A Novel Photo-Acid Generator Bound Molecular Glass Resist with a Single Protecting Group

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ABSTRACT: A novel photo-acid generator (PAG) bound molecular glass photoresist with a single protecting group has been developed as a promising resist material for use in microelectronics. This single component molecular resist was prepared in four steps starting from 9,9-*bis*(4-hydroxyphenyl)fluorene. The single component molecular resist exhibited good thermal properties, such as a 10% weight loss temperature of 200 °C and a glass transition temperature of 91 °C. This resist showed a good sensitivity of 60 μC/cm^2 with e-beam exposure (50 keV). On the other hand, the fine pattern with a half-pitch of 50 nm in the presence of 4 wt % quencher, trioctylamine, was obtained using electron-beam (100 keV) lithography. The LER value was 8.2 nm (3σ, 60 nm half-pitch patterns). © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1956–1962

KEYWORDS: electron beam irradiation; molecular glass resist; lithography; photoresist; photo-acid generator

INTRODUCTION Chemically amplified resists (CARs)[1] have contributed to the continuous evolution of electronic device performance. The density of the patterning has been continued to rapidly increase according to Moore's Law. In general, it is necessary for modern CARs to improve their resolution, sensitivity, and Line-Edge-Roughness (LER). Particularly, the LER must be improved because a high LER leads to a decrease in the electronic device performance. The target LER value is less than 1.5 nm (3σ) according to the ITRS roadmap 2011 for the next generation of CARs.[2] However, there is a trade-off relationship among the resolution, sensitivity and LER of CARs, which has been the barrier of meeting the requirement of a low LER.[3]

Molecular glass resists are known as one of the ways to reduce the LER.[4] They have several advantages compared with conventional polymer photoresists, such as their monodispersity and small molecular size. A high resolution and low LER are expected by using the molecular glass resist because these advantages reduce defects at the boundary area between the exposed and unexposed areas. Furthermore, the chemical structures of the molecular glass resists can be precisely designed; therefore, their chemical properties can be faithfully modified. For example, Shiono et al. controlled the number of protecting groups in the molecular glass resists in order to control the distribution of solubility of the molecular glass resists to an alkaline developer. They revealed that a precise solubility control significantly affects the lithographic performance, and the molecular glass resists with a single acid-labile protecting group showed a high resolution of 25 nm and low LER of 3.6 nm (at 100 nm half-pitch) by electron-beam (e-beam) exposure. These lithographic performances were better than that of the conventional poly(4-hydroxy styrene)-based photoresists.[5,6]

Another approach to improve the LER is reducing the number of photoresist components. For the CAR, it is necessary to blend the resist resin, photo-acid generator (PAG) and cross-linker in some cases; however, aggregation sometimes occurred due to the immiscibility of each component. This aggregation negatively affects the LER, therefore, the reduction of the number of resist components is an effective way to improve the LER.[7,8] In particular, the incorporation of PAG moieties into the resists can not only avoid the negative effects of aggregation, but also reduces the photo-generated acid diffusion length due to large anionic species. A low acid-diffusion length leads to an improved resolution and LER due to the increased image contrast. Therefore, an ionic photo-generated acid with large-sized anion moieties,[9] PAG-bound polymer photoresists,[10] and PAG-bound molecular glass resists[11] were evaluated. Especially, Lawson et al. reported that the ionic single molecular resist based on a triarylsulfonium PAG showed 55 nm lines and 105 nm spaces that were nominally patterned at 80 nm 1:1 lines/spaces using electron beam (e-beam) lithography. The LER was found to be 3.9 nm.[12] This resist suffered from a significant

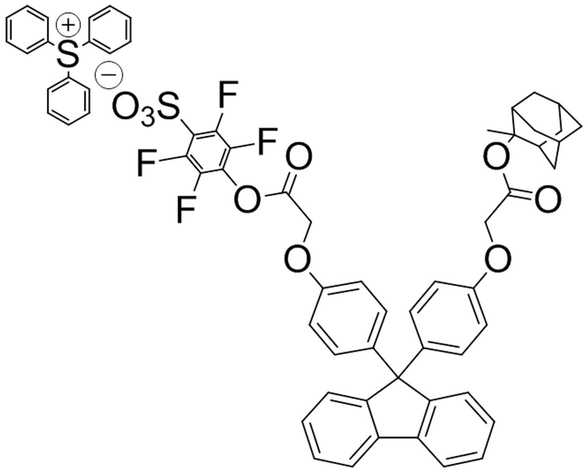


FIGURE 1 Chemical structure of the single component molecular resist **4**.

dark loss due to the intrinsic solubility of the ionic compounds in water, which limits the positive tone imaging. Although it has several problems regarding its solubility, glass transition temperature, and sensitivity, this single-component molecular resist provided all the basic requirements to serve as functional chemically amplified resists, which prompted us to develop another single-component molecular resist.

In this study, we designed a novel PAG bound molecular glass resist (single component molecular resist **4**, Fig. 1). The features of the single component resist **4** are as follows: (i) single component resist **4** has just one acid-labile methyladamanthyl ester group as a protecting group, therefore, the distribution of the dissolution rate in the alkaline developer will be suppressed. (ii) As an anionic moiety of the PAG is incorporated into the resist core, it is expected to make the diffusion length shorter. (iii) The problem of the low glass transition temperature (T_g) of the molecular resists will be resolved by increasing the molecular weight of the molecular resists. These well-controlled solubilities and acid diffusion lengths would lead to an improve the lithographic performance.

EXPERIMENTAL

Materials

Sodium hydride was used after washing with hexane to remove oil. Anhydrous tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), acetone, and acetonitrile were used in all cases. Sodium 2,3,5,6-tetrafluoro-4-hydroxybenzenesulfonate[13] and 2-methyl-2-adamantyl bromoacetate[14] were synthesized according to the literatures. Other reagents and solvents were used as received.

Measurements

^1H NMR spectra and ^{13}C NMR were recorded in chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) on a BRUKER DPX-300 spectrometer. ^{19}F NMR spectra were recorded in chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) on a JEOL JNM-AL400 spectrometer. Fourier-transferred (FT-IR) spectra were recorded on Horiba FT-720. Thermal analysis was 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 9-(4-Hydroxyphenyl)-9-(4-(2-methyl-2-adamantyloxycarbonylmethyloxy)phenyl)fluorene (1)

To a solution of 9,9-*bis*(4-hydroxyphenyl)fluorene (13.0 g, 37.2 mmol) and 2-methyl-2-adamantyl bromoacetate (5.34 g, 18.6 mmol) in anhydrous acetonitrile (160 mL), potassium carbonate (20.5 g, 149 mmol) and 18-crown-6 (0.39 g, 1.49 mmol) were added and the solution was stirred overnight at 60 °C. Then, the reaction solution was added to water and neutralized by 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 then 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 (5.08 g, yield:49%).

^1H NMR (300 MHz, DMSO-d_6, ppm, TMS); 9.21 (s, 1H, –O*H*), 7.9–6.6 (16H, Ar*H*), 4.65 (s, 2H, –OC*H*$_2$C(=O)O–), 2.2–1.2 (17H, adamantyl group). ^{13}C NMR (75 MHz, DMSO-d_6, ppm, TMS); 167.70, 156.38, 156.11, 151.36, 139.39, 138.51, 135.74, 128.70, 128.64, 127.77, 127.44, 125.92, 120.45, 115.01, 114.14, 87.81, 64.74, 63.63, 37.52, 35.71, 33.84, 32.19, 26.00, 22.06. IR (KBr, cm^{-1}); 1727 (–C(=O)O–). Anal. Calcd. for $C_{38}H_{36}O_4$: C, 81.99; H, 6.52; found: C, 81.39; H, 6.56.

Synthesis of 9-(4-Hydroxycarbonylmethoxyphenyl)-9-(4-(2-methyl-2-adamantyloxycarbonylmethyloxy)phenyl)fluorene (2)

The solution of **1** (3.18 g, 5.71 mmol) in THF (25 mL) was slowly added to a solution of sodium hydride (1.10 g, 8.65 mmol) in THF (25 mL) at 0 °C, and the solution was stirred for 1 h at room temperature. To this solution, the solution of bromoacetic acid (1.19 g, 8.56 mmol) in THF (25 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 (2.89 g, yield: 82%).

^1H NMR (300 MHz, DMSO-d_6, ppm, TMS); 7.9–6.6 (16H, Ar*H*), 4.65 (s, 2H, –OC*H*$_2$C(=O)O–), 4.52 (s, 2H, –OC*H*$_2$C(=O)OH), 2.2–1.2 (17H, adamantyl group). ^{13}C NMR (75 MHz, DMSO-d_6, ppm, TMS); 170.14, 167.40, 156.81, 156.34, 151.06, 139.23, 138.11, 137.46, 128.51, 128.39, 127.59, 127.34, 125.71, 120.26, 114.12, 87.70, 65.46, 64.89, 63.53, 37.35, 35.65, 33.70, 32.12, 26.53, 25.87, 21.94. IR (KBr, cm^{-1}); 1751 (–C(=O)O–), 1718 (–C(=O)OH). Anal. Calcd. for $C_{40}H_{38}O_6$: C, 78.15; H. 6.23, found: C, 78.04; H, 6.33.

Synthesis of Sodium 4-(9-(4-(2-methyl-2-adamantyloxycarbonylmethyloxy)phenyl) fluorene-9-yl)phenoxyacetyl-2,3,5,6-tetrafluorobenzenesulfonate (3)

A solution of **2** (1.03 g, 1.68 mmol), sodium 4-hydroxy-2,3,5,6-tetrafluorobenzenesulfonate (0.456 g, 1.68 mmol) and *N,N′*-dicyclohexylcarbodiimide (1.05 g, 5.10 mmol) in the mixture of acetone (34 mL) and DMF (1.7 mL) was stirred for 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. The solid was purified by silica gel column chromatography (eluent: acetone: chloroform = 6:4, Rf = 0.25) and dried *in vacuo* at 60 °C to give **3** as a white solid (0.76 g, yield: 52%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 7.9–6.6 (16H, Ar*H*), 5.25 (s, 2H, –OCH_2C(=O)OAr–), 4.65 (s, 2H, –OCH_2C(=O)O–), 2.2–1.2 (17H, adamantyl group). ^{13}C NMR (75 MHz, DMSO-d_6, ppm, TMS); 169.88, 167.42, 156.42, 156.37, 151.01, 143.08 (J = 251 Hz), 139.26, 138.02, 137.97, 137.72 (J = 251 Hz), 136.05, 128.51, 127.61, 127.38, 125.73, 120.29, 114.14, 87.69, 64.84, 64.49, 63.52, 37.40, 35.64, 33.71, 32.13, 26.55, 25.86, 21.90. ^{19}F NMR (DMSO-d_6, ppm, CCl_3F): −145.9, −160.1. IR (KBr, cm^{-1}); 1812 (–C(=O)OAr–), 1751 (–C(=O)O–), 1180, 1049(–SO_3^-). Anal. Calcd. for $C_{46}H_{37}F_4NaO_9S \cdot 1.02H_2O$: C, 62.56; H, 4.46, found: C, 62.60; H, 4.50.

Synthesis of Triphenylsulfonium Chloride Aqueous Solution

Chlorotrimethylsilane (30.0 mmol, 2.65 mL) was slowly added to a solution of diphenyl sulfoxide (2.02 g, 10.0 mmol) in dichloromethane at 0 °C.[15] After stirring for 1 h at room temperature, 2 M phenylmagnesium chloride in THF solution (15 mL) was slowly added to this solution at 0 °C and the solution was stirred for 1 h at room temperature. Then, small amount of water was added to this solution to quench excess amount of phenylmagnesium chloride, and 30 mL of 0.2 N HCl aqueous solution was added to acidify the solution. After removing organic phase, the remaining aqueous solution was washed with ether twice. The triphenylsulfonium (TPS) chloride aqueous solution was used without further purification.

^{1}H NMR (300 MHz, DMSO-d_6, TMS); 7.9–7.7 (Ar*H*).

Synthesis of Triphenylsulfonium 4-(9-(4-(2-methyl-2-adamantyloxycarbonylmethyloxy)phenyl) fluorene-9-yl)phenoxyacetyl-2,3,5,6-tetrafluorobenzenesulfonate (4)

A solution of **3** (0.317 g, 0.366 mmol) in dichloromethane was added to an aqueous solution of TPS 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 = 0.25) and dried *in vacuo* at 60 °C to give single component resist **4** as a white solid (0.334 g, yield: 83%).

^{1}H NMR (300 MHz, DMSO-d_6, ppm, TMS); 7.9–6.6 (31H, Ar*H*), 5.25 (s, 2H, –OCH_2C(=O)OAr–), 4.65 (s, 2H, –OCH_2C(=O)O–), 2.2–1.2 (17H, adamantyl group). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, TMS); 167.90, 165.29, 156.86, 156.29, 151.50, 143.92 (J = 253 Hz), 140.57 (J = 252 Hz), 140.01, 140.00, 138.69, 134.66, 134.62, 131.63, 131.37, 129.53, 129.30, 127.86, 127.55, 126.15, 124.68, 120.26, 114.46, 114.34, 89.36, 65.65, 64.75, 64.22, 38.12, 36.27, 34.60, 32.99, 27.29, 26.62, 22.45. ^{19}F NMR ($CDCl_3$, ppm, CCl_3F): −144.8, −160.3. IR (KBr, cm^{-1}); 1808 (–C(=O)OAr–), 1743 (–C(=O)O–), 1180, 1041 (–SO_3^-). Anal. Calcd. for $C_{64}H_{52}F_4O_9S_2 \cdot 1.76H_2O$: C, 67.61; H, 4.92, found: C, 67.49; H, 4.79.

Fabrication of the Fine Patterns using High-Pressure-Mercury-Lamp Exposure

The photoresist films with 0.7 μm thickness on a silicon wafer were prepared from a cyclopentanone solution of single component resist **4**. After the pre-bake (PB) (70 °C, 3 min), the prepared resist films were exposed using super-high-pressure mercury lamp (250 W) without any optical filter for 45 min. The resist film was then post-exposure-baked (PEB) (70 °C for 2 min) and developed with 2.38 wt % tetramethyl ammonium hydroxide (TMAH) aqueous solution, and obtained fine patterns were observed by field emission scanning electron microscopy (SEM).

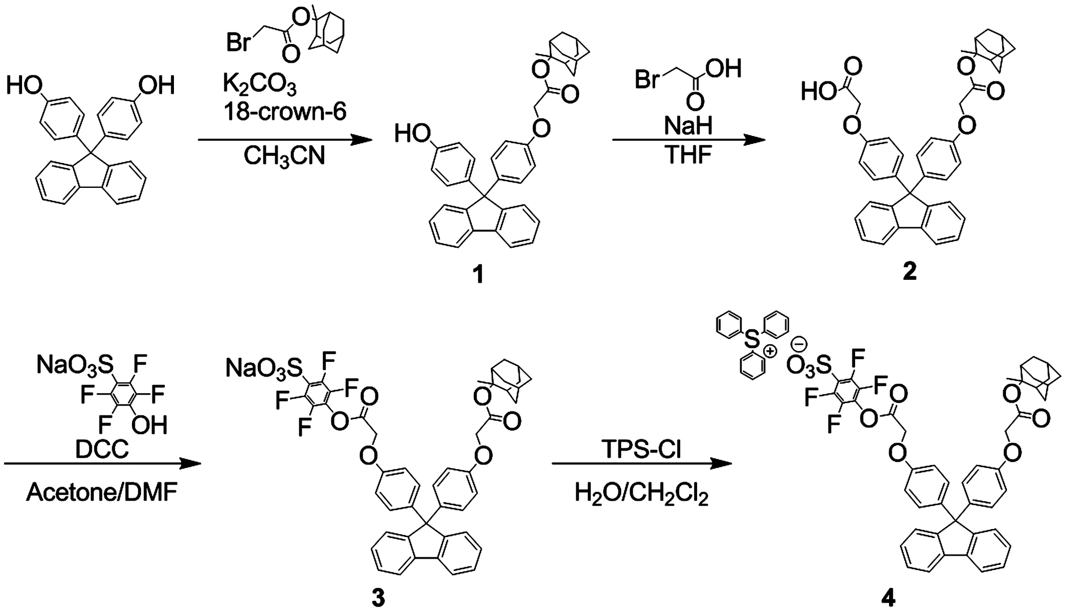
Fabrication of the Fine Pattern with Electron-Beam Exposure

The photoresist films with 70 nm thickness on a silicon wafer were prepared from a cyclopentanone solution of single component resist **4** and trioctylamine in some cases. The PB temperature, PB time, PEB temperature, and PEB time were 80 °C for 90 s, 80 °C for 90 s, respectively. The obtained resist films were exposed to electron-beam (100 keV), and developed with 2.38 wt % TMAH aqueous solution. Obtained fine patterns were observed by SEM.

RESULTS AND DISCUSSION

Design of Single Component Resist 4

A new single component resist **4** was designed according to the basic three concepts described in the introduction. Furthermore, a rigid and bulky fluorene structure was introduced into the core of the molecular glass resist in order to increase its glass transition temperature, because molecular glass resists generally show a low glass temperature and high crystallinity which lead to a negative effect on the lithographic performance, such as a high LER and poor film-forming property. Also, when the resist **4** is used as a single component resist, the PAG loading in a resist becomes relatively high due to the existence of one PAG group per molecule. As a high PAG loading is effective for a high sensitivity



SCHEME 1 Synthesis of the single component resist **4**.

and low LER,[16] it is expected that single component resist **4** shows a better lithographic performance. Furthermore, single component resist **4** can avoid such a negative effect of aggregation of each resist component due to the incorporation of the PAG group into the photoresist. For the conventional resists, positive-type resists are generally a mixture of resist polymers, PAG etc., however, it have been reported that the aggregation of each resist component leads to a poor lithographic performance.[7]

Synthesis of Single Component Resist 4

The single component resist **4** was prepared in four steps according to Scheme 1. The chemical structure of each compound was determined by ^{1}H, ^{13}C, ^{19}F-NMR, IR, and elemental analyses.

For the synthesis of **1**, the feed ratio of 9,9-bis(4-hydroxyphenyl)fluorene to 2-methyl-2-adamantyl bromoacetate was fixed at 2:1 in order to suppress the formation of the derivatives with two protecting groups, and compound **1** was obtained in the good yield of 49%. Next, the nucleophilic substitution reaction between **1** and α-bromoacetic acid was conducted, producing compound **2** in an excellent yield. The ^{1}H-NMR spectrum of **2** showed characteristic signals at 4.65 ppm and 4.52 ppm, which correspond to the α-methylene of methyladamantyl ester and acetic acid, respectively, and signals of the methyladamantyl group were observed at 1.2 to 2.0 ppm. The FT-IR spectrum of **2** exhibited characteristic absorptions of the C=O of carboxylic acid at 1718 cm^{-1} and the C=O of the methyladamantyl ester at 1751 cm^{-1}. Compound **3** was then prepared from **2** and sodium 2,3,5,6-

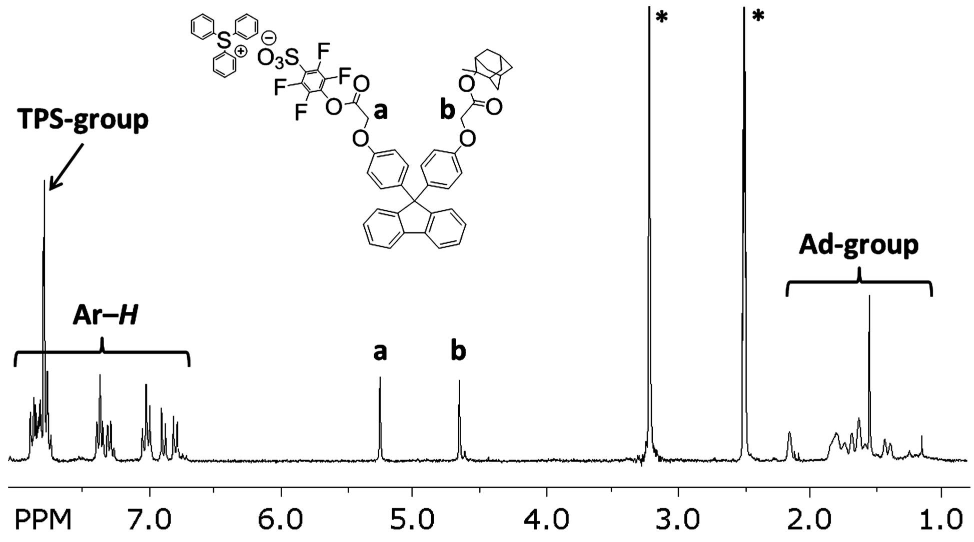


FIGURE 2 ^{1}H-NMR spectrum of the single component resist **4** in DMSO.

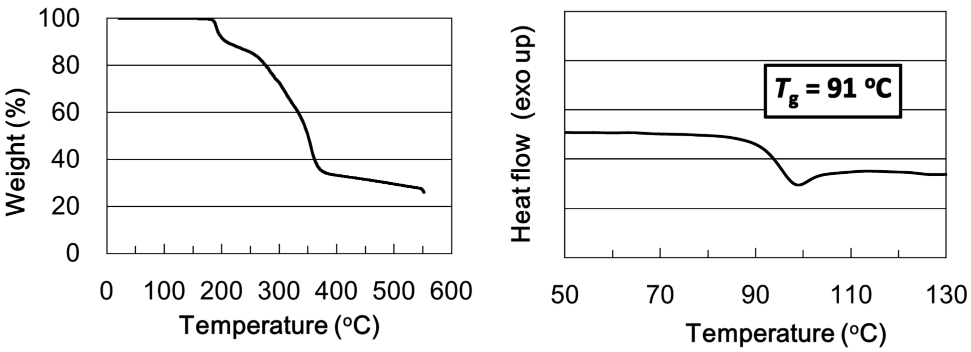


FIGURE 3 TGA and DSC curves of the single component resist **4**.

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 4.52 ppm to 5.25, and the FT-IR spectrum of **3** also showed the characteristic ester absorption at 1812 cm^{-1}. The spectral evidence clearly supported the formation of the expected ester bond. Finally, the single component resist **4** was prepared by the salt exchange reaction of **3** with TPS-chloride at room temperature. The ^{1}H-NMR spectrum of the single component resist **4** is shown in Figure 2. The characteristic signals of the TPS group are observed around 7.7 to 7.9 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. The single component resist **4** was soluble in the common organic solvents, such as dichloromethane, chloroform, acetone, cyclopentanone, and dimethyl sulfoxide, probably due to the introduction of the bulky fluorene unit which contributes to weakening the molecular interaction. Furthermore, the elemental analyses also supported the formation of each compound.

Evaluation of Chemical Properties and Lithographic Performance

Thermal Properties of Single Component Resist 4

The thermal properties of the single component resist **4** were measured by TGA and DSC at the heating ratio of 10 °C/min and 20 °C/min, respectively (Fig. 3). The single component resist **4** possessed a relatively high thermal stability over 192 °C ($T_{d5\%}$) and the weight loss around 200 °C corresponded to the weight ratio of the adamantyl group to the single component resist **4**, which indicated that the decomposition of the adamantyl ester group occurs around 200 °C. The single component resist **4** showed the glass transition at 91 °C, which is higher than that of previously reported PAG-bound molecular glass resists.[12] Therefore, the following evaluation of the lithographic performance for the single component resist **4** was decided to be done at a temperature lower than 91 °C.

Pattern Formation with High Pressure Mercury Lamp Exposure

At first, whether or not the single component resist **4** after UV exposure and PEB treatment became soluble in an alkaline developer was investigated. The solution of the single component resist **4** (15 wt %) in cyclopentanone was spin-coated on a Si wafer. PB was then conducted at 70 °C for 3 min. Next, the resist films were exposed to a high pressure mercury lamp without any optical filters for 45 min due to the very weak absorption of the compound **4** under this exposure. Subsequently, the PEB was performed at 70 °C for 2 min, and the films were dipped in a 2.38 wt % TMAH alkaline developer for 1 min. The fine patterns of the single component resist **4** were observed as shown in Figure 4. These results indicated that the catalytic deprotection reaction proceeded using the photo-generated acids, and the single component resist **4** became soluble in the alkaline developer by exposure to a high pressure mercury lamp and subsequent PEB treatment. Therefore, the single component resist **4** resist has the ability to fabricate fine patterns by exposure to certain wavelength light.

Characteristic Photosensitive Curve of the Single Component Resist 4 for e-Beam Exposure

Based on the UV lithography, the sensitivity of the single component resist **4** for e-beam exposure (50 keV) was measured using a 70-nm thick film, PB at 80 °C for 2 min, PEB at 80 °C for 90 s, and developed in a 2.38 wt % TMAH aqueous solution for 30 s at 25 °C. The photosensitive curve of the single component resist **4** is shown in Figure 5. This single component resist **4** has a good sensitivity of 60 μC/cm^2 and contrast of 1.7 with e-beam exposure.

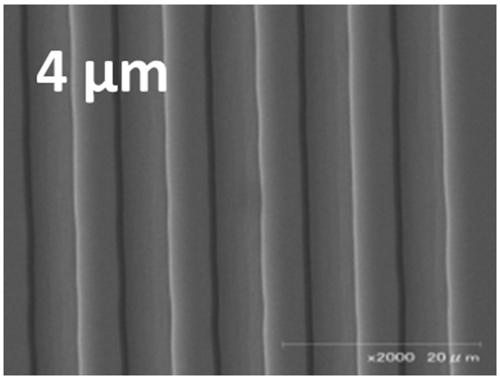


FIGURE 4 SEM image of positive patterns by high pressure mercury lamp exposure.

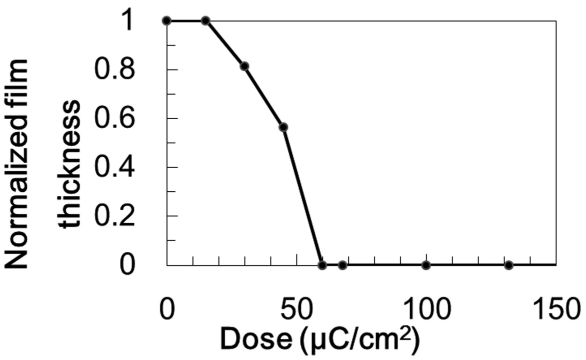


FIGURE 5 Characteristic photosensitive curve of the single component resist **4** by 50 keV e-beam exposure.

Pattern Formation with Electron-Beam Exposure

The pattern formation by e-beam lithography was carried out by 100 keV electron-beam exposure. The lithographic condition was as follows: a 2 wt % solution of the single component resist **4** in cyclopentanone was spin-coated on the silicon wafer, prebaked at 80 °C for 90 s on the hot plate, exposed to the e-beam, PEB at 80 °C for 90 s, then developed with 2.38 wt % TMAH for 60 s at 25 °C. The film thickness before and after the development were 70 nm and 50 nm, respectively. The lithographic performance of the single component resist **4** without a base quencher is shown in Figure 6. The resolution limit of this resist is around 80 nm, and smaller patterns suffer from no pattern formation (less than 40 nm line) due to the high acid diffusion length and

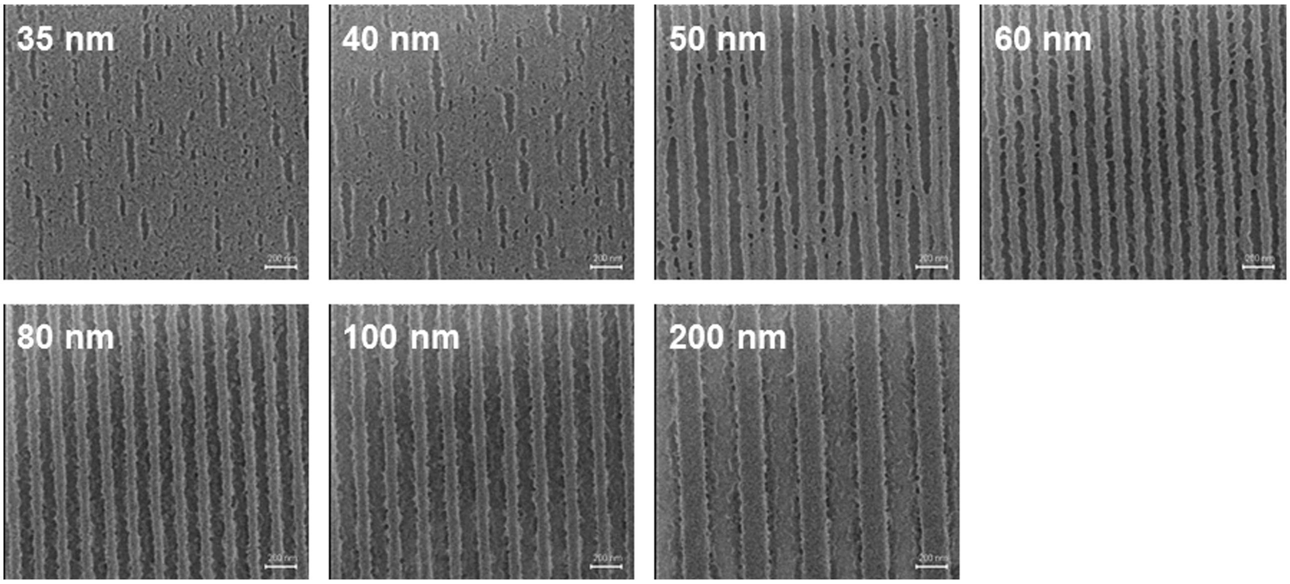


FIGURE 6 SEM images of the positive patterns by e-beam exposure.

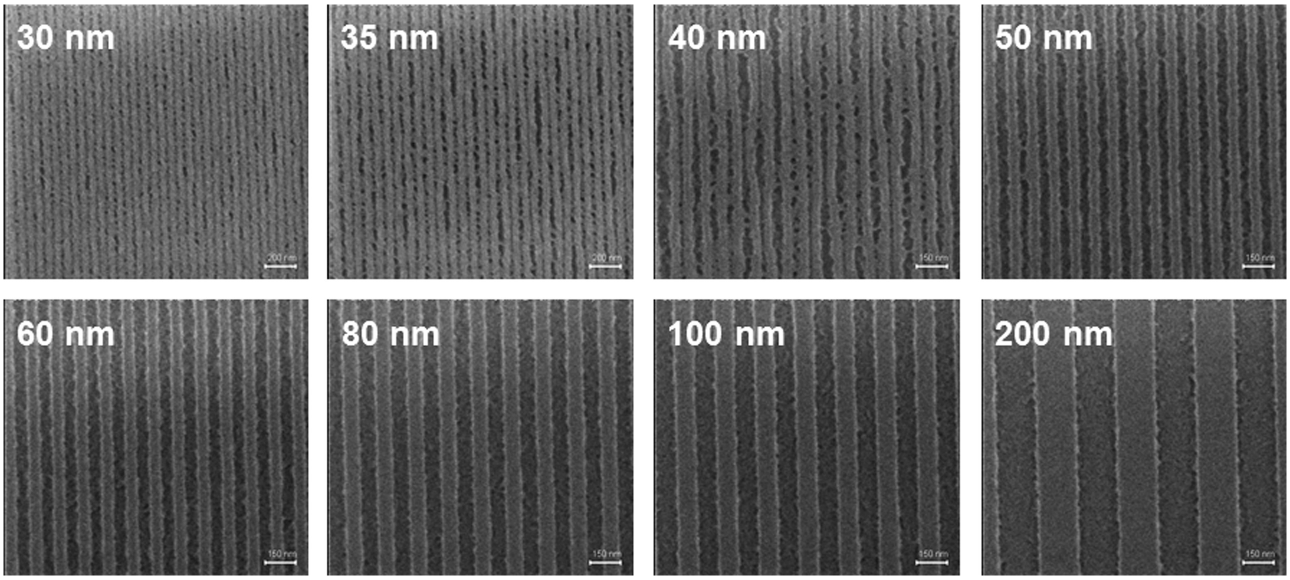


FIGURE 7 SEM images of positive patterns by e-beam exposure with a 4 wt % quencher.

severe pattern collapse (50 nm line) because the high hydrophilicity of the single component resist **4** results in strong capillary forces during development and drying.

Figure 7 shows SEM images of the positive patterns by e-beam exposure for the dose of 500 μC/cm^2 with a 4 wt % quencher, trioctylamine. In this evaluation, the addition of a base results in the reduced diffusion of the photo-generated acid and better patterns are obtained. The fine pattern with a half-pitch of 50 nm is formed and the blurred patterns are observed in the patterns with a half-pitch of less than 40 nm. Serious bridging randomly appeared between the resolved resist lines that limited the resist resolution to an approximate 50 nm half-pitch. The bridging problem may be due to some combination of a lack of compatibility between the single component resist **4** and the base, trioctylamine, insufficient image contrast, and pattern collapse by capillary force during the rinse process because of the hydrophilic single component resist **4**. The LER value calculated from the 60-nm line-and-space pattern is 8.2 nm, which is still higher than the target value.

CONCLUSIONS

A new single component molecular glass resist **4**, which has a single acid-labile protecting group and a PAG functional group within its molecule structure, has been developed. The single component resist **4** has a relatively good thermal stability and the high glass transition temperature of 91 °C. This resist showed the good sensitivity of 60 μC/cm^2 with e-beam exposure (50 keV). On the other hand, and the fine patterns with a half-pitch of 50 nm in the presence of 4 wt % quencher, trioctylamine, were obtained using e-beam (100 keV) lithography and the LER value was 8.2 nm (3σ, 60 nm half-pitch patterns). Further optimization is required to obtain a sub-30 nm half-pitch and lower LER. Future work will focus on the design of a single-component resist material with a more reduced hydrophilicity by using a non-ionic PAG unit and higher T_g to control the acid diffusion length.

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