Sensitive Polysulfone Based Chain Scissioning Resists for 193 nm Lithography

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ABSTRACT

Chain scissioning resists do not require addition of photoacid generators to function. Previously reported chain scissioning polysulfone resists were able to achieve enhanced sensitivity by incorporation of absorbing repeat units, but these groups also inhibited the depolymerization reaction, which could further enhance sensitivity. Here we report the development of sensitive polysulfone chain scissioning resists for 193 nm that are able to undergo depolymerization. The effect of depolymerization of LER is also discussed. These polymers underwent CD shrinkage upon overdose, which may be useful for double patterning processes.

Keywords: polysulfones, absorbing, chain scission, depolymerisation

1. INTRODUCTION

The semiconductor industry is continually seeking to improve the performance of integrated circuits. In the main is achieved by reducing the size of features that are printed onto silicon wafers. Over the past 30 years, the density of transistors on computer chips has doubled every 18-24 months and this is used as a benchmark for the industries plans for manufacture into the future. One of the primary ways of achieving smaller feature sizes has been to decrease the wavelength of the source. However, there have been cases where this has not been feasible. For example the introduction of 157 nm VUV technology was unsuccessful because of unachievable requirements on certain critical components, such as the lens materials, the pellicle[1-5] and the resist itself.[6] Thus, much recent activity has concentrated on extending the life of 193 nm lithography through various means, such as immersion lithography (193i) in which the final lens element is water. It is expected that 193i lithography will allow the industry to move beyond the current 65 nm node to the 45 nm node. Initially, it was thought that the use of higher refractive index fluids[7] and photoresists,[8-13] 193i+ lithography would be able to tackle the 32 nm node. However, the significant challenges associated with this technology have meant that it has been surpassed by double patterning technologies.[14, 15] EUV lithography is likely to be introduced into some sectors of the industry over the next few years.

Most resist formulations currently use chemical amplification / catalysis to achieve the desired sensitivity. The concept of chemical amplification for photolithography was originally proposed by Ito, Willson, and Fréchet[16] In this scheme, a single photochemical event induces a cascade of subsequent chemical transformations in the resist film, which results in a switch in solubility of the photosensitive material. Typically this is achieved through the use of photoacid generators (PAGs), which upon photodegradation form strong acids that catalyze the formation of polar carboxylic acids or phenols and forms an almost exclusive foundation for an entire family of advanced resist systems. Diffusion of photoacid is believed to be a dominant cause of LER for CAR platforms.[17,19] However, a number of other factors are believed to contribute to LER and the major contributors include mask roughness,[20] aerial image contrast,[21] polymer-developer interactions,[22, 23] and energy blur such as diffusion of secondary electrons in the case of EUV lithography.[24, 25]

Despite the large amount of work investigating issues that affect LER a global understanding of the precise contribution of all the different components is yet to be achieved. Furthermore, LER values for patterning at 32 or 22 nm...
nodes is yet to reach the goals set by the ITRS for immersion double patterning or EUV. Given that LER can have a significant effect on device performance,[26] it still remains important to develop polymers and processes that minimize LER and also to gain further understanding of the processes involved.

As part of this search for a solution, we are considering chain scissioning resists for 193 nm and EUV lithography.[27-33] An issue with this class of resists has been the poor sensitivity.[34] The next generation of excimer lasers have a more powerful laser source which will provide the capability to deliver significantly larger doses to the resist at current scan speeds. Hence, for 193 nm Immersion lithography in particular it is likely that the industry will accept less sensitive resists. However despite this further effort is still required to increase the sensitivity of non-CAR resists.

Our 193 nm scission resist platform is based on polysulfones. Polysulfones are copolymers of a vinyl monomer and sulfur dioxide. Typically, this class of polymer exhibits high sensitivities to ionizing radiation, where the rate of chain scission is as high as 6 times greater than that of PMMA. Another advantageous property is that they are thermodynamically unstable in the presence of radicals above a critical temperature, termed the ceiling temperature (Tc). Hence, once a radical forms as a result of a chain scission, polysulfones have a tendency to spontaneously depolymerize when heated above their Tc. This provides a possible mechanism for further decreasing the molecular weight of the polymer during a post exposure (PEB) step, which is conducted outside of the exposure tool. Hence, the amount of SO₂ released in the tool can be minimized and the sensitivity of the resists can also be increased.

Copolymers of norbornene and sulfur dioxide form the basis of our 193 nm scissioning resist platform, because this copolymer has a high Tg and Tc. From spectroscopic ellipsometry studies it was found that this polymer had an absorbance of 0.17 µm⁻¹ at 193 nm.[27] Hence, it was not unexpected that the dose to clear (E₀) for this polymer was in the order of 1000 mJ.cm⁻². The amount of film thinning during the PEB step was found to increase with increasing baking temperatures. It was also found that the E₀ could be decreased by over an order of magnitude to 80 mJ.cm⁻² when the PEB temperature was 170 °C. Using grazing angle attenuated total reflectance FTIR it was also shown that irradiated films that underwent an annealing step, exhibited a decrease in the SO₂ band at 1302 cm⁻¹, which is consistent with loss of sulfur dioxide during depolymerization. All these results demonstrated that depolymerization was occurring during the PEB and that this could be used to enhance the effective sensitivity of polysulfone based chain scissioning photoresists. However, pure poly(norbornene sulfone) is only useful as a model resist, because the PEB temperatures required to obtain the highest sensitivities were well above the Tg.

To increase the sensitivity of these resists a controlled amount of an absorbing comonomer was incorporated during polymerization.[31, 35] In the first instance the amount of allyl benzene was varied and polymers with absorbance values between 3.0 and 6.1 µm⁻¹ at 193 nm were obtained. E₀ values as low as 50 mJ.cm⁻² were obtained for some of these polymers. This demonstrated that by controlling the absorbance at 193 nm the sensitivity of the chain scissioning resists could be controlled. However, when these polymers were subjected to a PEB, no enhancement in sensitivity was observed. This was attributed to the allyl benzene repeat unit being stable towards depolymerization. This article focuses identifying absorbing repeat units to replace allyl benzene in our polysulfone formulations for 193 nm scission resists.

2. EXPERIMENTAL

2.1 Synthesis of vinyloxybenzene

A solution of crude 1-phenoxy-2-bromoethane (25.7 g) in dry benzene (75 mL) was slowly added to a refluxing potassium t-butoxide solution over a period of 6 h. After cooling to room temperature, the solution was diluted with H₂O (150 mL) and extracted several times with Et₂O. After removing the solvent under vacuum, the residue was distilled at reduced pressure: bp 54–55 °C (10 mm Hg) giving phenyl vinyl ether (12 g, 0.1 mol, 62 % overall yield).¹H NMR (CDCl₃), δ (ppm): 7.45–6.97 (m, 5H, Ar), 6.71 (dd, 1J = 13.2 Hz, 2J = 6.7 Hz, 1H.), 4.85 (dd, 1J = 13.2 Hz, 2J = 1.6 Hz, 1H.), 4.50 (dd, 1J = 6.7 Hz, 2J = 1.6 Hz, 1H).

2.2 Synthesis of polysulfones

In a typical polymerization, bicyclo[2.2.1]hept-2-ene, (1 g, 1.06 × 10⁻² mol) in THF (2.67 mL) were transferred to a 50 mL reaction vessel and deoxygenated using three successive freeze-evacuate-thaw cycles before sulfur dioxide (~25 mL) was added. The polymerization was carried out at -15 °C to -20 °C and was initiated with t-butyl hydroperoxide for 2 h. The polymer was purified via precipitation in diethyl ether. All other experiments were carried out in the same way but with the addition of varying different monomers, compositions and temperatures.
2.3 Measurements

$^1$H NMR spectroscopy was carried out using a Bruker Avance DRX 500 spectrometer operating at 500.13 MHz and equipped with a 5 mm triple resonance z-gradient probe. Deuterated chloroform (CDCl$_3$) was used to dissolve the organic samples. An internal standard, either tetramethysiliane (TMS) or the residual proton signal of the deuterated solvent was used. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min in N$_2$ on a METTLER TOLEDO instrument STARé Thermogravimetric analyzer. Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C/min on a METTLER TOLEDO instrument STARé DSC. Molecular weights of polymers were measured using gel permeation chromatography. The chromatographic system consisted of a 1515 isocratic pump (Waters), a 717 autosampler (Waters), Styragel HT 6E and Styragel HT 3 columns (Waters) run in series, a light scattering detector DAWN 8+ (Wyatt Technology Corp.) and a 2414 differential refractive index detector (Waters). Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL/min. ASTRA (Wyatt Technology Corp.) and Empower 2 (Waters) were used for data collection and processing. For the determination of molar mass by conventional SEC, the columns were calibrated by polystyrene standards (Waters) covering the molar mass range of 1.06–1,320 kDa. Optical properties of the thin films, phi and delta, were measured using a J.A. Woollam Vacuum UV – Variable Angle Spectroscopic Ellipsometer (VUV-VASE). Using a model these parameters were used to calculate, film thickness, refractive index and absorbance.

3. RESULTS AND DISCUSSION

Allylbenzene was previously used as the chromophore to raise the absorbance of resists at 193 nm. However, it was found that its incorporation resulted in inhibition of depolymerization during the PEB, having an adverse effect on the sensitivity. This was attributed to the stability of the radical that formed during photodegradation, which inhibits depolymerization. To improve sensitivity a more reactive absorbing unit was sought. Vinyloxybenzene was chosen due to the aromatic group for absorbance, but with the addition of an oxygen atom. Inclusion of this monomer has been reported to enhance scission of other systems upon irradiation with ionizing radiation.[36]

![Chemical structure of terpolymer of vinyloxybenzene(VOB), bicyclo[2.2.1]hept-5-en-2-yl ethyl carbonate (NBEC) and sulfur dioxide.](image)

To verify that vinyloxybenzene was a better absorbing unit than allyl benzene, it was copolymerized with bicyclo[2.2.1]hept-5-en-2-yl ethyl carbonate (NBEC) and sulfur dioxide, using tert-butylperoxide as initiator and tetrahydrofuran as a solvent, at a reaction temperature of -45 °C for 3 h. The copolymers (3KG_PS_R25(A-C)) that were prepared are listed in Table 1 along with their compositions and optical properties at 193 nm. For 3KG_PS_R25(A-C), a higher mol% of vinyloxybenzene was incorporated into the copolymer compared to the initial feed ratio, which can be attributed to the higher reactivity of vinyloxybenzene. This is in contrast to the copolymerization using allylbenzene that was reported previously, where the stability of propagating radical resulted in a lower rate of propagation during polymerization. Initially, 3KG_PS_R25A was prepared with 40 mol% of vinyloxybenzene incorporated, but the absorbance value of 10.6 µm⁻¹ (at 193nm) is higher than the target value of 3µm⁻¹. The feed ratios (3KG_PS_R25B-C) were subsequently reduced from 40 to 20 and 10 mol% to adjust the absorbance to 6.88 and 3.04 µm⁻¹ respectively.

Figure 2 shows the SEM micrographs of 130 nm line/space patterns for 3KG_PS_R25C that have been generated using dry 193nm interference lithography, where the NA was 0.32, the PEB conditions were 100 °C for 60s and the developer conditions were MIBK for 60s. At 20 mJ.cm⁻² exposure, the dissolution of the exposed area with organic solvent, MIBK gives a positive image. Based on the SEM image (Figure 7 (C)), the half-pitch and LER were analyzed using SUMMIT software. At 20 mJ.cm⁻², an average half-pitch of 116.3 nm was measured and the LER was calculated to be approximately 11.7 nm. In addition, a 10.5% shrinkage of CD was observed. The shrinkage became more distinct as the dose was increased to 90 mJ.cm⁻², where shrinkage of ~63% (48.1nm) was observed. However, qualitatively the LER seemed to be improved at higher doses (90 mJ.cm⁻²) based on the images from (C) & (D) in Figure 2. This shrinkage of CD may be useful for a double patterning process.
Table 1. Terpolymerization of bicyclo[2.2.1]hept-5-en-2-yl ethyl carbonate (NBEC), vinyloxybenzene(VOB) and sulfur dioxide, using 2mol% of tert-butylperoxide as initiator in tetrahydrofuran at -45 °C for 3h.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Molecular Weighta (Da)</th>
<th>Feed Ratio (x:y:z)</th>
<th>Mole Ratiob (x:y) (NMR)</th>
<th>n193nm</th>
<th>k193nm</th>
<th>Abs193nm (µm-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3KG_PS_R25A</td>
<td>Mw: 176 k Da: 2.43</td>
<td>70:30</td>
<td>60:40</td>
<td>1.74</td>
<td>0.33</td>
<td>10.6</td>
</tr>
<tr>
<td>3KG_PS_R25B</td>
<td>Mw: 99 k Da: 2.36</td>
<td>80:20</td>
<td>70:30</td>
<td>1.74</td>
<td>0.21</td>
<td>6.88</td>
</tr>
<tr>
<td>3KG_PS_R25C</td>
<td>Mw: 71 k Da: 2.12</td>
<td>90:10</td>
<td>81:19</td>
<td>1.73</td>
<td>0.09</td>
<td>3.04</td>
</tr>
<tr>
<td>*3KG_PS_R13b</td>
<td>Mw: 173 k Da: 2.47</td>
<td>60:40</td>
<td>83:17</td>
<td>1.75</td>
<td>0.165</td>
<td>5.36</td>
</tr>
</tbody>
</table>

aMolecular weight characteristics are measured using polystyrene as standard at 40 °C in THF.
bMole ratio is calculated using 1H NMR.
cn & k are measured using VUV ellipsometer.
dAbsorbance value is calculated using this equation:
*Note: Allylbenzene is used as the absorbing monomer unit.

Figure 2 SEM images of the interferometric patterning of 3KG_PS_R25C (0.32NA_Air). (A) 20 mJ.cm-2 at 16 k× magnification, (B) 90 mJ.cm-2 at 23 k× magnification (C) 20 mJ.cm-2 at 71 k× magnification and (D) 90 mJ.cm-2 at 125 k× magnification. *Conditions: (I) Thickness: 64nm; (II) PAB: 110 °C, 60s; (III) PEB 100 °C, 60s; (IV) developed with MIBK, 60s. *Note: BARC29A coated prior coating.

Figure 3 shows 193 nm interferometric imaging of 3KG_PS_R25C where a higher PEB temperature (120 °C) was used. Similar trends (such an increase in shrinkage of cd and lower LER at higher energy exposure) were observed, which is similar to the lower PEB temperature (100 °C) except that the increased PEB increased the degree of cd shrinkage. For example, at 20 mJ.cm-2 the shrinkage was 10.5% for a 100 °C PEB but for a 120 °C PEB, the shrinkage almost doubled to 17%. Figure 4 shows a typical plot of (a) dose versus CD and (b) dose versus % shrinkage which shows the reduction in CD from 105.9 nm (20 mJ.cm-2) to 44.5nm at 90 mJ.cm-2, causing shrinkage to rise from 17.5% (20 mJ.cm-2) to 65% (90 mJ.cm-2).
Figure 3 SEM images of 3KG_PS_R25C (0.32NA_Air) line/space pattern. (A) 20 mJ.cm$^{-2}$ at 11 k× magnification, (B) 30 mJ.cm$^{-2}$ at 17 k× magnification, (C) 40 mJ.cm$^{-2}$ at 20 k× magnification and (D) 50 mJ.cm$^{-2}$ at 11 k× magnification. (E) 20 mJ.cm$^{-2}$ at 54 k× magnification, (F) 50 mJ.cm$^{-2}$ at 64 k× magnification. *Conditions: (I) Thickness: 64nm; (II) PAB: 110 °C, 60s; (III) PEB 120 °C, 60s; (IV) developed with MIBK, 60s. *Note: BARC29A coated prior coating.

Figure 4 Plot illustrates the effect of (a) Dose vs. Critical dimension and (b) Dose vs. % shrinkage. *Note: Conditions: (I) Thickness: 64nm; (II) PAB: 110 °C, 60s; (III) PEB 120 °C, 60s; (IV) developed with MIBK, 60s. *Note: BARC29A coated prior coating.

The cross-sectional SEM images of the interferometric patterning of 3KG_PS_R25C for doses between 30-50 mJ.cm$^{-2}$ with 120 °C PEB are shown in Figure 5(A-C). The resist thickness was retained, however, rounded profiles were observed for all images.
SUMMIT software was used to analyze the LER and LWR for the high magnification images from Figure 2 and Figure 3 (20 and 50 mJ/cm$^2$ exposures) and these are summarized in Table 2. The LER decreases when the PEB temperature is increased. This decrease in LER can be attributed to increased depolymerization, which will lead to decreased molecular weight of the polymer chains. At higher doses the LER was also observed to decrease, although the as a percentage of the CD the value remains the same.

Table 2 LER and LWR analysis of 3KG_PS_R25C

<table>
<thead>
<tr>
<th>PEB (°C)</th>
<th>Irradiation Dose (mJ/cm$^2$)</th>
<th>CD (nm)</th>
<th>LWR'</th>
<th>% LWR</th>
<th>LER'</th>
<th>%LER</th>
<th>SEM magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>20</td>
<td>107.8</td>
<td>16.0</td>
<td>14.8%</td>
<td>11.7</td>
<td>10.9%</td>
<td>70.8k ×</td>
</tr>
<tr>
<td>120</td>
<td>20</td>
<td>105.9</td>
<td>13.8</td>
<td>13.0%</td>
<td>9.1</td>
<td>8.6%</td>
<td>54.4k ×</td>
</tr>
<tr>
<td>120</td>
<td>50</td>
<td>62.3</td>
<td>7.7</td>
<td>12.4%</td>
<td>5.5</td>
<td>8.8%</td>
<td>60.5k ×</td>
</tr>
</tbody>
</table>

*Note: All measurements are determined by SUMMIT software to 3σ.

4. CONCLUSIONS

A chain scissioning polysulphone resist has been developed that has excellent sensitivity (< 20 mJ cm$^{-2}$). This has been achieved by replacing the allylbenzene absorbing unit with a vinylxybenzene repeat unit. In a similar fashion to the allylbenzene the vinylxybenzene unit increases the absorbance compared to pure polynorbornene sulfone and acts as a centre for chain scission. The vinylxybenzene copolymer also was able to undergo depolymerization during the PEB, which further enhanced the sensitivity of the polymer. The polymers exhibited shrinkage of the CD upon overdose, which may make them useful in a double patterning process. It was also found that by increasing the PEB temperature that the LER could be decreased. Variants that are able to be developed by an aqueous based developer are currently being investigated in out labs.

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