Novel Ionic Photoacid Generators (PAGs) and Corresponding PAG Bound Polymers

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Three novel polymeric anionic and one cationic photoacid generators(PAGs), as well as corresponding PAG bound polymers, were prepared in moderate to good yield and characterized. As for the lithographic properties, the anionic PAG bound polymers showed improved resolution and photospeed than the cationic PAG bound polymer. Especially, the fluorine PAG bound polymer resist HS-EA-PAG(c) showed high photospeed and improved resolution than other PAG bound polymer. Therefore, it should be potential for these new PAG and PAG bounder polymers to be applied to EUV lithography.

Keywords: lithography; photoacid generator (PAG); anionic PAG; polymer resist

1. Introduction

Extreme ultraviolet (EUV) lithography at 13.5 nm wavelength has emerged as a promising candidate to meet the resolution requirements of the microelectronic industry roadmap [1]. Although some advanced exposure tools have been developed, significant challenges remain in developing photore sist materials with all of the required imaging properties. Conventional chemically amplified photore sist formulations are complex mixtures of a protected polymer matrix and a small molecule photoacid generator (PAG).

The inherent incompatibility can lead to PAG phase separation, non-uniform initial PAG and photoacid distribution, as well as acid migration during the post-exposure baking (PEB) processes [2]. To alleviate these problems, several systems with ionic or non-ionic PAG grafting into the main-chain of polymer have been reported [3-11]. The incorporation of ionic PAG units into the main chain of the hydroxystyrene and adamantyl methacrylate based polymers showed improved EUV lithographic performance, such as faster photospeed and higher stability, lower outgassing, and lower line edge roughness (LER) than corresponding blend resists [10,11]. Here we report novel ionic bound PAGs and a series of new photoresists incorporating them in the main chain (Figures 1 and 2). Figure 2 also outlines the anticipated advantages of polymer microstructures incorporating PAGs in the resist backbone.

2. Experimental Section

2.1. Materials

2,3,5,6-Tetrafluoro-phenol, sodium sulfite, 2, 2′-azobisisobutyronitrile (AIBN), and triflic acid were purchased from Aldrich. 4-Vinylbenzyl chloride was from Fluka, Acetic acid 4-vinylphenyl ester were purchased from Tokyo

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Kasei Kogyo Co., Ltd. Japan. Methacrylic acid, sodium 4-phenosulfonate were purchased from ACROS ORGANICS. Triphenylsulfonium chloride 50% aqueous solution was purchased from City Chemical Ltd. 2-Ethyl-2-adamantyl-methacrylate (EAMA) was supplied by AZ Electronic Materials Ltd. All chemicals and solvents were used as received unless otherwise noted. AIBN was recrystallized from methanol before use, and tetrahydrofuran (THF) and acetonitrile were dried (over sodium, calcium hydride) before use. Hydroxystrene (HOST) was prepared by the hydrolysis of acetic acid 4-vinylphenyl ester.

2.2. Characterization

The NMR was performed on a JEOL 500 spectrometer with DMSO-d₆ and TMS as the solvent and internal standard, respectively. Elemental analyses were performed at Atlantic Microlab Inc. Gel permeation chromatography (GPC, Waters Breeze software) was performed with THF as the eluent. The molecular weights of polymers were calculated with respect to polystyrene as narrow Mₙ standards. Thermogravimetric analyses (TGA) were performed on a TA instrument, Hi-Res TGA 2950 Thermogravimetric Analyzer 7, at a rate of 10 °C/min, heating to 800 °C with N₂ gas flow of 25 cm³/min. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument (DSC 2920) at a heating rate of 10 °C/min. For acid generating measurements, a 254 nm UV lamp (model R 52 G UVP Inc) was used. For imaging, a Quintel Ultraline Q4000-6,1:1 contact mask alignment systems, Laser: 80 MHz Ti: sapphire femtosecond pulses Oscillator (Spectra-physics), center wavelength 800nm, generating 400nm wavelength laser through frequency doubling the output of the oscillator. Focus condition: N.A = 0.55.

2.3. Synthesis of photocacid generators (PAGs)

These novel polymerizable PAGs were synthesized as shown in scheme 1.

2.3.1. Bound PAG (c) Triphenylsulfonium salt 4-(vinyl benzyloxy) 2,3.5.6-tetrafluoro benzenesulfonate (F4-VBzBS-TPS)

P-chloromethylstyrene (20 mmol, 3.04g) in 10 ml aceton was added dropwise to the aqueous solution of sodium 4-hydroxy-2,3,5,6-tetrafluoro benzenesulfonate [7] (22 mmol, 5.90g) under nitrogen, refluxed over 24 hours. After cooling to room temperature, the solid was filtered, washed with acetone, and dried overnight under high vacuum. Sodium salt of 4-(vinyl benzyloxy) 2,3.5.6-tetrafluoro benzenesulfonate (F4-VBzBS-Na) was obtained as a white solid with 72 % yield. Characterized by ¹H NMR (25°C, ppm) 87.49 (d, J = 8.1 Hz, 2H); 7.45 (d, J = 8.1 Hz, 2H); 6.72 (dd, J = 11.2 and 17.8 Hz, 1H); 5.85 (d, J = 17.8 Hz, 1H); 5.26 (d, J = 11.2 Hz, 3H), and ¹³C NMR (25 °C, ppm, ext.CF₃COOH): δ -156.35 (m, 2F); -139.68 (m, 2F). Then (F4-VBzBS-Na) was reacted with 50% aqueous solution of triphenylsulfonium chloride in water, at room temperature overnight. The product was refined with dichloromethane and hexane. Triphenylsulfonium salt 4-(vinyl benzyloxy) 2,3.5.6-tetrafluoro benzenesulfonate (F4-VBzBS-TPS) was obtained as a colorless crystal with 76% yield. Characterized by ¹H NMR (25°C, ppm) 87.42-7.92 (m, 19H); 6.73 (dd, J = 11.2 and 17.8 Hz, 1H); 5.86 (d, J = 17.8 Hz, 1H); 5.27 (dd, J = 11.2 Hz, 3H). ¹³C NMR (25°C, ppm) δ 146.1, 144.1, 142.2, 141.7, 141.0, 139.2, 137.6, 136.2, 135.2, 134.4, 132.5, 131.4, 130.4, 128.9, 126.3, 125.2, 124.2, 121.3, 115.1, and 75.8. ¹³F NMR (25°C, ppm, ext. CF₃COOH): δ -156.55 (m, 2F); -139.82 (m, 2F).

2.3.2. Bound PAG (a) Triphenylsulfonium salt 4-vinylbenzylsulfonate (VBzS-TPS)

P-chloromethylstyrene (20 mmol, 3.04g) in 10 ml aceton was added dropwise to the aqueous solution of sodium sulfite (22 mmol, 2.77g) under nitrogen, and refluxed over 12 hours. After cooling to room temperature, the solid was filtered, washed with acetone, and dried overnight under high vacuum. Sodium salt of 4-vinylbenzylsulfonate (F4-VBzS-Na) was obtained as white solid with 80 % yield. Characterized by ¹H NMR (25°C, ppm) 87.34 (d, J = 9.1 Hz, 2H); 7.26 (d, J = 9.1 Hz, 2H); 6.72 (dd, J = 10.7 and 18.6 Hz, 1H); 5.79 (d, J = 18.6 Hz, 1H); 5.20 (d, J = 10.7 Hz, 3H); 3.68 (s, 3H). Then the (VBzS-Na) was reacted with 50 % aqueous solution of triphenylsulfonium chloride in water, at room temperature overnight. The product was refined with dichloromethane and hexane. Triphenylsulfonium salt of 4-vinylbenzylsulfonate was obtained as a colorless crystal with 85 % yield. ¹H NMR (25°C, ppm) 87.42-7.92 (m, 151H); 7.32 (d, J = 8.7 Hz, 2H); 7.24 (d, J = 8.7 Hz, 2H); 6.68 (dd, J = 11.2 and 18.0 Hz, 1H); 5.75 (d, J = 18.0 Hz, 1H); 5.17 (d, J = 11.2 Hz, 3H); 3.66 (s, 2H). ¹³C NMR (25°C, ppm) δ 145.0, 139.1, 136.7, 135.6, 135.0, 134.4, 132.4, 131.0, 130.5, 125.3, 124.1, 112.8, and 57.4.
2.3.3. Bound PAG (b) Triphenylsulfonium salt 4-(vinyl benzyloxy) benzenesulfonate (VBzBS-TPS)

P-chloromethylstyrene (20 mmol, 3.04g) in 10 ml acetone was added dropwise to the aqueous solution of sodium 4-hydroxy-benzenesulfonate (22 mmol, 4.31g) under nitrogen, and refluxed over 12 hours. After cooling to room temperature, the solid was filtered, washed with acetone, and dried overnight under high vacuum. Sodium salt of 4-(vinyl benzyloxy) benzenesulfonate (VBzBS-Na) was obtained as a white solid with 76% yield. Charactarized by $^1$H NMR (25°C, ppm) $\delta$ 7.46-7.54 (m, 4H); 7.41 (d, $J = 9.0$ Hz, 2H); 6.93 (d, $J = 9.3$ Hz, 2H); 6.72 (dd, $J = 11.0$ and 18.4 Hz, 1H); 5.83 (d, $J = 18.4$ Hz, 1H); 5.27 (d, $J = 11.0$ Hz, 1H); 5.1 (s, 2H). Then the (VBzBS-Na) was reacted with 50% aqueous solution of triphenylsulfonium chloride in water, at room temperature overnight. The product was refined with dichloromethane and hexane. Triphenylsulfonium salt of 4-(vinyl benzyloxy) benzenesulfonate (VBzBS-TPS) was obtained as a colorless crystal with 73% yield. $^1$H NMR (25°C, ppm) $\delta$ 7.39-7.90 (m, 21H); 6.92 (d, $J = 9.1$ Hz, 2H); 6.73 (dd, $J = 11.0$ and 18.2 Hz, 1H); 5.82 (d, $J = 18.2$ Hz, 1H); 5.25 (d, $J = 11.0$ Hz, 1H); 5.1 (s, 2H). $^{19}$F NMR (25°C, ppm ext. CF$_3$COOH): $\delta$ -125.25 (m, 3F); -120.87 (m, 2F); -114.43 (m, 2F); -80.58 (m, 2F). $^{13}$C NMR (25°C, ppm) $\delta$ 145.9, 141.3, 141.0, 140.8, 136.4, 135.2, 134.3, 132.5, 131.3, 130.3, 129.6, 128.7, 127.8, 126.9, 125.1, 124.2, 121.3, 114.5, 113.6, and 68.6.

2.3.4. Bound PAG (d) 4-(Vinyl benzyloxy)phenyl-dimethylsulfonium nonaflate (VBz-Nf)

A mixture of P-chloromethylstyrene (1.4 mmol), intermeidiate (2, 0.7 mmol) [9], dried potassium carbonate (3.5 mmol) and 18-crown-6 (0.28 mmol) in dry acetone (15 ml) was heated to reflux and stirred vigorously under nitrogen atmosphere for 48 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane. The aqueous layer was washed twice with dichloromethane and combined the organic layers. The crude product was recrystallized from dichloromethane and hexane. Yield 30 %, $^1$H NMR (DMSO- D$_6$) $\delta$ 7.49 (d, $J = 7.8$ Hz, 2H); 7.40 (d, $J = 7.8$ Hz, 2H); 7.22 (d, $J = 8.2$ Hz, 2H), 6.99 (d, $J = 8.2$ Hz, 2H); 6.73 (dd, $J = 11.0$ and 18.2 Hz, 1H); 5.86 (d, $J = 18.2$ Hz, 1H); 5.28 (ds $J = 11.0$ Hz, 1H); 5.08 (s, 2H); 3.35 (s, 6H). $^{19}$F NMR (25°C, ppm ext. CF$_3$COOH): $\delta$ -125.25 (m, 3F); -120.87 (m, 2F); -114.43 (m, 2F); -80.58 (m, 2F). $^{13}$C NMR (25°C, ppm) $\delta$ 136.7, 136.2, 132.1, 128.9, 128.6, 127.8, 126.2, 115.7, 114.3, 69.4, 69.0, and 16.5.

2.4. Synthesis of Polymers

Terpolymers were prepared by free radical polymerization in sealed pressure vessels (Scheme 3). Hydroxystrene (HOST), 2-ethyl-2-adamantyl-methacrylate (EAMA), PAGs (a, b, c, d), and 2, 2'-azobisisobutyronitrile (AIBN), as a free radical initiator (5 mole % to the monomers) were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) and acetonitrile. Polymerization was performed at 65 °C for 24 hrs. The polymer solutions were precipitated with
large amount of diethyl ether or petroleum ether and dried in vacuum.

Table 1. Polymerization results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Site Ratios</th>
<th>Monomer Composition</th>
<th>Yield (%)</th>
<th>Intrinsic</th>
<th>PAG</th>
<th>Tg/°C</th>
<th>PAG/°C</th>
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</thead>
<tbody>
<tr>
<td>HS-EA</td>
<td>0.2 - 0.4</td>
<td>Cyclohexanone</td>
<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
<td>0.0283</td>
<td>0.23</td>
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<tr>
<td>HS-EA</td>
<td>0.2 - 0.4</td>
<td>Cyclohexanone</td>
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<td>0.6</td>
<td>0.2</td>
<td>0.4060</td>
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<tr>
<td>HS-EA</td>
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<td>0.6</td>
<td>0.2</td>
<td>0.4070</td>
<td>0.23</td>
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<tr>
<td>HS-EA</td>
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<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
<td>0.4090</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The glass transition temperature of HS-EA-PAG (d) was 116°C. The other PAG bound polymers showed no obvious Tg, suggesting that these anionic PAG bounded polymers are probably quite rigid, resulting from the restrictive motion of the bulky triphenylsulfonium moiety of the PAG in the polymer chain. As reported previously for analogous rigid polymers [7,11], no transitions were observed below the decomposition temperature for the polymers in this study also.

**Resist Processing**

For resist formulation, 0.2 g of PAG bound polymer resists were dissolved in 3.4 g of cyclohexanone. The resist solutions were filtered through 0.2 µm filter, and spin-coated (3000 rpm, 60s) onto silicon wafers primed with a 20% 1,1,3,3,3-hexamethyl-disilazane (HMDS)/ 80% propylene glycol-1-monomethyl ether 2-acetate (PGMEA) solution. The post apply bake was carried out at 100°C for 90 seconds. The thickness of the resists was determined to be in the range of 110 -150 nm. The exposed wafers were baked at 100°C for 90 s. The development was conducted in conventional 2.38-wt % tetramethylammonium hydroxide (TMAH) for approximately 20s and rinsed with de-ionized water.

**3. Results and Discussion**

The anionic and cationic bound PAGs were designed and prepared in good yield, as well as characterized by 1H, 19F and 13C NMR. The terpolymers (HS-EA-PAG a, b, c, and d) were prepared by free radical polymerization and obtained in moderate yield from 27.5 to 37.3%, and the PAG contents were 7.8, 6.5, 6.8, and 8.3% (mole ratio) for HS-EA-PAG (a), HS-EA-PAG (b), HS-EA-PAG (c) and HS-EA-PAG (d), respectively. The intrinsic viscosity ranged from 0.0283 to 0.0506 dl/g, which indicates the molecular weight of these polymers are similar. The polymer HS-EA-PAG (a) and HS-EA-PAG (d) have a Mw of 1800, 3900 respectively, as determined by GPC using THF as mobile phase, but the polymer HS-EA-PAG (b) and HS-EA-PAG (c) have poor solubility in THF. The thermostability of these PAG bound polymers, TDecomp of HS-EA-PAG (a), HS-EA-PAG (b), HS-EA-PAG (c), HS-EA-PAG (d) are 158, 162, 145, and 155, respectively.

The glass transition temperature of HS-EA-PAG (d) was 116°C. The other PAG bound polymers showed no obvious Tg, suggesting that these anionic PAG bounded polymers are probably quite rigid, resulting from the restrictive motion of the bulky triphenylsulfonium moiety of the PAG in the polymer chain. As reported previously for analogous rigid polymers [7,11], no transitions were observed below the decomposition temperature for the polymers in this study also.

Fig. 3. Exposed by 365-436 nm contact printer

Fig. 4. Exposed by 400 nm FS-Laser

Although full field EUV lithography tools are now being developed and installed at multiple sites, access to EUV patterning capabilities is still limited and preliminary screening of these polymers was carried out by contact printer.
(wavelength from 365-436 nm). The anionic PAG (a, b, c) bound polymers showed improved photospeed and good resolution compared with the cationic PAG(d) bound polymer. Probably due to the acid from anionic PAG (a, b, c) still bounded to the polymers after exposure, while the acid from cationic PAG(d) being free after exposure. As for the anionic PAG (a, b, c) bound polymers, the performance was in the following order: HS-EA-PAG (c) > HS-EA-PAG (b) > HS-EA-PAG (a), they gave 1:2 L/S (about 2 μm) and showed good resolution at 68 mJ/cm² and 135 mJ/cm², while, the cationic PAG bound polymer HS-EA-PAG (d) showed unresolved 1:2 L/S at 204 mJ/cm², even at 612 mJ/cm². We do not have any data correlating the doses for EUV and 365nm lithography, but would expect that the doses required for EUV to be much lower since most PAG materials show low sensitivity at wavelengths longer than 300 nm. The images obtained using optical microscope are shown in Figure 3. These samples were also exposed with 400 nm laser by using different power and scanning speed (see Fig. 4). We found that the fluorinated anionic PAG(c) bound polymer was very sensitive compared with other three samples, which is consistent with the electron with-drawing power of the substituents. We have demonstrated the synthesis of these new PAGs and PAG bound polymers, and have demonstrated their lithographic capabilities.

We believe that these polymers may be candidates for EUV lithography based on previously published results on F4 PAG bound polymer for EUV photoresists [11]. However further testing at EUV wavelengths, and optimization of the platforms is required to demonstrate the resolution and sensitivity targets required of EUV resists.

4. Conclusion

Three new anionic bound PAGs and one cationic bound PAG, as well as corresponding polymers, were prepared in moderate to good yield and characterized. As for the lithographic properties, they are in the following order: HS-EA-PAG (c) > HS-EA-PAG (b) > HS-EA-PAG (a) > HS-EA-PAG (d), the anionic PAG bound polymers showed improved resolution and photospeed than the cationic PAG bound polymer. Especially, the fluorine anionic PAG bound polymer resist HS-EA-PAG(c) showed high photospeed and improved resolution than other PAG bound polymers, which depends on the exposure mechanism of different kind of PAGs. Therefore, it should be potential for these new PAGs and PAG bound polymers to be applied to EUV lithography. Further investigations on EUV lithography imaging, outgassing and acid diffusion studies will be reported subsequently.

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References