Development of Dissolution Inhibitor in Chemically Amplified Positive Tone Thick Film Resist

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Thick film resist is applied to a template for microelectrode used in semiconductor device integration. Utilization of positive type resist in chemically amplified system for thick film is expected to improve production efficiency of semiconductor device integration, but improvement of resolution is required. In order to improve the resolution of chemically amplified positive tone thick film resist, chemical structure of the dissolution inhibitor (DI) was designed for the control of solubility in resist polymer. The increase of molecular size in DI improved the dissolution inhibiting ability for the resist polymer in the unexposed area and the high acidity of the deprotected DI having carboxyl group improved dissolution promoting ability for the resist polymer in the exposed area. The resist containing DI possessing a large molecular size and high acidity improved its sensitivity and resolution.

Keywords: Thick film resist, Dissolution inhibitor, Positive tone resist, Chemically amplified system

1. Introduction

Along with high performance of electronic devices typified by recent mobile phones, high density and integration of semiconductor devices have been promoted [1-5]. In three-dimensional mounting, which is one of the integration technologies, a technique of conducting a semiconductor element by using a wire and a microelectrode (bump) is used [6,7]. Bumps are made by electrolytic plating, and a resist is used as a template [8-10]. In order to prevent short-circuiting between the elements when integrating the semiconductor elements, the bumps have a certain thickness to keep the distance between the elements. Therefore, thick resist film from a few tens to hundreds of micrometers is used for manufacturing bumps.

In the case where the resist is used as a thick film, there is concern that the resolution may be lowered due to an increase in development time as compared with a thin film [11]. A negative tone resist using a crosslinking reaction is mainly used because it is excellent in this point [12,13]. SU-8 is currently the most widely used negative tone resist, and it is possible to produce a pattern of 20 μm with a film thickness of 200 μm [14-16]. These crosslinked polymers have low removability, and in that respect, positive tone resists are superior. The positive tone resist is easy to lift off, and the development of a positive tone resist that can be used for a thick film is expected from the viewpoint of improving production efficiency of three-dimensional mounting. However, the problem of development resistance has not been solved yet, and the processing limit of the positive resist is 10 μm, and only films up to 60 μm have been commercialized.

In this study, we aimed at improving the resolution of positive tone novolak resist, and designed the structure of a low molecular weight compound called dissolution inhibitor (DI) which works as an inhibitor for the OH-group in novolak resin and has high dissolution inhibiting ability of polymer in unexposed area [17]. DI is deprotected by acid, and the compound after deprotection promotes dissolution of the polymer in exposed area, so it is called a dissolution accelerator (DA). By designing a structure that likewise increases this dissolution accelerating ability, the dissolution rate ratio between the unexposed area and the exposed area was increased to improve the resolution. For
the deprotection of DI, we attempted to improve sensitivity and resolution by incorporating chemical amplification mechanism using acid catalyst [18].

2. Experimental

Two types of novolak resins ($M_n$: 4600-5600 and 6500-7900) were utilized as a base resin. Propylene glycol monomethylether acrylate (PGMEA) was utilized 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 aqueous solution was utilized as a developer. Hydroquinone (DA1), 4,4′-(propane-2,2-diyl)diphenol (DA2), 4,4′,4″-methylidynetrisphenol (DA3), 4,4′-[1-[4-bis-phenol (DA4) were used as DA. DI was prepared according to the methods reported in the literature [19]. 2,2′-[[1-[4-[4-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]phenyl]-1-methylethyl]phenyl]ethylidene]bis(4,1-phenyleneoxy)]bis-,1,1′-bis(1,1-dimethyl-ethyl) ester ($t$-Bu-DI5) was obtained by reacting DA2 with $t$-butyl bromoacetate under basic conditions [20]. The chemical structure of the synthesized DI is shown in Scheme 1. 2,2′-[[1-[4-[4-[2-(1,1-Dimethylethoxy)-2-oxoethoxy]phenyl]-1-methylethyl]phenyl]ethylidene]bis(4,1-phenyleneoxy)]bis acetic acid ($t$-Bu-DI5) was obtained by thermally decomposing $t$-Bu-DI5.

The polymer solution was prepared by dissolving equal amounts of two novolak resins in PGMEA and the concentration of was 40 wt%. When observing the influence of DI and DA on polymer solubility, appropriate amounts of DI and DA were added to the polymer solution. When observing the influence of DI on resist characteristics, $t$-Boc-DI4 or $t$-Bu-DI5 and PAG were added to the polymer solution and the concentration of DIs and PAG was 15-17 and 3 wt% relative to base polymer. The concentration of DIs was adjusted so that the substance amount to 1 g of polymer was the same.

The prepared solution was spin-coated on a three or four inches silicon wafer. Silicon wafers were treated with hexamethyldisilazane. After spin-coating, the wafer was prebaked on a hot plate at 100 °C for 5 min, and the film thickness was measured using stylus surface profilometer (Bruker Co., Ltd., Dektak 6M). The prebaked resist was then exposed and baked again at 100 °C for 2 min. All films were developed with 2.38% of TMAH aqueous solution for 2 min. The film thickness remained after development was measured. The exposure conducted using M-1S (Mikasa Co., Ltd.).

3. Results and discussion

In order to investigate the effect on inhibiting dissolution of novolak resin by DI, a polymer film to which was added varying amount of DI was prepared and its Alkali dissolution rate (ADR) was measured under non-exposure condition. The correlation between the ADR of the polymer film and the substance quantity of DI per gram of polymer is shown in Fig. 1. It is found that increase

![Scheme 1. Chemical structure of DIs.](image)
in the additive amount of DI resulted in exponentially decrease in ADR of the polymer film. In addition, when comparing the ADR of the polymer film containing DI, the ADR of the polymer film containing t-Boc-DI4 and t-Bu-DI5 was the smallest, followed by the polymer film containing t-Boc-DI3, t-Boc-DI2, and t-Boc-DI1. Since the ADR of the polymer film became smaller as the molecular size of the contained DI was larger, it was found that DI having a larger molecular size greatly suppresses dissolution of the polymer. In the subsequent experiments, t-Boc-DI4 and t-Bu-DI5 which sufficiently inhibited the dissolution of the polymer were used.

Next, in order to investigate the effect on promoting dissolution of novolak resin due to the difference in acidity of DA, the ADR of the polymer film containing DA4 or DA5 was measured under non-exposure condition. DA4 is derived from phenol, DA5 is derived from carboxylic acid, and the acidity of DA5 is larger. The correlation between the ADR of the polymer film and the amount of DA per gram of polymer was shown in Fig. 2. It was found that increase in the amount of DA added resulted in a linear increase in ADR of the polymer film. In addition, when comparing the ADR of a polymer film containing the same substance quantity of DA, the ADR was larger in the polymer film containing DA5 than that containing DA4. From this, it was found that the higher the acidity of DA is, the higher the dissolution promoting ability is. From the above results, it was anticipated that by increasing the acidity of DA, the difference in ADR between the polymer film of the unexposed and the exposed area becomes large and resist to which was added DA having high acidity possesses high-resolution.

The influence of DI on resist characteristics was evaluated. The t-Boc-DI4 and t-Bu-DI5, which differed in acidity after deprotection, were used for the evaluation. The sensitivity curve is shown in Fig. 3. The resist film containing t-Boc-DI4 started to dissolve with less exposure than that containing t-Bu-DI5. This is presumed to be because the activation energy of the t-Boc group is smaller than that of the t-Bu group. However, the amount of exposure necessary for complete dissolution of each resist film was 282 mJ/cm² for the resist film containing t-Boc-DI4 and 252 mJ/cm² for that containing t-Bu-DI5. The resist film containing t-Bu-DI5 gave higher sensitivity due to satisfactory promoting effect on dissolution of polymer. Also, the resist film containing t-Bu-DI5 has high contrast and it was expected to have high resolution.
A pattern was actually prepared by using a resist to which t-Boc-DI4 and t-Bu-DI5 was added, and the shape of the pattern was observed. Each pattern image is shown in Fig. 4. In the pattern prepared with the t-Bu-DI5 added resist, the inclination of the pattern wall was small and a good pattern shape was shown. This is considered to be because the solubility promoting effect of the polymer in the exposed part was large. In addition, when a t-Boc-DI4 added resist was used, a pattern of 19 μm can be formed with a film thickness of 11 μm, and, when a t-Bu-DI5 added resist was used, a pattern of 7 μm can be formed with a film thickness of 9 μm. Resist to which t-Bu-DI5 was added could improve resolution by raising the acidity of DA.

4. Conclusion

The inhibiting ability of DI to the dissolution of polymer was improved by increasing the molecular size of DI. The promotion ability of DA for dissolution of polymers was improved by increasing acidity of DA. Improvement in sensitivity was achieved by adding DI with high acidity after decomposition to the resist. Resist containing DI with large molecular size and high acidity after decomposition was improved in resolution. When a t-Bu-DI5 added resist was used, a pattern of 7 μm can be formed with a film thickness of 9 μm.

Fig. 4. SEM micrographs of pattern prepared by resist containing t-Bu-DI5 (a), (b) and resist containing t-Boc-DI4 (c), (d).

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