Fullerene Grafted Photoacid Generator (PAG) Bound Polymer Resists

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Two polymeric fullerene derivatives and corresponding fullerene grafted, PAG bound polymer resists (HS-EM-HM/Fuller-PAG) based on hydroxystyrene (HS), 2-ethyl-2-adamantyl methacrylate (EM), 3-hydroxy-1-adamantyl methacrylate (HM) were prepared and characterized. The preliminary lithographic performance of these polymers were conducted with a contact printer, e-beam, and structure-function relationships were also studied. The results demonstrated that the thermostability and glass transition temperatures increased, but sensitivity and resolution decreased. Further investigations about microstructure modification, composition effect, exposure conditions on the lithographic properties will be carried out.

Keywords: Anionic PAG, PAG bound polymer resist, Fullerene, EUV, e-beam.

1. Introduction
The microelectronic industry has made remarkable progress with the development of integrated circuit (IC) technology, which depends on the fabrication of smaller feature sizes. Extreme ultraviolet (EUV) lithography at 13.5 nm wavelength has been positioned as a promising candidate to meet the resolution requirements of the microelectronic industry roadmap.¹² Therefore, one of the major subjects of current lithography research is to develop novel resist materials with all of the required imaging properties: high resolution, high sensitivity, lower line edge roughness, and lower outgassing. Conventional chemically amplified resist (CAR) formulations are blends of a protected polymer matrix and a small molecule photoacid generator (PAG). This kind of PAG blend CAR materials have inherent incompatibility. This can lead to a tradeoff in achieving the desired characteristics of high resolution, high sensitivity, and low line edge roughness through formulation changes to PAG blend CAR systems.³ The incorporation of anionic PAG units into the main chain of the hydroxystyrene (HS) and 2-ethyl-2-adamantyl methacrylate (EM) based polymers showed improved EUV lithographic performance, such as high PAG loading, and higher stability, lower outgassing, and lower line edge roughness (LER) than PAG blend polymer resists.⁴⁻¹⁰ On the other hand, as the patterned feature size diminishes, the film thickness must also be reduced to avoid aspect ratio related pattern collapse.¹¹ For subsequent pattern transfer, high etch durability of resist materials is required. Fullerene derivative molecules have a diameter of approximately 1 nm and have been shown to act as negative resists with etch durability and a resolution of < 20 nm when exposed via electron beam lithography.¹²,¹³ Herein we report fullerene grafted polymer bound PAG resists based on vinyl perfluoro alkanesulfonic PAG (MTFB PAG), hydroxystyrene (HS), 2-ethyl-2-adamantyl methacrylate (EM). Polymers containing the fullerene derivative or
3-hydroxy-1-adamantyl methacrylate (HM) were prepared and characterized (Schemes 1 and 2).

2. Experimental Section

2.1. Materials

2, 2’-Azobisobutyronitrile (AIBN) and propylene glycol-1-monomethyl ether 2-acetate (PGMEA) and trifluoroacetic acid were purchased from Sigma Aldrich. 1,1,1,3,3,3-Hexamethyl disilazane (HMDS) was from ICN Biomedicals, Inc. 2-Ethyl-2-adamantyl-methacrylate and 3-hydroxy-1-adamantyl methacrylate were supplied by Rohm Haas. 2.38 wt% tetramethylammonium hydroxide (TMAH) were supplied by AZ Electronic Materials Ltd. Hydroxytrene was prepared by the hydrolysis of 4-acetoxytrene purchased from TCI America. Allyloxybenzaldehyde was obtained from Alfa Aesar, Buckminster fullerene (C60) was obtained from Fullerene Enterprises and used as purchased. Heptaldehyde was obtained from Aldrich. Tetrahydrofuran (THF) and acetonitrile were dried (over sodium, calcium hydride) before use. PAGs were prepared as reported previously. All chemicals and solvents were used without further purification unless otherwise noted.

2.2. Characterization

NMR spectroscopy was performed on a JEOL500 spectrometer with DMSO-d6 or CDCl3 and TMS as the solvent and internal standard, respectively. 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 Mw standards. Thermal analysis was performed on a TA instrument, Hi-Res TGA 2950 Thermogravimetric Analyzer 7, and Differential Scanning Calorimetry (DSC 2920) under a nitrogen atmosphere at a heating rate of 10 °C/min. TGA was used to determine the decomposition temperature (T_d at 5% weight loss). The thickness of the films was measured with a Woollam Variable Angle Spectroscopic Ellipsometer. Film thicknesses were in the range of 110-130 nm.

2.3. Synthesis of polymeric fullerene derivatives

2.3.1. 2-(4-(4-penyloxy-phenyl)-3,4-fulleropyrrolidine(I)2-(4-Glycine)(75mg, 1 mmol), 4-(2-penyloxy) benzaldehyde(400mg, 2.5 mmol), and C60 (360 mg, 0.5 mmol) were dissolved in chlorobenzene, and the mixture was refluxed for 6 hours under stirring in a N2 atmosphere. After cooling, the solvent was evaporated under reduced pressure. The crude solid was purified on silica gel column using toluene as the eluent, yielding a black powder (45 %). 1H NMR (25°C, CDCl3, ppm), δ = 7.73(d, J= Hz, 2H), 7.03(d, J=8.6 Hz, 2H), 5.76(s, 1H), 5.099d, J=10.4 Hz, 1H), 4.87 (d, J=10.4 Hz, 1H), 4.70(s, 2H), 3.26(s, 1H), 2.51 (s, 1H). 13C NMR (25°C, CDCl3, ppm) δ 157.77, 156.08, 153.94, 153.68, 153.32, 147.02, 146.85, 146.64, 146.32, 146.03, 145.97, 145.86, 145.78, 145.63, 145.45, 145.04, 144.98, 144.83, 144.76, 144.54, 144.25, 144.13, 142.87, 142.75, 142.64, 142.32, 142.21, 142.06, 141.97, 141.85, 141.63, 141.43, 141.25, 139.87, 139.73, 139.54, 136.21, 135.94, 135.72, 134.74, 128.93, 117.25, 114.83, 77.21, 75.04, 55.92.

Scheme 1. Synthetic scheme of fullerene derivatives (see reference 15).

2.3.2. N-Heptal-2-(4-penyloxy-phenyl)-3,4-fulleropyrrolidine(II) 2-(4-penyloxy-phenyl)-3,4-fulleropyrrolidine(135mg, 0.15 mmol) and heptaldehyde(0.75 mmol) were mixed in dichloromethane (50 mL) and then treated with sodium triacetoborohydride (159 mg, 0.75 mmol) and AcOH (35 µL). The mixture was stirred at room temperature under a N2 atmosphere for 12 h until the reactants were consumed as determined by TLC analysis. The reaction mixture was quenched by adding aqueous saturated NaHCO3 solution, and the product was extracted with dichloromethane. The extract was dried over MgSO4, and the solvent was evaporated. The final product was purified on silica gel using hexane-toluene(5:1), yield 74%. 1H NMR (25°C, CDCl3, ppm), δ = 7.74(d, J= Hz, 2H), 7.02(d, J=8.6 Hz, 2H), 5.09 (d, J=10.4 Hz, 1H), 5.02 (s, 1H), 4.69 (s, 2H), 4.12 (d, J=9.2 Hz, 1H), 3.20 (m, 1H), 2.52 (m, 1H), 2.17(s, 1H), 1.90-1.86 (m, 2H), 1.67-1.29 (m, 18H), 0.89 (t, J=6.72 Hz,
3H). $^{13}$C NMR (25°C, CDCl$_3$, ppm) δ 157.93, 156.58, 154.74, 154.61, 153.57, 147.32, 147.05, 146.84, 146.52, 146.35, 146.23, 145.97, 145.84, 145.73, 145.65, 145.34, 145.12, 144.92, 144.83, 144.74, 144.55, 144.34, 142.97, 142.74, 142.53, 142.31, 142.26, 142.10, 141.94, 141.83, 141.57, 141.45, 140.07, 139.93, 139.75, 136.87, 136.24, 135.95, 135.04, 130.75, 130.54, 117.86, 115.03, 69.43, 56.24, 54.12, 32.48, 30.83, 30.54, 29.65, 29.54, 29.32, 28.65, 27.76, 23.14, 14.43.

2.4. Synthesis of Polymers

Scheme 2. Synthetic scheme of polymers

Table 1. Polymerization results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer Feed Ratio</th>
<th>Polymer composition</th>
<th>Total yield (%)</th>
<th>Mw (kg/mol)</th>
<th>PDI</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-EM-MTB-PAG</td>
<td>35</td>
<td>60</td>
<td>75</td>
<td>6.4</td>
<td>1.5</td>
<td>190</td>
<td>203</td>
<td>130</td>
</tr>
<tr>
<td>HEA-PAG</td>
<td>35</td>
<td>7.7</td>
<td>7.5</td>
<td>8.4</td>
<td>1.5</td>
<td>210</td>
<td>203</td>
<td>120</td>
</tr>
<tr>
<td>HEA-PAG</td>
<td>35</td>
<td>9.7</td>
<td>9.5</td>
<td>10.5</td>
<td>1.5</td>
<td>220</td>
<td>203</td>
<td>110</td>
</tr>
<tr>
<td>HS-EM-Fullerene</td>
<td>35</td>
<td>9.7</td>
<td>9.5</td>
<td>10.5</td>
<td>1.5</td>
<td>220</td>
<td>203</td>
<td>110</td>
</tr>
</tbody>
</table>

*The decomposition temperature was determined according to weight loss below 5.0%.
**Could not be determined by DSC.

2.5. Resist processing

For resist formulation, 66 mg of polymer bound PAG resists were dissolved in 1.0 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 HMDS / PGMEA (20/80 weight ratio) solution. The post apply bake was carried out at 110°C for 90 seconds. The thickness of the resists was determined to be in the range of 110-130 nm. The exposed wafers were baked at 110°C for 90 s. The development was conducted in conventional 2.38-wt % TMAH for approximately 20 s and rinsed with de-ionized water.

3. Results and Discussion

The fullerene derivatives were designed and prepared as outlined in scheme-1 with moderate to good yield and characterized by $^1$H and $^{13}$C NMR.

The polymers were prepared by free radical polymerization with AIBN as initiator, yield from 45.5-52.5%. PAG loading ranged from 6.4, 8.2, 6.6 and 6.3 % (mole ratio) for HS-EM-MTB-PAG, HS-EM-HM-MTB-PAG, HS-EM-Fullerene-MTB-PAG, and HS-EM-FullereneMTB-PAG, respectively. The molar composition of each unit in the polymers was determined by $^1$H NMR. The characteristic peaks have the following assignments: around 9.1ppm is assigned to the proton of hydroxyl group of HOST, 7.6-7.8 ppm is assigned to the protons from PAG’s cation TPS and fullerene derivatives, 6.6-7.1ppm from HOST and PAG’s anionic part, 4.6 ppm from OCH2 of fullerene derivative, 4.3 ppm (multiplet) from –CF2-CHF- and –COOCH2-, 3.7-3.8 ppm (multiplets) from fullerene derivatives, 0.7-2.8 ppm from the EAMA, HAMA and main-chain of polymer. The molar composition was calculated based on the integration ratios of the above corresponding peaks. The molecular weights were determined by GPC with THF as mobile phase. The results showed the polymer HS-EM-MTB-PAG, HS-EM-HM-MTB-PAG had $M_w$ of 3200 with PDI 1.9 and 2900 with PDI 1.7, and the polymers HS-EM-FullereneNH-MTB-PAG of $M_w$ of 4500 with PDI 2.1; HS-EM-FullereneNC7-MTB-PAG of $M_w$ of 4300 with PDI 2.2. The thermal stability of the polymers was identified by estimating the percentage of the weight loss of the polymer on thermal decomposition using TGA. The fullerene grafting polymers HS-EM-FullereneNH-MTB-PAG and HS-EM-FullereneNC7-MTB-PAG ($T_d$: 190, 203, respectively) showed higher thermostability than HS-EA-MTB-PAG and HS-EM-HM-MTB-PAG ($T_d$: 190, 203, respectively). The glass transition

Fig.1. Contact-printed images obtained, unprimed wafer
temperature of polymers HS-EM-FullerenNH-MTFB PAG and HS-EM-FullerenNC7-MTFB PAG (153, 162, respectively) were also superior to that of HS-EA-MTFB PAG and HS-EM-HM-MTFB PAG (142, 145, respectively), suggesting that the polymers are probably quite rigid, resulting from the fullerene bulky group in the main-chain of the polymers.

4. Conclusion

Two polymeric fullerene derivatives and corresponding fullerene grafted, PAG bound polymer resists based on hydroxystyrene, 2-ethyl-2-adamantyl methacrylate, or 3-hydroxy-1-admantyl methacrylate were prepared in moderate yields and characterized by NMR, GPC, and thermal-analysis. The lithographic performance of these polymers was conducted with contact printer, e-beam. The sensitivity decreased by grafting the amino-fullerene units, due to their basic properties. The microstructure optimization, high resolution EBL and EUV imaging, etching durability, outgassing, structure-function relationship will be reported subsequently.

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References