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A Chemically Amplified Molecular Glass Resist with an Ionic Photoacid Generator and a Single Protection Group

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ABSTRACT: A molecular glass resist with an ionic photoacid generator and a single protection group (MR-1) has been developed. MR-1 exhibited good thermal properties, such as a 5% weight loss temperature ($T_{d5\%}$) of 167°C and a glass transition temperature (T_g) of 80°C. MR-1 showed the good sensitivity of 80 μC/cm^2 and high contrast of 4.9 with e-beam exposure (50 keV). A relatively high resolution of 50 nm and low Line-Edge-Roughness of 3.8 nm were obtained by e-beam exposure (100 keV). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39769.

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INTRODUCTION

Chemically amplified resists (CARs)[1,2] have been widely used for the fabrication of integrated-circuits. In general, it is necessary for modern CARs to simultaneously improve their resolution, sensitivity and Line-Edge-Roughness (LER), which represents the roughness of the fabricated fine patterns. In particular, the LER must be improved because a high LER produces a low-performing electric device.[3] However, there is a trade-off relationship among the resolution, sensitivity, and LER of the CARs. For example, a long diffusion length in the lithography process leads to a high sensitivity, however, simultaneously leads to an image blur resulting in negative effects on the resolution and LER.[4,5]

One of the approaches to improve the LER is the use of molecular glass resists.[6–8] They have several advantages compared to conventional polymer photoresists, such as low molecular weights, small molecular sizes, and well-defined structures.[9] These unique properties contribute to the improvement of the resolution and LER.

Another approach for a low LER is the reduction in the number of components in the resist films. In general, the mixture composed of a resist resin, photoacid generator (PAG), and cross-linker in some cases is used as CARs. However, the aggregation of each component sometimes occurs because of their immiscibility, and this aggregation increases the LER value.[10,11] Therefore, a decrease in the number of resist components is an effective way to improve the LER.

Also, the reduction in the diffusion length of the photogenerated acid is known as a way to improve the LER, because a low acid diffusion length leads to an increase in the image contrast, and the resolution and LER can then be improved.[12] Therefore, many approaches for reducing the acid diffusion length have been developed, such as ionic PAGs with large-sized anion moieties,[13] PAG bound polymer photoresists[14] and PAG bound molecular glass resists.[15,16]

Henderson et al. reported an ionic single molecular resist based on a triarylsulfonium PAG, which showed 55 nm lines and 105 nm spaces that were nominally printed at 80 nm 1:1 lines/spaces, but line sliming because of photoacid diffusion reduced the lines to 55 nm using electron beam (e-beam) lithography. The LER was found to be 3.9 nm.[16] This resist suffered from a resolution limitation because of diffusion of a small and free photoacid. Although there are several problems regarding its solubility, glass transition temperature, and sensitivity, this single-component molecular resist provided all the basic requirements to serve as functional CARs, which prompted us to develop another single-component molecular resist.

In this study, we developed a novel molecular glass resist with an ionic PAG and a single protection group (MR-1, Figure 1). The features of the MR-1 are as follows: (i) MR-1 has a single acid-labile protecting group, therefore, the distribution of the dissolution rate in the alkaline developer can be suppressed. (ii) An anionic moiety of PAG is bound to MR-1. Hence, the number of resist components and the diffusion length can be decreased. (iii) MR-1 has been designed based on a rigid and bulky spirocyclic structure to achieve a high T_g, because molecular glass resists generally show a low glass temperature and

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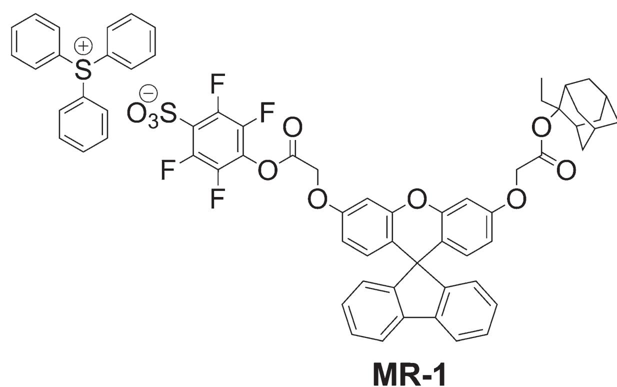


Figure 1. The chemical structure of MR-1.

high crystallinity that lead to a negative effect on the lithographic performance, such as a high LER and poor film-forming property.

EXPERIMENTAL

Materials

Sodium hydride was used after washing with hexane to remove oil. Anhydrous tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and acetone were used in all cases. Sodium 2,3,5,6-tetrafluoro-4-hydroxybenzenesulfonate[17] was synthesized according to the literatures. Other reagents and solvents were used as received.

Measurements

^{1}H and ^{13}C NMR spectra were recorded in chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) on a BRUKER DPX-300 spectrometer. Fourier-transferred IR (FT-IR) spectra were recorded on Horiba FT-720. Thermal analyses were performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10°C/min for thermogravimetry (TG) and a Seiko EXSTAR 6000 DSC 6200 connected to a cooling system at a heating rate of 10°C/min or 20°C/min for differential scanning calorimetry (DSC). The film thickness was measured by Veeco Instrument Dektak^3 surface profiler.

Synthesis of 3′-(2-Ethyl-2-adamantyloxycarbonylmethyloxy)-6′-hydroxyspiro[fluorene-9,9′-xanthene] (1)

Spiro[fluorene-9,9′-(3′,6′-dihydroxyxanthene)] (0.73 g, 2.0 mmol) was slowly added to a solution of sodium hydride (0.33 g, 1.4 mmol) in DMF (7 mL), and the solution was stirred for 1 h at room temperature. To this solution, the solution of 2-ethyl-2-adamantyl bromoacetate (0.35 g, 1.2 mmol) in DMF (3 mL) was slowly added at 0°C, and then the solution was refluxed overnight at 80°C. After the reaction, 0.1*M* citric acid aqueous solution was added to the solution, and the solution was extracted with ethyl acetate. Subsequently, the organic layer was separated, washed with water three times, and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a white solid. The solid was purified by silica gel column chromatography (eluent: ethyl acetate : hexane = 1 : 3, Rf = 0.40) and dried at 60°C *in vacuo* to give **1** as a white solid (0.39 g, yield: 57%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 9.52 (s, 1H, –O*H*), 7.9–6.0 (14H, Ar*H*), 4.75 (s, 2H, –OCH_2C(=O)O–), 2.2–0.6 (19H, adamantyl group).

^{13}C NMR (75 MHz, DMSO-d_6, ppm, TMS); 167.03, 157.38, 157.21, 154.71, 151.38, 151.27, 138.92, 128.19, 127.96, 127.63, 124.84, 120.11, 117.13, 114.53, 111.59, 110.73, 102.44, 101.93, 89.90, 64.77, 52.71, 37.50, 33.41, 33.11, 32.17, 26.30, 26.28, 24.35, 6.35.

IR (KBr, cm^{-1}); 1726 (–C(=O)O–).

Anal. Calcd for $C_{39}H_{36}O_5$: C, 80.1; H, 6.21. Found: C, 80.32; H, 6.31.

Synthesis of 3’-(2-Ethyl-2-adamantyloxycarbonylmethyloxy)-6’-hydroxycarbonylmethoxy Spiro[fluorene-9,9’-xanthene] (2)

The solution of **1** (0.58 g, 1.0 mmol) in THF (3 mL) was slowly added to a solution of sodium hydride (0.20 g, 8.3 mmol) in THF (3 mL) at 0°C, and the solution was stirred for 1 h at room temperature. To this solution, the solution of bromoacetic acid (0.21 g, 1.5 mmol) in THF (3 mL) was slowly added at 0°C, and then the solution was refluxed for 24 h. After the reaction, water was added to the solution to quench the residual sodium hydrate, and the reaction mixture was neutralized with citric acid. The solution was extracted with ethyl acetate, and then the organic layer was separated, washed with water three times, and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a white solid. The solid was purified by silica gel column chromatography (eluent: ethyl acetate : hexane = 1 : 3, then acetone) and dried at 60°C *in vacuo* to give **2** as a white solid (0.57 g, yield: 89%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 8.0–6.0 (14H, Ar*H*), 4.75 (s, 2H, –OCH_2C(=O)O–), 4.16 (s, 2H, –OCH_2C(=O)OH), 2.3–0.6 (19H, adamantyl group).

IR (KBr, cm^{-1}); 1752 (–C(=O)O–), 1719 (–C(=O)OH).

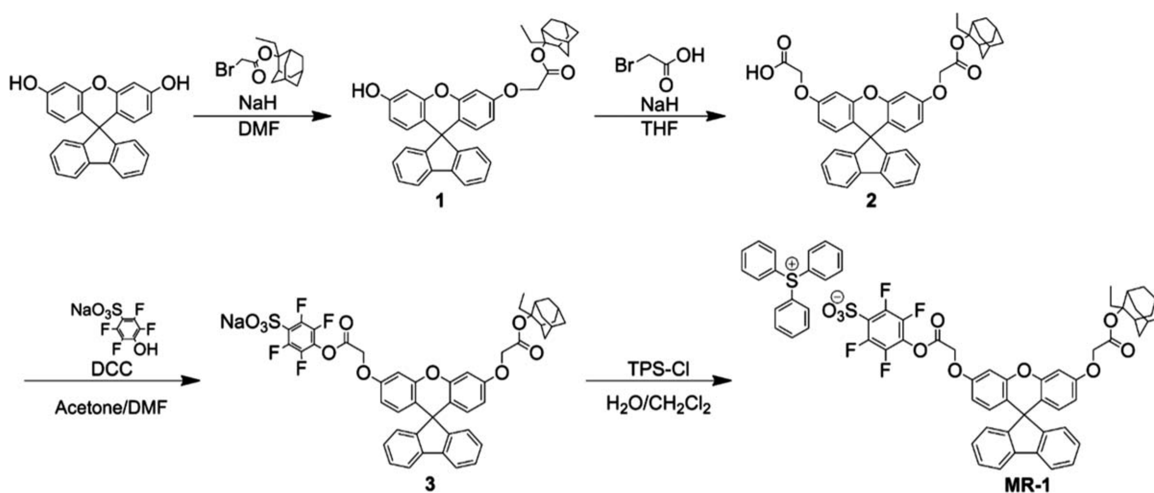
Anal. Calcd for $C_{41}H_{38}O_7$ 0.78H_2O: C, 75.0; H, 6.07. Found: C, 74.9; H, 5.96.

Synthesis of Sodium 4-((3′-(2-Ethyl-2-adamantyloxycarbonylmethyloxy)-Spiro[fluorene-9,9′-xanthene]-6′-yl)oxyacetoxy)-2,3,5,6-tetrafluorobenzenesulfonate (3)

A solution of **2** (2.11 g, 3.28 mmol), sodium 4-hydroxy-2,3,5,6-tetrafluorobenzenesulfonate (0.925 g, 3.45 mmol) and *N,N′*-dicyclohexylcarbodiimide (1.35 g, 6.56 mmol) in the mixture of acetone (60 mL) and DMF (12 mL) was stirred overnight at 50°C. The precipitate was then filtrated by suction through Celite on a sintered glass funnel, and the filtrate was removed under reduced pressure to afford a white solid. Then, water was added, and the solution was extracted with ethyl acetate. Then, the organic layer was separated, washed with water three times, and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a white solid.The solid was purified by silica gel column chromatography (eluent: acetone : chloroform = 6 : 4, Rf = 0.35) and dried *in vacuo* at 60°C to give **3** as a white solid (1.16 g, yield: 40%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 8.0–6.0 (14H, Ar*H*), 5.37

(s, 2H, –OCH_2C(=O)OAr–), 4.79 (s, 2H, –OCH_2C(=O)O–), 2.3–0.6 (19H, adamantyl group).



Scheme 1. Synthesis of MR-1.

^{13}C NMR (75 MHz, DMSO-d_6, ppm, TMS); 169.89, 167.16, 158.80, 157.57, 157.53, 156.94, 151.30, 151.23, 146.36 (J = 243 Hz), 139.04, 137.31 (J = 242 Hz), 128.47, 128.14, 127.96, 124.99, 120.35, 117.01, 111.36, 110.98, 102.04, 101.80, 89.96, 64.73, 64.65, 64.26, 53.69, 37.56, 33.47, 33.16, 31.21, 27.92, 26.35, 24.40, 6.50.

IR (KBr, cm^{-1}); 1805 (–C(=O)OAr–), 1743 (–C(=O)O–), 1180, 1049 (–SO_3^-).

Anal. Calcd for $C_{47}H_{37}F_4NaO_{10}S$ 0.67H_2O: C, 62.4; H, 4.27. Found: C,62.1; H, 4.02.

Synthesis of Triphenylsulfonium 4-((3′-(2-Ethyl-2-adamantyloxycarbonylmethyloxy)-spiro[fluorene-9,9′-xanthene]-6′-yl)oxyacetoxy)-2,3,5,6-tetrafluorobenzenesulfonate (MR-1)

A solution of **3** (0.52 g, 0.58 mmol) in dichloromethane was added to an aqueous solution of triphenylsulfonium chloride, and stirred for 1 h at room temperature. The organic layer was separated, and washed with 0.1 M citric acid aqueous solution twice, water three times, and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a white solid. The solid was purified by silica gel column chromatography (eluent: acetone : chloroform = 6 : 4, Rf = 0.40) and dried *in vacuo* at 60°C to give MR-1 as a white solid (0.45 g, yield: 68%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 8.0–6.6 (29H, Ar*H*), 5.32 (s, 2H, –OCH_2C(=O)OAr–), 4.77 (s, 2H, –OCH_2C(=O)O–), 2.3–0.6 (19H, adamantyl group).

^{13}C NMR (75 MHz, $CDCl_3$, ppm, TMS); 167.47, 165.00, 157.89, 157.21, 155.22, 152.22, 151.99, 147.17 (J = 245 Hz), 141.48 (J = 243 Hz), 139.62, 136.55, 135.43, 134.49, 134.41, 131.99, 131.84, 131.58, 131.54, 131.16, 131.11, 130.59, 130.36, 130.29, 129.32, 129.04, 128.57, 128.50, 128.38, 127.92, 125.78, 125.19, 125.05, 120.03, 119.44, 118.84, 117.76, 110.09, 110.80, 102.67, 102.36, 91.68, 65.51, 64.90, 53.42, 38.29, 34.28, 33.79, 33.17, 27.16, 26.91, 25.15, 6.95.

IR (KBr, cm^{-1}); 1743 (–C(=O)O–), 1808 (–C(=O)OAr–) 1180, 1041 (–SO_3^-).

Anal. Calcd for $C_{65}H_{52}F_4O_{10}S_2$ 1.43H_2O: C, 67.36; H, 4.77. Found: C, 67.13; H, 4.53.

Fabrication of the Fine Pattern with Electron-Beam Exposure

The photoresist films with 70 nm thickness on a silicon wafer were prepared from a cyclopentanone solution of MR-1 and trioctylamine in some cases. The prebake temperature, prebake time, postexposure bake temperature and postexposure bake time were 70°C for 120 seconds, 70°C for 90 seconds, respectively. The obtained resist films were exposed to electron-beam using spot e-beam tools (100 keV), and dipped in a 2.38 wt % TMAH aqueous solution for 60 sec. Obtained fine patterns were observed by SEM.

RESULTS AND DISCUSSION

Synthesis of MR-1

MR-1 was prepared in four steps according to Scheme 1. The chemical structure of each compound was determined by ^{1}H, ^{13}C-NMR, IR, and elemental analyses.

For the synthesis of **1**, the nucleophilic substitution reaction of spiro[fluorene-9,9′-(3′,6′-dihydroxyxanthene)] with 2-ethyl-2-adamantyl bromoacetate produced compound **1** in good yield of 57%. Next, compound **1** was treated with α-bromoacetic acid, producing compound **2** in an excellent yield. The ^{1}H-NMR spectrum of **2** showed characteristic signals at 4.75 ppm and 4.16 ppm, which correspond to the α-methylene of ethyladamantyl ester and acetic acid, respectively, and signals of the ethyladamantyl group were observed at 2.3–0.6 ppm. Compound **3** was then prepared from **2** and sodium 2,3,5,6-tetrafluoro-4-hydroxybenzenesulfonate using *N,N′*-dicyclohexylcarbodiimide as a condensation agent. In the ^{1}H-NMR spectrum of **3**, the signal of the α-methylene of acetic acid was shifted from 4.16 to 5.37 ppm, and characteristic C=O absorption was shifted from 1719 to 1805 cm^{-1} in the FT-IR spectrum of compound **3**. These spectral evidences clearly supported the formation of the expected ester bond. Finally, the single component resist MR-1 was prepared by the salt exchange reaction of **3** with triphenylsulfonium chloride at room temperature. The ^{1}H-NMR spectrum of MR-1 is shown in Figure 2. The

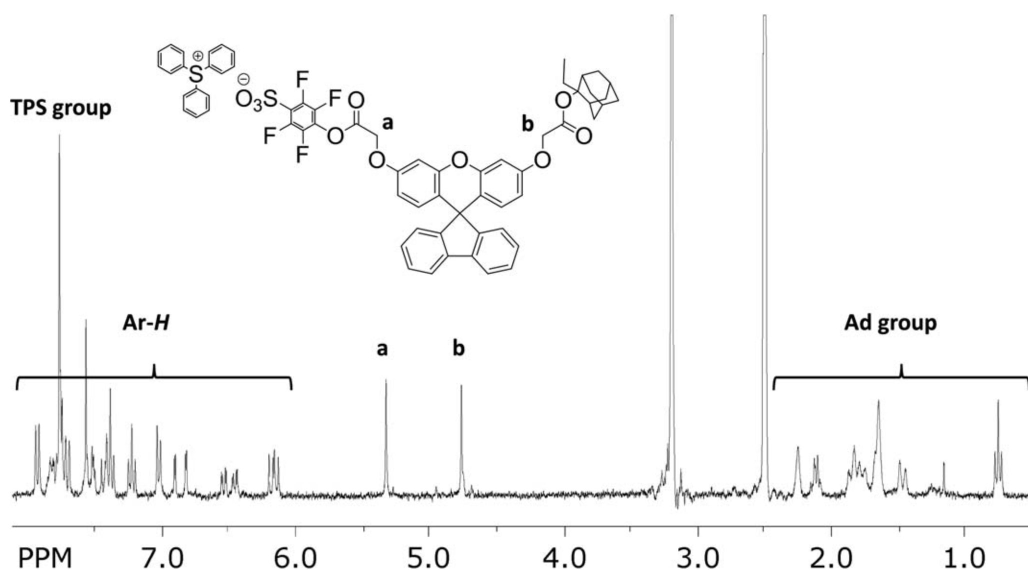


Figure 2. ^{1}H-NMR spectrum of MR-1 in DMSO.

characteristic signals of the TPS group are observed around 7.8 ppm, and the conversion of the salt exchange reaction calculated from the integration ratio of the TPS groups to the α-methylene of the ester groups was quantitative. Furthermore, the elemental analyses also supported the formation of each compound.

MR-1 can be dissolved in common organic solvents such as chloroform, acetone, cyclopentanone, and dimethyl sulfoxide. The high solubility of MR-1 might be because of its bulky structure.

Evaluation of Chemical Properties and Lithographic Performance

Thermal Properties of MR-1

The thermal properties of MR-1 were evaluated by TG and DSC at the heating ratio of 10°C/min and 20°C/min, respectively (Figure 3). MR-1 possessed a relatively high thermal stability over 167°C ($T_{d5\%}$), and MR-1 showed the glass transition at 80°C, which was comparable to that of previously reported PAG bound molecular glass resist,[16] The following evaluation of the lithographic performance of MR-1 was determined to be done at a temperature lower than 80°C.

Characteristic Photosensitive Curve of MR-1 for e-Beam Exposure

In order to study the sensitivity of MR-1 with e-beam exposure (50 keV), a cyclopentanone solution of MR-1 was spin-coated on a Si wafer. The wafer was then prebaked at 70°C for 2 min to fabricate a 70-nm-thick resist film. The resulting resist film was exposed to the e-beam, and postexposure baked at 70°C for 90 sec. Subsequently, the resist film was developed with a 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution, and the remaining film thickness was measured to provide the sensitivity curve. The photosensitive curve of MR-1 is shown in Figure 4. MR-1 has a good sensitivity of 80 μC/cm^2 and high contrast of 4.9 with e-beam exposure.

Pattern Formation with Electron-Beam Exposure

The pattern formation was then carried out by e-beam exposure (100 keV). The 2 wt % cyclopentanone solution of MR-1 was spin-coated, and prebaked at 70°C for 2 min. Subsequently, the obtained 70-nm-thick resist film was exposed to the e-beam (550 μC/cm^2) and post-exposure baked at 70°C for 90 sec. The film was then developed with a 2.38 wt % TMAH aqueous

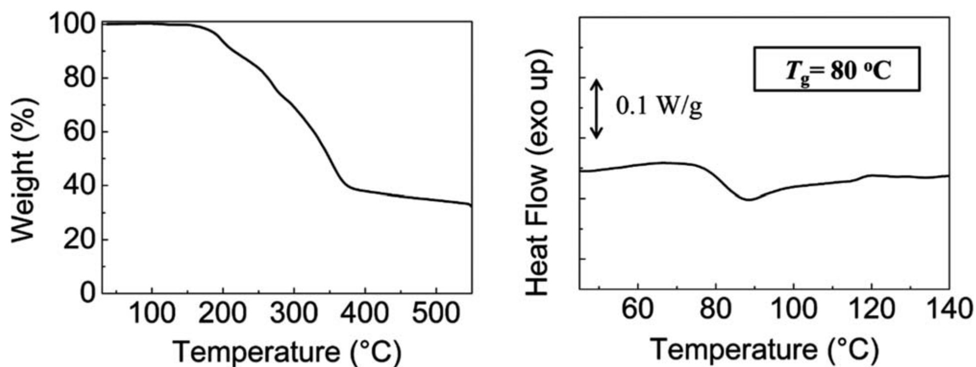


Figure 3. TGA (left) and DSC (right) curves of MR-1.

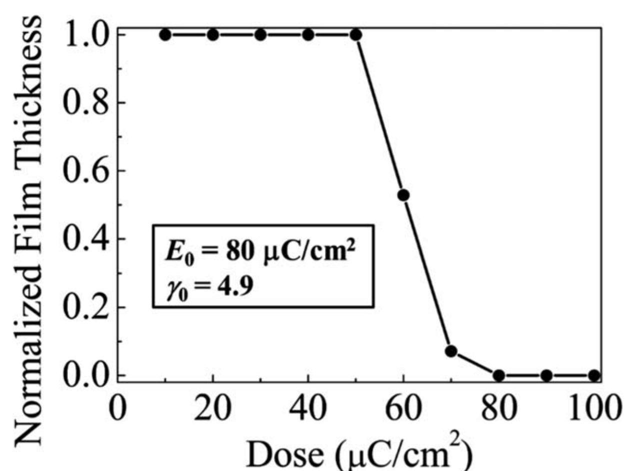


Figure 4. Characteristic photosensitive curve of MR-1 by 50 keV e-beam exposure.

solution and the obtained fine patterns were observed by scanning electron microscopy (SEM).

Figure 5 shows the SEM images of the obtained fine patterns. The resolution of MR-1 is around 80 nm and the fine pattern with a half-pitch below 40 nm cannot be obtained. The LER value calculated from the fine patterns with a half-pitch of 80 nm was 5.1 nm (3σ). The high acid diffusion during the PEB might degrade the resolution and LER.

Therefore, to regulate the diffusion of photo generated acid from PAG, 4 wt % trioctylamine was added to the resist solution as a quencher, and the fabrication of the fine patterns by e-beam exposure was carried out according to a procedure similar to the previous ones.

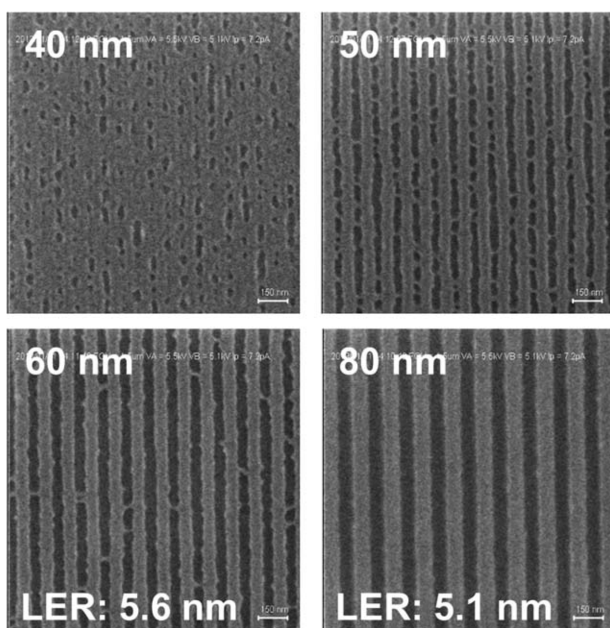


Figure 5. SEM images of the positive patterns by e-beam (100 keV) exposure for the dose of 550 μC/cm^2.

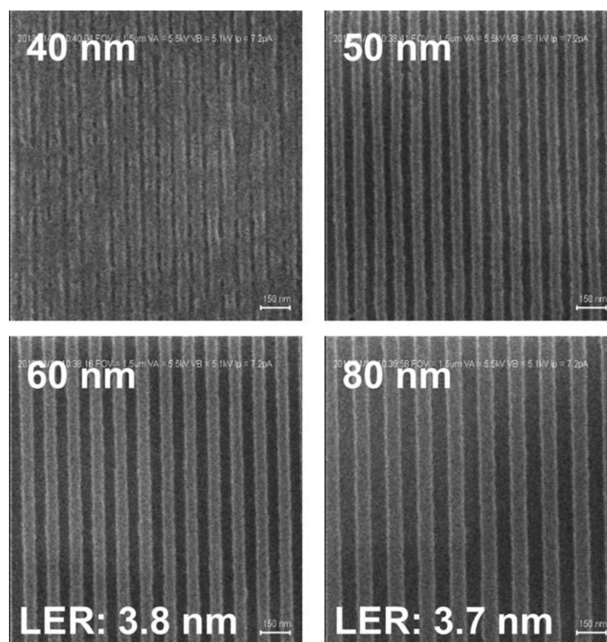


Figure 6. SEM images of the positive patterns by e-beam (100 keV) exposure for the dose of 800 μC/cm^2 with a 4 wt % trioctylamine.

The SEM images of the obtained fine patterns are shown in Figure 6. The fine pattern with a half-pitch of 50 nm can be observed, and the LER value calculated from the fine patterns with a half-pitch of 60 nm was 3.8 nm (3σ). Unfortunately, the sensitivity was not good for the patterning process because of too large moiety of acid components, which might limit the diffusion of photo-generated acid. Further improvements should be needed for higher sensitivity.

Because of the low PEB temperature, a high exposure dose is required to fabricate the fine patterns. On the other hand, the low LER of 3.8 nm and relatively high resolution of 50 nm were obtained using the MR-1. The incorporation of the PAG groups into the resist and the well-defined number of protection groups might contribute to the low LER and relatively high resolution.

CONCLUSIONS

A chemically amplified molecular glass resist, called MR-1, which has an ionic photo-acid generator and a single protection groups in its structure has been developed. MR-1 showed a relatively high thermal stability and T_g of 80°C. The sensitivity and contrast of MR-1 by e-beam exposure (50 keV) were 80 μC/cm^2 and 4.9, respectively. On the other hand, the fine patterns with a half-pitch of 50 nm in the presence of 4 wt % quencher, trioctylamine, were obtained using the e-beam (100 keV) and the low LER value of 3.8 nm (3σ) could be achieved. It should be mentioned that, in case of supplying higher accelerating voltage for e-beam, the higher resolution could generally be achieved because the beam diameter becomes smaller. Fifty keV was weak to produce the higher resolution patterns at the present time. Therefore, 100 keV has been applied for fine patterning process. This kind of molecular glass resist might become a powerful candidate of next generation photoresists after further increasing the T_g value.

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