Dissolution Promotion Effect of Addition of Low Molecular Compounds to Positive Tone Chemically Amplified Photoresist System

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Three-component chemically amplified photoresists which are consisted of a base resin, a photo acid generator and a dissolution inhibitor are promising because the high sensitivity and the high resolution can be satisfied at the same time. We studied about the dissolution promotion effect of hydroquinone (HQ) in the exposed area. HQ is a model compound of the photo induced product of the dissolution inhibitor. We disclosed that HQ depressed a glass transition temperature ($T_g$) of the base resin and the sensitivity was improved by enhancing the dissolution rate in the exposed area. It is expected that the dissolution rate was promoted when the post exposure bake temperature exceeded $T_g$ because the acid diffuse more easily.

Keywords: Chemically amplified photoresist, Dissolution inhibitor, Three-component photoresist, High sensitivity

1. Introduction

In order to achieve high throughput in manufacturing electronic devices, such as integrated circuits (IC) and micro electro mechanical systems (MEMS), chemically amplified (CA) photoresists are applied in a semiconductor manufacturing process [1-3]. The concept of CA photoresist was introduced by Ito et al. in 1982 [4-6]. Generally, CA photoresists are composed of two components, that is, base resin and photo acid generator (PAG). A kind of aqueous-base soluble polymer with acid labile protecting group is used for base resin [7,8]. tert-Butoxycarbonyl (t-Boc) group is a known example of such a protecting group. t-Boc protected poly(p-hydroxystyrene) is one of the most common base resin [9,10]. Figure 1 shows the reaction mechanism of the CA photoresist. In positive-tone CA photoresists, photochemically generated acid catalyzes cleavage of pendant protecting groups to generate base-soluble acidic functionalities. The acid is regenerated during the deprotection reaction, and consequently the amount of acid is conserved [11]. Thus, CA photoresists exhibit excellent apparent quantum yields.

CA photoresists were originally developed for use in krypton fluoride photoresists, and they have been applied to i-line photoresists to improve lithographic properties [12]. In the meantime, there were some studies on adding low molecular lipophilic compounds to conventional two-component CA photoresists [13-16]. This new photoresist is called the three-component CA photoresist. The added compound is named dissolution inhibitor or dissolution reverser. Several types of dissolution inhibitors have been investigated by some groups. Most of the
dissolution inhibitors have acid labile groups such as t-Boc groups in their structure [17]. The small lipophilic molecule inhibits the dissolution of the base resin in an unexposed area, and this is considered as the consequence of interaction between base resin and dissolution inhibitors via hydrogen bonding [15,18]. On the other hand, in the exposed area, photo induced acid alters lipophilic molecules into hydrophilic, thus dissolution inhibitor molecules cannot inhibit the dissolution of the polymer film any more, but assist dissolution of the polymer film in aqueous developer. On account of these superior characteristics of dissolution inhibitors, high resolution and high sensitivity may be realized in the same time. Clarifying how dissolution inhibitors work in the polymer film is important to design novel CA photoresist systems but few researches on dissolution promotion mechanism in the exposed area have been reported.

In this study, we investigated the mechanism of dissolution promotion effect of dissolution inhibitors in an exposed area by comparing a two-component photoresist and a three-component photoresist. We added hydroquinone (HQ) into the two-component photoresist because 1,4-bis(tert-butoxy carbonyloxy)benzene (B-HQ) which is a kind of the dissolution inhibitor changes into HQ by a photo induced acid.

2. Experimental

Poly(p-vinylphenol) (PVP, Maruzen Petrochemical CO., LTD., $M_w$: 5,200, $M_n$: 2,700) (product name: Maruka lyncur S-2P) and poly(p-hydroxystyrene-co-p-(1-ethoxyethoxy)stylene) (EE PVP) were used as base resin. Propylene glycol monomethylether acetate (PGMEA) was utilized as a solvent for base resin. The PAG 2-Methyl-α-[2-[(propylsulfonyl)oxy]imino]-3(2H)-thiénylidene]benzeneacetonitrile (product name: Irgacure PAG103) was obtained from BASF. Tetramethylammonium hydroxide 2.38 wt% aqueous solution (Tokyo Ohka Kogyo CO., LTD.) was utilized as a developer. B-HQ and HQ (Wako Pure Chemical Industries, Ltd.) were utilized as low molecular compounds. B-HQ was synthesized from HQ. The two-component resist solution was prepared by dissolving the base resin and the PAG in PGMEA. The concentration of the polymer solution was prepared 20.5 wt%. The three-component photoresist solution was made by mixing HQ into the two-component photoresist solution.

EE PVP was synthesized by a polymer reaction of PVP with distilled ethyl vinyl ether as previously reported [19,20]. 5.0 g of PVP, 1.5-6.0 g of ethyl vinyl ether and a catalytic amount of $p$-toluenesulfonic acid were charged into a flask with 50 mL of tetrahydrofuran (THF). The mixture was stirred for few hours under the room temperature. The mixture was evaporated and washed with ethyl acetate after adding a little triethylamine into the reaction mixture to quench reaction. Then, the mixture was dissolved into small amount of acetone, and precipitated in n-hexane. The polymer was collected and dried under vacuum.

The photoresist solution was spin-coated on a three inches silicon wafer. Silicon wafers were treated with hexamethyldisilazane. After spin-coating, the wafer was prebaked on a hot plate at 100 °C, and observed film thickness followed by the radiation of an i-line and post-exposure baking at 100 °C for 1 min. The resist films were developed with 2.38 wt% aqueous TMAH for 1 min. The film thickness was observed using stylus surface profilometer Dektak 6M (Bruker Nano). The exposure was conducted using M-1S (Mikasa Co., Ltd.).

Glass transition temperature ($T_g$) of the polymer film was analyzed using a DSC (Seiko Instruments Inc., DSC6200). The measurement was conducted under N₂ flow. The samples were heated and cooled at 10 °C/min.

3. Results and discussion

The control of the copolymer composition of EE PVP is important to adjust its solubility in the developer. We defined the protection degree of EE PVP as (the number of $p$-(1-ethoxyethoxy)stylene units) / (the number of $p$-(1-ethoxyethoxy)stylene units and $p$-hydroxystyrene units). Some stirring times are attempted and we disclosed that we could hardly control the protection degree when stirred 3-5 hours, therefore 7 hours was chosen for the stirring time. Then, the reactant charging rate was optimized. Figure 2 shows the relationship between the charge ratio of ethyl vinyl ether and the protection degree of EE PVP. We could control the protection degree by feeding more than equivalent amount of ethyl vinyl ether.

First, the sensitivity enhancement effect of B-HQ was confirmed by comparing the two-component photoresist and three-component photoresis. The two-component photoresist was composed of the base resin and the PAG and the three-component photoresist was composed of the base resin, the PAG and B-HQ. The sensitivity was improved as
previously reported although the exposure wavelength and the base resin differ from the previous work. Then, to study the sensitivity enhancement mechanism in the exposed area, the sensitivity of the two-component photoresist and the three-component photoresist which contained 4 wt% of HQ was compared. Dissolution inhibitor B-HQ changes into HQ in the exposed area, this is the reason why HQ was chosen as an additive low molecular compound. In this work, the sensitivity is defined as the minimum exposure dose at which 1 cm×1 cm square film could be dissolved in 2.38 wt% TMAH developer within 1 minute. Figure 3 shows the relationship between the film thickness and the sensitivity when the 35% protected EE PVP was utilized as the base resin. As shown in Figure 3, although the sensitivity of the two-component CA photoresists was in the range of 5-10 mJ/cm², the sensitivity of the HQ added three-component CA photoresists was below 5 mJ/cm². Figure 4 shows the relationship between the film thickness and the sensitivity when the EE PVP whose protection degree was 47% was utilized. We anticipated that the sensitivity improved by adding HQ in like manner as the previous experiment but the sensitivity of the three-component CA photoresists was not risen. Moreover, sensitivity enhancement could not be observed when 26 and 68% protected EE PVP was used as the base resin.

In order to study the protection degree-dependent sensitivity enhancement, $T_g$ of EE PVP and the mixture of EE PVP and HQ was evaluated by DSC measurement. Figure 5 stands for $T_g$ at each protection degree. $T_g$ was depressed along with increase of protection degree. Addition of HQ depressed $T_g$ of EE PVP. Some interactions between HQ and EE PVP may create. What is notable is that...
the diminution in $T_g$ was occurred when 19, 45 and 68% even though sensitivity improvement was not occurred at these protection degrees. In this study, the PEB temperature was set to be 100 °C thus it is expected that the sensitivity was enhanced only when the 35% protected EE PVP was used as the base resin because $T_g$ of EE PVP decreased from 108.7 °C to 86.0 °C by HQ addition. The $T_g$ decrease below PEB temperature could promote acid diffusion in exposed area.

4. Conclusion
HQ worked as a dissolution promoter only when 35% protected EE PVP was utilized as a base resin. However, when 26 or 45% protected EE PVP was utilized as a base resin, there was no dissolution promote effect though HQ interacted with the base resin. The mechanism of dissolution enhancement in an exposed area was revealed by our study. From $T_g$ analysis of EE PVP and the mixture of EE PVP and HQ, dissolution was enhanced because the PEB temperature exceed $T_g$. The photo induced acid can diffuse more easily across a bulky polymer film. In designing dissolution inhibitor molecules, the ability to lower the $T_g$ of the base resin is important.

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