Acid-Catalyzed Silanol Condensation Reaction Mechanism in a Chemical Amplification Negative Resist System

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It has been shown that chemical amplification resist systems have a lot of useful capabilities for various microlithography techniques[1]. Recently, chemical amplification resists which use a novolak matrix resin and can be developed in aqueous alkaline solutions have been reported[2][3][4]. One of such resists, SAL-601, developed by Rohm & Haas / Shipley Co. is a negative electron-beam resist for aqueous alkaline-developers that provides high sensitivity and high resolution[3][5]. Electron-beam lithography is one of the most promising candidates for microfabrication. The biggest problem with electron-beam lithography is its low throughput compared with that of conventional photolithography. In order to solve this problem, more sensitive electron-beam resists are required. In the previous paper[6], we proposed a solubility reversal mechanism to enhance the performance of a chemical amplification resist. This paper deals with another chemical amplification negative resist, which exhibits very high sensitivity to electron irradiation with a solubility reversal mechanism.

The novel resist system consists of an acid generator, a novolak matrix resin, and a silanol compound. Silanol compounds show chemical affinity to aqueous alkaline solution and can act as a dissolution promoter in the aqueous alkali-development. In fact, one of silanol compounds, cis-\((1,3,5,7\)-tetrahydroxy\)-\(1,3,5,7\)-tetraphenylcyclotetrasiloxane (Ph\(_4\)T\(_4\)O\(_4\)) was found to be soluble in aqueous alkali-developer[7]. Figure 1 shows the dissolution rate of Dihenylsilanediol (DPS) / novolak mixture film as a function of DPS content in the film. As shown in the figure, DPS can act as dissolution promoter in aqueous alkali-solution. On the other hand, the condensation reaction products of silanol compounds, polysiloxanes, are typical hydrophobic materials and therefore can act as a dissolution inhibitor in aqueous alkaline developers. Exposure of the resist generates an acid from the acid generator. In a subsequent post-exposure baking (PEB) step, the acid catalyzes the condensation reaction of the silanol compound, and the condensation product acts as a dissolution inhibitor in the exposed areas. In contrast, the silanol compound in the unexposed areas promotes aqueous alkaline solubility.

Onium salts are effective acid generators in various chemical amplification resists[1]. In this paper, triphenylsulfonium triflate (Ph\(_3\)S\(^+\)OTf\(^-\)) is used as the acid generator. Various silanol compounds are investigated...
in this study. The electron-beam exposure characteristics (at 30kV) of the new resist systems using three kinds of silanol compounds are shown in Figure 2. Diphenylsilanediol(DPS) has two OH groups, triphenylsilanol (TPS) has one, and Ph₄T₄(OH)₄ has four. These are solid at room temperature and compatible with novolak resins. The composition of these resist systems is Ph₃S⁺OTF⁻/novolak resin/silanol compound = 3/80/20 (weight ratio). Coating solvent is ethylcellosolve acetate. The PEB step was 80°C for 10min on a hot plate. The developer was an aqueous tetramethylammoniumhydroxide (TMAH) solution (2.38wt%). The development was stopped at about twice the immersion time to clear the 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 is shown in Figure 3. As shown in this figure, 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 no such phenomenon was seen in the case of using TPS or Ph₄T₄(OH)₄. This indicates 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. The electron-beam lithographic performance of the new resist is shown in Figure 4. The electron-beam sensitivity of it reached 0.8 μC/cm² at 30kV.

This resist system is also sensitive to deep-UV exposure. Deep UV exposure characteristics of the resist using DPS as the silanol component are shown in Figure 5. The samples were irradiated through an interference filter (250nm) with a 600W Xe-Hg lamp (Conrad-Hanovia, Incorporated). Details of deep-UV lithographic performance of this system were reported elsewhere[8].

Figure 1. Dissolution rate of the film of novolak resin/diphenylsilanediol mixture as a function of diphenylsilanediol content. Aqueous alkaline-solution: tetramethylammoniumhydroxide 2.38 wt%.

Figure 2. Electron-beam exposure characteristics of Ph₃S⁺OTF⁻/novolak resin/silanol compound systems using (a) diphenylsilanediol, (b) Ph₄T₄(OH)₄, (c) triphenylsilanol. Acceleration voltage: 30kV.
Figure 3. Post-exposure baking temperature effect on electron-beam exposure characteristics of \( \text{Ph}_3\text{S}^+\text{OTf}^- / \text{novolak resin} / \text{diphenylsilane-diol} \). Baking temperature: (a) 80°C x 10min, (b) 100°C x 10min.

Figure 4. Scanning electron micrograph of 0.3\( \mu \text{m} \) line & space patterns delineated by electron-beam. Acceleration voltage: 30kV, exposure dose: 0.8 \( \mu \text{C/cm}^2 \).

Figure 5. Deep-UV exposure characteristics of the system \( \text{Ph}_3\text{S}^+\text{OTf}^- / \text{novolak resin} / \text{diphenylsilane-diol} \).

Figure 6. Molecular weight distributions of resist composition using oligomer-free novolak resin. (a) before deep-UV exposure, (b) after deep-UV exposure (10mJ/cm\(^2\)) / post-exposure baking (80°C x 10min).
In order 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 / PEB were measured. It can be seen that there is an absorption at 910 cm\(^{-1}\) due to silanol in unexposed sample, and that there appears an absorption at 1110 cm\(^{-1}\) due to the siloxane structure in the exposed and baked sample. These spectra changes are too small to be detected clearly, because the absorption bands of the novolak matrix resin spectra are superimposed on the signals. These samples were measured by gel permeation chromatography (GPC) to detect silanol-condensation reaction product directly. Conventional novolak resins contain a lot of oligomer-components and unfortunately the dimer or trimer peaks of the resin coincide with that of DPS in gel permeation chromatogram. Therefore, we made a model experiment using a novolak matrix resin in which the oligomer components had been removed. Figure 6 shows the molecular weight (MW) distributions of the unexposed model composition (a), and of the deep UV exposed (about 10mJ/cm\(^2\)) and baked sample(b). A sharp peak at a polystyrene equivalent MW of 300 in Figure 6 (a) is due to DPS. As can be seen, new peaks appeared in the oligomer region and the sharp peak of DPS disappeared in Figure 6 (b).

Siloxane oligomer samples were synthesized from diphenyldichlorosilane to evaluate their dissolution inhibitor capability. As the synthesized samples contained some amount of DPS, they were washed with aqueous alkali-developer. The siloxane oligomer was mixed with the novolak resin and the dissolution rates of the film of the novolak and of the mixture were measured. The dissolution rate of the novolak film was 25nm/s, whereas that of the mixture containing about 10wt% of the siloxane oligomer was 21nm/s. The rate difference is too small to form patterns by aqueous alkali-development. When the resist was fully deep-UV exposed and post-exposure baked, it showed a very small dissolution rate( 0.03nm/s). The exposed film was once dissolved in ethylcellosolve acetate and then re-coated from the solution. The re-coated film showed a large dissolution rate (22nm/s). These results indicate that the insolubilization of the resist is affected by the site or orientation of the silanol-condensation products in the novolak matrix resin.

REFERENCES