exposure and PEB. The model composition was $Ph_3S^+OTf^-$/oligomer-free novolak resin/DPS = 3/80/20 (weight ratio). As can be seen in this figure, new peaks appeared in the oligomer region even at a 1 $\mu C/cm^2$ dose. The same peaks also appeared in the case

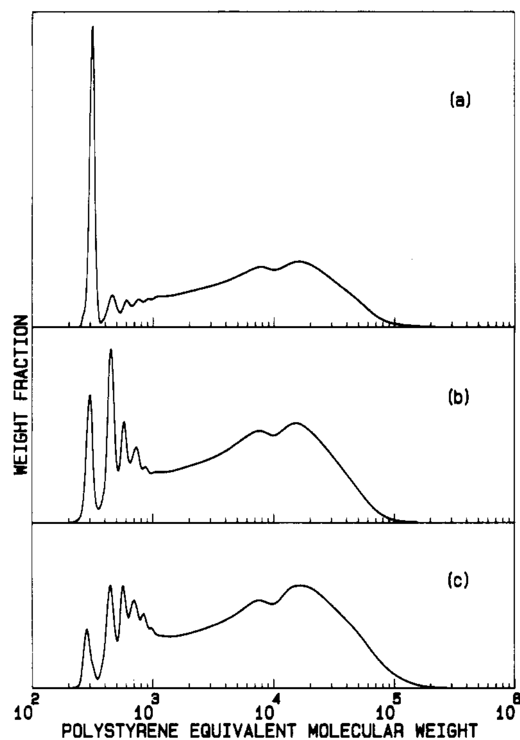

Figure 7. Molecular weight distributions of a triphenylsulfonium triflate/oligomer-free novolak resin/diphenylsilanediol mixture film exposed to electron beam and baked: (a) reference before exposure, (b) dose 1 $\mu C/cm^2$, (c) dose 10 $\mu C/cm^2$.

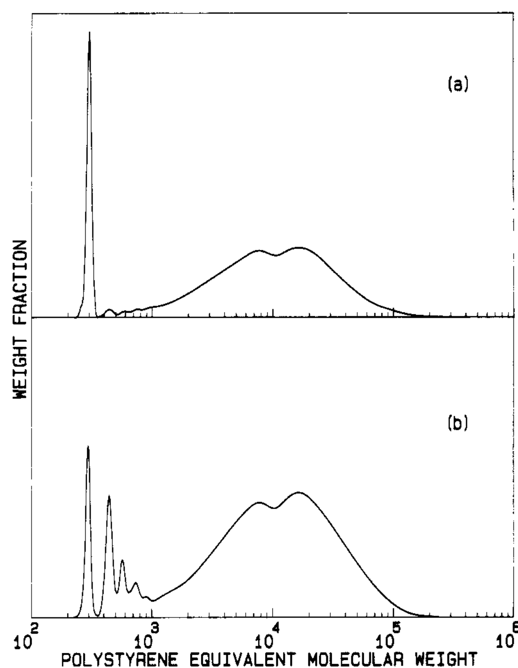

Figure 8. Molecular weight distributions of a triphenylsulfonium triflate/oligomer-free novolak resin/diphenylsilanediol mixture film (a) before exposure, (b) after deep-UV exposure and baked. Deep-UV dose 1 mJ/cm^2 at 250 nm; baking temperature 80 °C for 10 min.

of deep-UV exposure. Figure 8 shows the molecular weight distributions of the model composition films before and after deep-UV exposure and PEB. The exposure dose was only 1 mJ/cm^2. Figure 9 shows the molecular weight distribution changes as a function of deep-UV dose. According to exposure dose increase, the relative area of the oligomeric siloxane peaks increases and DPS peak decreases as shown in this figure. Figure 10 shows DPS and siloxane–oligomer contents in the postexposure baked film

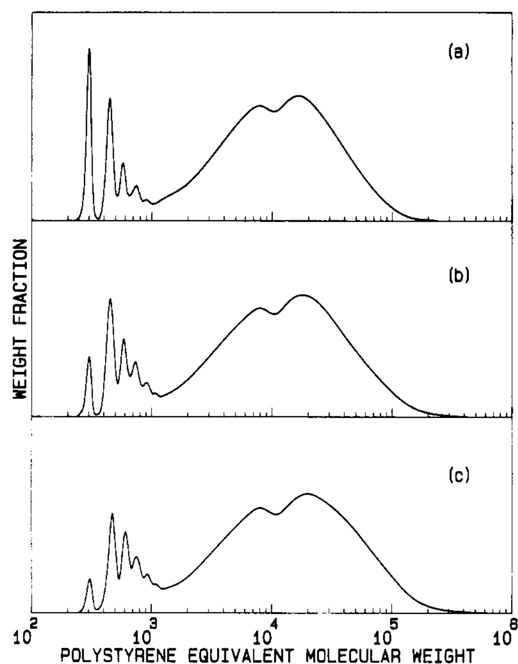

Figure 9. Molecular wieght distribution changes of a triphenylsulfonium triflate/oligomer-free novolak resin/diphenylsilanediol mixture film as a function of deep-UV dose: (a) 1 mJ/cm^2, (b) 5 mJ/cm^2, (c) 10 mJ/cm^2. Baking temperature 80 °C for 10 min.

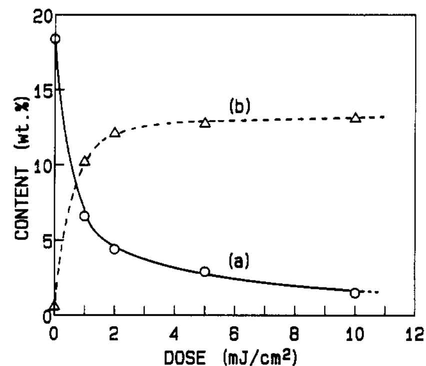

Figure 10. Diphenylsilanediol and siloxane oligomer contents in a triphenylsulfonium triflate/oligomer-free novolak resin/diphenylsilanediol mixture film deep-UV exposed and baked as a function of exposure dose. Baking temperature 80 °C for 10 min. (a) Diphenylsilanediol, (b) siloxane oligomer.

as a function of deep-UV dose. These contents were calculated from the gel permeation chromatogram. The oligomer regions in all plots were defined as less than polystyrene equivalent molecular weight, 1000 in this calculation. As shown in this figure, it was considered that almost all the decreasing DPS converted to siloxane–oligomer.

Dissolution Inhibition by the Siloxane Structure in a Phenolic Resin Matrix. To evaluate the dissolution inhibitor capability of siloxane–oligomer, a mixture film of the novolak resin and a synthesized siloxane–oligomer were prepared, and the dissolution rate of the film was measured. Figure 11 shows molecular weight distributions of the novolak resin used in the resist system and the synthesized siloxane–oligomer. The synthesized siloxane–oligomer was insoluble in an aqueous alkali developer. However, no remarkable dissolution inhibition effect was found in the mixed film. Therefore, dissolution rates of various sample films were compared. The results are shown in Table I. The dissolution rate of the novolak film was 25 nm/s, whereas that of the mixture containing the

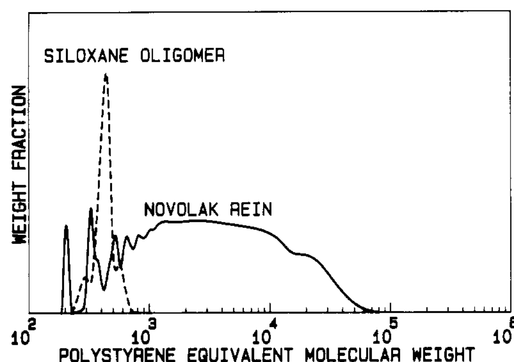

Figure 11. Molecular weight distributions of novolak resin and synthesized siloxane oligomer.

Table I. Dissolution Rates of Sample Films to Aqueous Tetramethylammonium Hydroxide Solution (2.38 wt %, 0.261 N)[a]

no.	sample film	rate, nm/s
1.	novolak resin	25
2.	DPS/novolak resin = 10/100	50
3.	siloxane oligomer/novolak resin = 10/100	21
4.	$Ph_3S^+OTf^-$/DPS/novolak resin = 3/10/100 (unexposed)	25
5.	no. 4 film deep-UV exposed and baked	<0.03
6.	no. 5 film dissolved and coated again	22

[a] DPS, diphenylsilanediol; $Ph_3S^+OTf^-$, triphenylsulfonium triflate. Baking temperature 80 °C for 10 min; coating solvent 2-ethoxyethyl acetate.

siloxane-oligomer was 21 nm/s. The rate difference is too small to form patterns by aqueous alkali development. When the resist was fully deep-UV exposed and postexposure baked, it showed a very small dissolution rate (<0.03 nm/s). The exposed film was once dissolved in the coating solvent and then coated again from the solution. The coated film showed a large dissolution rate. From these results, the following dissolution promotion and inhibition mechanisms of this resist system are proposed. The model is shown in Figure 12. As silanol group is hydrophilic, silanol compounds are around the hydrophilic site, the phenol group, of the novolak resin matrix in the equilibrium state. When radiation-indued acid-catalyzed condensation takes place at the hydrophilic site, the reaction products, siloxanes, are produced around the phenol group and shield or block it. As the condensation products are bulky, the siloxanes cannot move in the resist matrix and such a state is metastable. When the metastable-state film is once dissolved and coated again from the solution, hydrophobic siloxane structures are around the hydrophobic site of the matrix in the equilibrium state and cannot shield or block the hydrophilic site of the matrix. According to the hydrophilic diffusion channel model for the dissolution of novolak resin,[18] hydrophilic additives can increase a succession of hydrophilic sites (diffusion channel) and promote the dissolution rate of the resin, whereas blocking the diffusion channel decreases the dissolution rate. In the case of this resist system, silanol compounds can be such hydrophilic additives and promote the dissolution rate. In contrast, hydrophobic siloxanes produced around the hydrophilic sites block the diffusion channel and decrease the dissolution rate effectively. As described above, it was found that the insolubilization mechanism of the resist is non-cross-linking but affected by the site or orientation of the silanol condensation products in the matrix.

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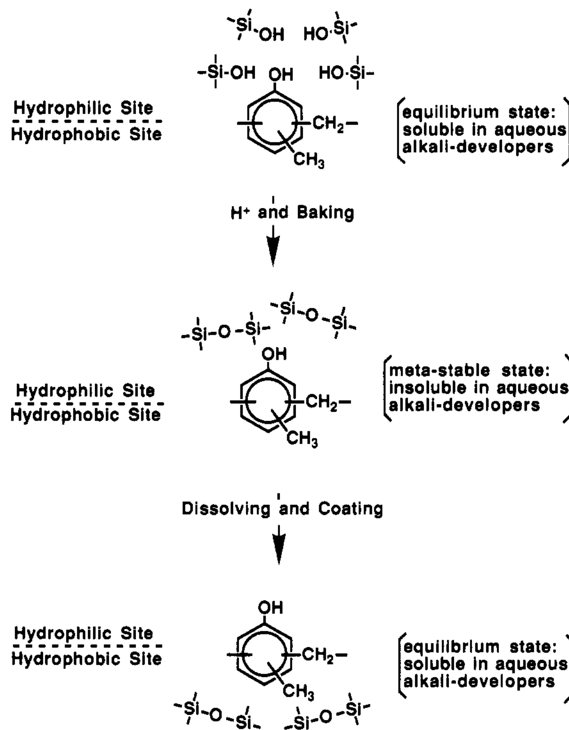

Figure 12. Model of dissolution promotion/inhibition mechanism in the resist system.

Conclusion

A chemical amplification negative-resist system utilizing acid-catalyzed silanol condensation reaction showed high sensitivity and high resolution to electron-beam and deep-UV exposure. The system consists of an acid generator, novolak resin, and a silanol compound. It resolved 0.3-μm line and space patterns by using electron-beam delineation. The acceleration voltage was 30 kV, and the exposure dose was 0.8 $\mu C/cm^2$. It has been shown that the resist system is a non-cross-linking type negative resist for aqueous alkali developer. The insolubilization mechanism to aqueous alkali developer was investigated by measurements of molecular weight distributions and dissolution rates of the exposed resist films. The results show that radiation-induced acid-catalyzed silanol condensation reaction renders siloxane–oligomer in the novolak resin matrix and that the orientation or position of the siloxane structure effectively decreases the dissolution rate of the matrix.

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