Improvement of Resist Characteristics by Synthesis of a Novel Dissolution Inhibitor for Chemically Amplified Three-Component Novolac Resist

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A photosensitive polymer called photoresist is used to create fine circuit patterns on the surface of semiconductors. The aim of this study was to improve the resist function by incorporating a chemical amplification mechanism into the base polymer, novolac resin. The resist is composed of three components: base polymer, dissolution inhibitor (DI), and photoacid generator. The ability to inhibit the dissolution of resist polymer in the unexposed area was improved by increasing the molecular size of DI. The high acidity of deprotected DI with carboxyl groups improved the ability to promote dissolution of resist polymer in the exposed area. The resists containing DIs with large molecular size and high acidity showed improved resolution.

Keywords: Novolac resist, Dissolution inhibitor, Positive tone resist, Chemically amplified system

1. Introduction

Semiconductors are used in a variety of electronic devices. In order to achieve high performance and miniaturization of these electronic devices, semiconductors must be made finer and denser [1-6]. A photosensitive polymer material called photoresist is used to form circuit patterns on the surface of semiconductors. When the resist is exposed, a chemical reaction occurs, which changes its solubility in alkaline developing solution. The procedure for forming the circuit pattern is shown below. After the formation of the oxide film on the Si substrate, resist is applied to its surface. The resist pattern is then formed on the substrate surface by exposure and development. The formed resist pattern serves as a mask in the etching process. After etching, the resist is removed and the electronic circuit is fabricated on the substrate.

In this study, we developed a three-component resist by applying the chemical amplification mechanism to novolac resin [7, 8]. A three-component resist consists of a novolac resin as the base polymer, a photoacid generator (PAG) that generates protons when exposed, and a dissolution inhibitor (DI) that controls the resist's solubility. Before exposure, the interaction between the novolac resin and DI, such as intermolecular forces and hydrogen bonds, prevents the resist film from dissolving into the developing solution [9-11]. First, exposure releases protons from the PAG, which cause the dissolution inhibitor to undergo a deprotection reaction and decompose into a dissolution accelerator (DA). Since DA is soluble in the developing solution, the resist film in the exposed area dissolves into the developing solution. When the dissolution inhibitor decomposes, protons are generated again. This generated proton repeatedly works for the dissolution reaction of the dissolution inhibitor, and the proton functions as a catalyst, which is the chemical amplification mechanism [12-14]. The chemical amplification mechanism is expected to improve sensitivity and resolution over conventional novolac positive resists, which consist of two components: a novolac resin and a diazonaphthoquinone (DNQ) derivative [15-17]. In addition, dissolution of the novolac resin
can be promoted by making the molecular weight distribution of the novolac resin wider. This is because if the novolac resin has a wide molecular weight distribution, the resin with the smaller molecular weight will dissolve in the developing solution, and the contact area between the resin with the larger molecular weight and the developing solution will increase. Therefore, the dissolution rate is faster than that of novolac resin with a narrow molecular weight distribution. Since DA is a low molecular weight compound compared to the resin, it is thought to function in the same way as a resin with a small molecular weight. Therefore, the addition of DI is expected to improve the dissolution promotion capability over normal resists.

We improved the dissolution inhibition ability of DI and the dissolution enhancement ability of DA for novolac resin by designing the molecules of DI. The dissolution inhibitor was designed to have different numbers of benzene rings in the molecule, and the molecular size was varied [18]. In addition, by increasing the acidity after decomposition, DA dissolves in the developing solution in a shorter time, and the contact between the resin and the developing solution occurs faster. Thinking that this would improve the dissolution promotion ability, we synthesized two types of DI: the phenol type, in which the decomposition product becomes phenol, and the carboxylic acid type, in which the decomposition product becomes carboxylic acid. In order to evaluate only the effect of acidity after degradation, the molecular sizes of phenolic and carboxylic acid type DIs were designed to be almost equal. These DIs made it possible to incorporate acid-catalyzed chemical amplification mechanism into the resists by protecting the dissolution promoters with tBoc and tBu groups that can be degraded by acid. Using the DIs synthesized by the above molecular design, we aimed to improve the sensitivity and resolution of three-component positive resists.

2. Experimental

Novolac resin (Mw 9000) were used as a base polymer. Propylene glycol monomethylether acetate (PGMEA) was used as a solvent for base resin. 2-Methyl-α-[2-[([propylsulfonyl]oxy)imino]-3(2H)-thienylidene]benzeneacetonitrile (product name: Irgacure PAG103) was obtained from BASF and used as a photo acid generator (PAG). 2.38% of tetramethylammonium hydroxide (TMAH) aqueous solution was used as a developer. Hydroquinone (DA1), 4,4’-[1-[4-[1-(4-hydroxyphenyl)-1-methylethyl]phenyl]ethylidene]bis[phenol] (DA2), 4,4’-((2-hydroxyphenyl)methylene)bis(2,6-dimethylphenol) (DA3) and 4,4’-methylenebis(2-(4-hydroxybenzyl)-3,6-dimethylphenol) (DA4) were used as DA. tBoc-DI1, tBoc-DI2, tBoc-DI3, and tBoc-DI4 were synthesized by the reaction of DA1-4 with Di-t-butyl Dicarbonate in the presence of 4-Dimethylaminopyridine (DMAP) [19]. di-tert-butyl 2,2’-(((1-(4-(2-(4-(2-(tert-butoxy)-2-oxoethoxy)phenyl)propan-2-yl)phenyl)ethane-1,1-diyl)bis(4,1-phenylene))bis(oxo))diacetate (tBu-DI2) and di-tert-butyl 2,2’-(((2-(2-(tert-butoxy)-2-oxoethoxy)phenyl)methylene)bis(2,6-dimethyl-4,1-phenylene))bis(oxo))diacetate (tBu-DI3) were synthesized as follows: DA2, DA3 and t-butyl bromoacetate were reacted in DMF in the presence of potassium carbonate and heated and stirred in an oil bath at 90 °C for 24 h while refluxing [20]. The chemical structure of the synthesized DI is shown in Scheme 1.

The polymer solution was prepared by dissolving novolak resin in PGMEA and the concentration of was 30 wt%. DIs was added at 0.10, 0.20, and 0.30.
decomposition product becomes carboxylic acid. In and the carboxylic acid type, in which the decomposition product becomes phenol, which the dissolution promotion ability, developing solution occurs faster. Thinking that this by increasing the acidity after decomposition, DA degraded by acid. Using the DIs synthesized by the promoters with tBoc and tBu groups that can be into the resists by protecting the dissolution acid-catalyzed chemical amplification mechanism addition of DI is expected to improve the dissolution with a small molecular weight. Therefore, the it is thought to function in the same way as a resin molecular weight distribution. Since DA is a low rate is faster than that of novolac resin with a narrow contact area between the resin with can be promoted by making the molecular weight equal. These DIs made it possible to incorporate carboxylic acid type DIs were designed to be almost degradation, the molecular sizes of phenolic and order to evaluate only the effect of acidity after completion, the ADRs of the resist films with the same substituent DIs, the ADRs of the films containing tBu-DI2 were smaller than those of tBoc-DI2 and those of the films containing tBu-DI3 were smaller than those of tBoc-DI3 (tBu-DI2, 3 < tBoc-DI2, 3). Therefore, it was found that the dissolution inhibition ability of DI protected by tBu group was larger than that of tBoc group.

The effect of DI on resist properties was evaluated using tBoc-DI2, 3 and tBu-DI2, 3 with different acidity after deprotection. The sensitivity curve is shown in Figure 2 and 3. Exposure dose at which the resist film began to dissolve was smaller for the tBoc group-protected resist than for the tBu

3. Results and discussion

To evaluate the dissolution inhibition ability of the synthesized dissolution inhibitors against novolac resin, resist films with various amount of DI were prepared and its Alkali dissolution rate (ADR) was measured. The correlation between the ADR of the resist film and the amount of DI per gram of polymer was shown in Figure 1. Without the dissolution inhibitor, the ADR of the polymer solution was 2700 nm/min. The ADR of the resist films with tBu-DI2 was the smallest, followed by tBoc-DI4, tBoc-DI2, tBu-DI3, tBoc-DI3, and tBoc-DI1 added films. Comparing the ADRs of the resist films with the same substituent DIs, the ADRs of the resist films became smaller in the order of tBoc-DI1, tBoc-DI3, tBoc-DI2, and tBoc-DI4 (tBoc-DI1 < tBoc-DI3 < tBoc-DI2 < tBoc-DI4). From these results, it was found that the dissolution inhibition ability increased as the molecular size of DI increased. When the ADRs of the resist films were compared by DI of the same structure, the ADRs of the films containing tBu-DI2 were smaller than those of tBoc-DI2 and those of the films containing tBu-DI3 were smaller than those of tBoc-DI3 (tBu-DI2, 3 < tBoc-DI2, 3). Therefore, it was found that the dissolution inhibition ability of DI protected by tBu group was larger than that of tBoc group.

The effect of DI on resist properties was evaluated using tBoc-DI2, 3 and tBu-DI2, 3 with different acidity after deprotection. The sensitivity curve is shown in Figure 2 and 3. Exposure dose at which the resist film began to dissolve was smaller for the tBoc group-protected resist than for the tBu group-protected resist. This may be attributed to the fact that tBoc groups are more easily decomposed than tBu groups. The sensitivity was 70, 85, 200, and 220 mJ/cm2 for tBoc-DI2, tBoc-DI3, tBu-DI2, and tBu-DI3 added resists, respectively, and resists including tBoc-protected DI had higher sensitivity. Since tBoc group-protected DI becomes phenol after decomposition and tBu group-protected DI becomes carboxylic acid after decomposition, we expected that tBu-DI2, 3 added resists with higher acidity after decomposition would have higher sensitivity, but the actual result was the opposite. Next, the γ value was calculated according to Equation 1.

![Fig. 1. ADR of polymer films containing tBoc-DI1(●), tBoc-DI3(▲), tBu-DI3(◆), tBoc-DI2(■), tBoc-DI4(■) and tBu-DI2(●).](image1)

![Fig. 2. Sensitivity curves of Novolac resist including tBoc-DI2 (▲) and tBu-DI2 (●)).](image2)

![Fig. 3. Sensitivity curves of Novolac resist including tBoc-DI3 (▲) and tBu-DI3 (●)).](image3)
\[ \gamma = 0.5 \log(D_0/D_{50})^{-1} \]  

The exposure amount when the residual film ratio is 0% is "\(D_0\)" and the exposure amount when the residual film ratio is 50% is "\(D_{50}\)". The \(\gamma\) values are 1.18, 0.87, 2.02, and 2.92 for the tBoc-DI2, tBoc-DI3, tBu-DI2, and tBuDI3 added resists, respectively, and the tBu group protected resist is expected to have better pattern resolution.

The shapes of the patterns created using tBoc-DI2 and tBu-DI2 added resists were observed using SEM to evaluate the pattern resolution. Each pattern image is shown in Figure 4. For patterning, a mask with L/S = 3 µm was used. The resist including tBoc-DI2 was exposed at 85 mJ/cm² and the resist including tBu-DI2 was exposed at 660 mJ/cm². Comparing the shapes of the patterns produced, it was found that the tBu-DI2 doped resist produced better shaped patterns. Therefore, it was found that the improvement in pattern resolution was achieved by using a carboxylic acid type DI.

![Figure 4](Image)

**Figure 4.** SEM images of the patterns prepared by resist containing (a) tBoc-DI2 and (b) tBu-DI2.

### 4. Conclusion

A three-component resist was developed by applying the chemical amplification mechanism to novolac resin. By increasing the molecular size of DI, the inhibitory ability of DI to dissolve the polymer was improved. In the case of the tBoc group-protected DI added resist, the sensitivity was improved compared to the tBu group-protected resist. Resists added with tBu group-protected DI, which have a higher acidity after decomposition, have improved contrast; when resists added with tBu-DI2 were used, 3 µm patterns could be formed.

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