Acid-breakable Resin-based Resist for Nanofabrication

Electron-beam Lithography

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A new chemical amplification positive resist system designed for nanofabrication electron-beam lithography is described. The positive resist system consists of an acid-generator and an acid-breakable (AB) resin that can be converted to polyphenol fragments by an acid-catalyzed reaction. The AB resin is synthesized through a co-condensation reaction between polyphenol and aromatic multi-functional vinyl ether compounds (bisvinylether and trisvinylether compounds). Molecular weight (MW) of the AB resin increases with an increase in the vinyl ether feed ratio. A condensation reaction with a polyphenol/vinyl ether feed ratio of 100/50 results in a high MW ($M_w > 5000$) AB resin which is insoluble in an alkali developer (tetramethylammonium hydroxide: 2.38 wt%). The acid-catalyzed fragmentation of the AB resin in the resist film was confirmed through gel permeation chromatography. The resist with the AB resin showed the high resolution of 80-nm line-and-space patterns with high sensitivity ($5.0 \mu\text{C}/\text{cm}^2$ at 30 kV).

Keywords: electron-beam, positive resist, acid-breakable resin, vinyl ether compound, acid-catalyzed fragmentation

1. Introduction

For the fabrication of nanoelectronic devices with sub-100-nm dimensions, electron-beam (EB) lithography is most useful technique. We have investigated a novolak resin-based chemical amplification (CA) positive resist, consisting of a novolak resin, an acetal-protected dissolution inhibitor, and an acid generator [1,2]. Although the resist enabled fabrication of 100-nm contact hole patterns with high sensitivity ($6.0 \mu\text{C}/\text{cm}^2$ at 50 kV), the resolution was still insufficient for sub-100-nm fabrication.

In a previous paper [3], we investigated nanometer-scale imaging characteristics of a novolak resin-based CA resist and the molecular weight (MW) distribution effects of the resin matrix. As described in the paper, the wide MW distribution, which results in high contrast of dissolution rates between exposed and unexposed regions of the resist, caused nanometer-scale line edge roughness in the fine pattern. However, the degree of edge roughness was greatly reduced in

the fractionated novolak resin-based resist which showed lower resolution than the conventional novolak resin-based one. This paper reports on a new resin matrix of a CA positive resist for alkali development. This resin has high dissolution contrast that can be independent of the MW distribution.

CA resists for aqueous alkali development have achieved great success in recent sub-0.5- μm lithography. However, PMMA has been widely used as a high-resolution positive EB resist for nanofabrication. This is because a reduction in MW through the radiation-induced main-chain scission enables a large dissolution contrast in an organic developer. In the early stages of developing CA resists, acid-degradable polymers have been studied [4,5]. These polymers were used as a self-development imaging material and/or dissolution inhibitor in a novolak resin-based CA positive resist. Recently, Schacht et al. reported the use of acid-labile cross-linking units in their CA positive resist [6]. These cross-linking units lead to

an increase in MW and improved dissolution inhibition, thus enhancing the thermal flow stability and resolution of the resist.

In this article, we describe acid-breakable (AB) resins synthesized by a co-condensation reaction between polyphenol and aromatic multi-functional vinyl ether compounds. Since polyphenol compounds are very soluble in aqueous alkali developer, such resins can act as an alkali-developable matrix resin in CA positive resists. Preparation and characteristics of the AB resins are investigated. We also discuss the exposure characteristics of the AB resin-based resist. In addition, we report on the preliminary lithographic performance of the resist.

2. Experimental

2.1 Preparation of multi-functional vinyl ether compounds

The phenols used as starting materials of the aromatic bis- and trisvinyl ether compounds were 4,4'-dihydroxydiphenylmethane, 4,4',4''-trihydroxytriphenylmethane, and phloroglucinol purchased from Tokyo Kasei Kogyo Co. The vinyl ether compounds shown in Figure 1 were synthesized by the reaction of 2-chloroethylvinyl ether with a phenol in DMSO as described in previous articles [7, 8].

2.2 Preparation of AB resins

A series of AB resins were synthesized in a similar manner as shown in Figure 2. We tested several vinyl ether compounds feed ratios (wt. ratios) for the preparation of the resins. The polyphenol/vinyl ether wt. ratios were 100/10, 100/30, and 100/50. A typical example (wt. ratio of 100/50) is as follows. The polyphenol (2 g) and EVE-1 (1 g) were dissolved in ethyl acetate solution (100 ml) and pyridinium p-toluenesulfonate (PTS) (0.01 g) was added to this solution as an acid catalyst. After the solution was stirred at room temperature for one day, the solution was washed with 3% NaOH twice, and distilled water once. The solution was then dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resin was precipitated in n-hexane and purified.

2.3 Materials

The polyphenol investigated as a polyphenol unit in the AB resin syntheses was supplied by Honshu Chemical Co. (Figure 1). The acid generators used in this study were N-

ethanesulfonyloxy-1,8-naphthalimide (NAIOET), N-nonafluoro-1-butanefulfonyloxy-1,8-naphthalimide (NAIONO) [9], and tri(ethanesulfonyloxy)benzene (EtSB) [10]. An alkyl-substituted onium iodide was used as the additive for acid-diffusion control [11]. The commercially available aqueous-alkali developer NMD-3 (tetramethylammonium hydroxide: 2.38 wt%, Tokyo Ohka Co.) was used as the developer. 2-heptanone (MAK) was used as a resist solvent.

Figure 1 Chemical structures of vinyl ether compounds and polyphenol

2.4 Characterization

The chemical structures of the synthesized compounds were identified from IR spectra (Perkin-Elmer FT-IR 1720X) and NMR spectra (Varian Mercury 200 MHz). Gel-permeation chromatography (GPC) was performed using a Hitachi L-6000 liquid chromatography system equipped with Gelpak A-150, A-140 and A-120 GPC columns (Hitachi Chemical Co.) The GPC solvent was tetrahydrofuran. Thermogravimetric analysis (TGA) was done on a Shimadzu TG-40M and differential scanning calorimetry (DSC) was applied using a Perkin-Elmer DSC-7 at a heating rate of 10°C/min for TGA and 20°C/min for DSC in nitrogen. Electron-beam exposure characteristics were measured by a scanning electron microscopy at 30 kV using a modified Hitachi S-570. Electron-beam lithography evaluations were conducted with a raster scan Gaussian beam EB writer at 30 kV. Deep-UV exposure at 250 nm was made with a Xe-Hg lamp through an interference filter. The

light intensity was determined with a calorimetric flux detector thermopile (JASCO INC.). The sample films were spin-coated onto silicon wafers and baked on a hot plate under various conditions. The film thickness was determined by using a profilometer, Alpha-step 200 (Tencor Instrument Co.). Fabricated patterns were observed by a scanning electron microscopy using a Hitachi S-4200.

Figure 2 Acid-catalyzed condensation of polyphenol with EVE-1

3. Results and Discussion

3.1 Physical properties of AB resins

The effects of the structure and content of the vinyl ether on the physical properties of the AB resin is summarized in Table 1. As expected, the MW of AB resins increased with an increasing vinyl ether content. In the case of trisvinylethers (EVE-1 and EVE-2), at 30 wt% the MW was increased by a factor of about 5 compared with that of the polyphenol (Mw: 1060). By contrast, the bisvinylether (EVE-3) needed 50 wt% to obtain a high MW resin (Mw>5000).

To estimate the flow stability of the resist patterns, we also measured Tg of several resins obtained with a vinyl ether content of 30 or 50 %, as shown in Table 1. AB-1c (50 wt%) showed the highest Tg (103°C), and this was close to that of most conventional novolak resins used in positive photoresists. We ascribe the difference in Tg among these resins (with the same wt. ratio) to the difference in the melting points of these vinyl ethers. In addition, although it is well-known that the Tg of acetal-protected PHS decreases with an increasing acetal-protection degree [12], there was no evidence of a decrease in the resin's Tg when the vinyl ether content was increased (AB-2b and AB-2c).

Table 1 Physical properties of AB resins

Resin	Vinylether	PP/VE feed ratio ^a	Mw	Mn	Tg (°C)
AB-1a	EVE-1	100/10	2150	1580	—
AB-1b	EVE-1	100/30	5700	2200	—
AB-1c	EVE-1	100/50	8200	2200	103
AB-2a	EVE-2	100/10	1570	1410	—
AB-2b	EVE-2	100/30	7700	2500	78
AB-2c	EVE-2	100/50	8600	2100	80
AB-3a	EVE-3	100/10	1500	1100	—
AB-3b	EVE-3	100/30	1800	1300	—
AB-3c	EVE-3	100/50	8650	2400	86

^aPolyphenol/vinylether feed ratio

The TGA trace of AB-1c, as an example, is shown in Figure 3. Up to 250°C there was little significant change in TGA, then at about 360°C thermal decomposition occurred. This behavior is similar to that of the novolak resin. Therefore, this decomposition temperature clearly demonstrates the high thermal stability that is obtained through the condensation between multi-functional vinyl ether and the polyphenol unit.

Figure 3 TGA curve of AB-1c

As AB resin is used as an insoluble matrix resin in the resist system, we evaluated the dissolution inhibition ability of the resins. The dissolution rates of the resins were measured as a function of the vinyl ether content, as shown in Figure 4. For the three vinyl ethers, a 50 wt% was enough to ensure negligible dissolution for alkali development. From this result, we expected the dissolution contrast between unexposed and exposed areas to be about four orders of magnitude, because the polyphenol unit should be regenerated in the exposed areas.

Figure 4 Change in the dissolution rate with an increase in the vinyl ether content. polyphenol/vinylether=100/X (wt. ratio)

Figure 5 Molecular weight distributions of polyphenol and AB-1c/NAIOET=100/5 mixture film after PB, after exposure, and after PEB.

3.2 Acid-catalyzed fragmentation of AB resin

To investigate whether a large decrease in the MW occurs, the MW distributions of a model resist film with AB-1c were measured after prebaking (PB) (90°C, 120 s), after deep-UV exposure (10 mJ/cm²), and after post exposure baking (PEB) (100°C, 120 s). The mode composition was AB-1c/NAIOET=100/5 (wt ratio). The results are shown in Figure 5. After PB there was no peak in lower MW region (Mw<1000), indicating that this resin was free from unreactive vinyl ether. Also, there was no difference in MW distribution before and after PB (not shown in this figure). After exposure there was little or no change in the MW distribution. This means the acidolysis of acetal moieties in the presence of a photogenerated acid does not occur at room temperature. By contrast, after PEB most of the higher MW components had disappeared, and both the polyphenol and the cleavage product (Mw: ~500) appeared. These results indicate this type of resin is susceptible to acid-catalyzed fragmentation.

A reaction mechanism for the acid-catalyzed hydrolysis of a thermally cross-linked resist using a vinyl ether compound as a cross-linker has already been described [13]. To explain the mechanism of acid-catalyzed fragmentation of an AB resin, we measured the ¹H-NMR spectra of AB-1c before and after adding methanesulfonic acid in (CD₃)₂CO solvent. Figure 6 shows the ¹H-NMR spectra and the assignments of AB-1c before and after the acid was added. The methyl proton (a) of acetal groups appeared at about 1.3 ppm in the spectrum of the neat AB-1c. The proton (a) disappeared when the acid was added, and this was accompanied by the appearance of new peaks ((f) and (g)) due to acetaldehyde. However, other proton peaks remained unchanged after the acid was added.

An acid-catalyzed fragmentation mechanism of AB-1 based on our ¹H-NMR spectroscopic study and GPC analysis is summarized in Figure 7. Protonated phenolic oxygen liberates a phenol and an oxocarbenium ion during PEB. This carbenium ion can react with water from the atmosphere to give the hydroxy intermediate and regenerate a proton. Finally the cleavage products, that is, alcohol and acetaldehyde are produced by protonation at ether oxygen. These results suggest that the main fragmentation products are the initial polyphenol unit, a phenoxyethyl alcohol derivative, and acetaldehyde.

Figure 6 ¹H-NMR spectra of AB-1c in (CD₃)₂CO before (a) and after (b) adding CH₃SO₃H

3.3 Exposure characteristics and lithographic evaluation of the AB resin-based resist system

To determine whether the expected dissolution contrast could be obtained or not, we measured the exposure characteristics of a model resist as the development time was varied (2, 10, 30, and 60 s). The model composition was AB-1c/EtSB=100/4 (wt ratio). The results are shown in Figure 8. Even at 2 s, a complete positive tone was obtained. In addition, we found that changing the development time did not affect the sensitivity or the contrast due to the large dissolution contrast.

The effects of the PB and PEB temperature on the exposure characteristics of the same resist composition are shown in Figures 9 and 10, respectively. In the PB temperature region investigated, the exposure characteristic curves of

Figure 7 An acid-catalyzed fragmentation of AB resin.

the resist were unchanged. Also, when the PEB temperature was varied in the range of 80-100°C, the sensitivity reached a plateau at or above 90°C.

The effects that the kind of AB resin have on the exposure characteristics are shown in Figure 11. The resist compositions were AB resin/EtSB=100/4 (wt. ratio). The evaluated AB resins were AB-1c, AB-2c, and AB-3c. Although these resins showed no significant contrast reduction, there was a large difference in their sensitivity. In particular, the sensitivity for AB-3c was about one order of magnitude higher than that for AB-1c. Since these resins (AB-1c and AB-3c) contain almost the same content of the acetal groups, we ascribe the difference in sensitivity to the molecular size of the vinyl ether backbone structure and/or the dissolution promotion of a cleavage product.

Figure 8 Effect of development time on the exposure characteristics of a resist with AB-1c. Resist composition: AB-1c/EtSB=100/4 (wt. ratio) PB: 100°C for 5 min. PEB: 100°C for 2 min. Film thickness: 350 nm

Figure 10 Effect of PEB temperature on the exposure characteristics of a resist with AB-1c. Resist composition: AB-1c/EtSB=100/4 (wt. ratio) PB: 100°C for 2 min.

Figure 9 Effect of PB temperature on the exposure characteristics of a resist with AB-1c. Resist composition: AB-1c/EtSB=100/4 (wt. ratio) PEB: 100°C for 2 min.

Figure 11 Exposure characteristics of resists with AB resins. Resist composition: AB resin /EtSB=100/4 (wt. ratio) PB: 100°C for 5 min. PEB: 100°C for 2 min. Development time: 60 s.

Preliminary patterning of the resist using AB-1c and AB-3c was carried out with a 30 kV EB writer. The resist compositions were AB resin/NAINO=100/4 (wt ratio). The observed patterns showed a T-top profile due to the formation of an insoluble surface layer. Therefore, patterning of the resist using AB-2b was carried out. As the dissolution rate of AB-2b was too high to use the 2.38% TMAH developer, dilute TMAH (1.19%) was used as a developer. Scanning electron micrographs of a typical delineated pattern are shown in Figure 12. Even though the optimization of the resist composition and process conditions was still insufficient, we were able to open 110-nm line-and-space (L/S) patterns at a dose of $4.0 \mu\text{C}/\text{cm}^2$ for an initial $0.22\text{-}\mu\text{m}$ film thickness, and 80-nm L/S patterns were resolved with a dose of $5.0 \mu\text{C}/\text{cm}^2$. However, each pattern tended to have a T-top profile and considerable line edge roughness. We are now investigating the cause of these phenomena.

4. Conclusion

We have developed a novel acid-breakable (AB) resin obtained through the condensation of polyphenol with multi-functional vinyl ether compounds. Synthesized resins made with a 50% vinyl ether feed ratio gave a high MW ($M_w > 5000$) and were insoluble in an aqueous alkali developer (2.38% TMAH). The photogenerated acid induced fragmentation of the resin to produce low MW components. Among these resins, the resin with bisvinylether (EVE-3) showed the highest sensitivity ($0.8 \mu\text{C}/\text{cm}^2$). The resist with AB-2b for a 30 kV EB writer could resolve 80-nm L/S patterns with a dose of $5.0 \mu\text{C}/\text{cm}^2$.

5. Acknowledgments

We express our gratitude to Dr. Sumio Hosaka for use of the EB writer, and to Takashi Hattori for his useful advice on NMR measurement.

6. References

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Figure 12 Scanning micrographs of (a) 110 nm L&S, (b) 100 nm L&S, (c) 80 nm L&S patterns obtained by electron-beam exposure at 30 kV. Process conditions: PB 90°C for 2 min, PEB 90°C for 2 min, development time of 60s, and exposure dose of (a), (b) $4.0 \mu\text{C}/\text{cm}^2$, and (c) $5.0 \mu\text{C}/\text{cm}^2$

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