Design, Synthesis, and Characterization of Poly(trimethylsilylmethyl methacrylate-co-chloromethyl styrene) for 193 nm Exposure

Bruce W. Smith
*Rochester Institute of Technology*

David A. Mixon
*AT&T Bell Labs*

Anthony E. Novembre
*AT&T Bell Labs*

Shahid Butt
*Rochester Institute of Technology*

Follow this and additional works at: [http://scholarworks.rit.edu/other](http://scholarworks.rit.edu/other)

**Recommended Citation**

Design, synthesis, and characterization of poly(trimethylsilylmethyl methacrylate-co-chloromethyl styrene)
for 193 nm exposure

Bruce W. Smith†, David A. Mixon†, Anthony E. Novembre*, Shahid Butt†
†Rochester Institute of Technology, Rochester, N.Y. 14623-5604
*AT&T Bell Laboratories, Murray Hill, N.J. 07974

ABSTRACT

Requirements of materials for lithography at 193 nm limit single layer resist candidates to those with high optical transmission. A random copolymer of trimethylsilylmethyl methacrylate (SI) and chloromethyl styrene (CMS), [P(SI-CMS)], has been shown to be highly sensitive negative 193 nm resist in both bi-layer and single layer modes. Such resists show maximum sensitivity with an optical absorbance of the coating of \( \log_{10} e \), or 0.434. Through control of the mole ratio of the monomers in the P(SI-CMS) copolymer, absorbance values have been optimized for film thicknesses of 0.2 - 0.3 μm for 90:10 SI:CMS, 0.35 - 0.45 μm for 95:5 SI:CMS and 0.55 - 0.65 μm for 98.2 SI:CMS. Optical absorbance of the CMS is at a maximum in the 190 to 205 nm range, allowing the copolymer to be tailored for a large degree of crosslinking at a relatively low CMS concentration. Spray development of these materials is performed with ethanol, followed by a two step methanol / isopropanol-water rinse. Sensitivities are on the order of 4 to 20 mJ/cm² at \( \mathcal{M}_n \) near 40 000 g/mol. Furthermore, these ratios have been found to produce optimum O₂ etch resistance.

1. INTRODUCTION

Resist materials based on silicon containing methacrylate monomers have been demonstrated to be effective positive patterning masks for O₂ RIE pattern transfer into hard-baked novolac-based resist for electron beam and 248 nm lithography. A random copolymer of trimethylsilylmethyl methacrylate (SI) and chloromethyl styrene (CMS) has been shown to be a sensitive negative-acting resist material for these exposure applications, exhibiting O₂ RIE resistance for use in bi-layer processing. Due to the high optical transmission properties of the silicon methacrylate monomer, this copolymer, designated P(SI-CMS), has potential for application at 193 nm.

An analysis of radiation attenuation within a resist film can be utilized to determine optimum optical properties of a resist material. In a crosslinking resist, a fully networked structure throughout the resist film is desired with a minimum amount of exposure. This is accomplished when the molar extinction coefficient of the component responsible for crosslinking is sufficiently high at the exposing wavelength. Through adjustment of the molar concentration of this component within a resist, the absorbed energy throughout the film thickness can be controlled. For a given film thickness, an optimum optical absorbance (\( \log_{10}(T) \)) of 0.434 is desired for minimum attenuation through the bulk of the resist film with sufficient absorption at the film base so that photochemistry may occur. By targeting this absorbance through control of the mole ratio of SI and CMS monomers, the optical properties of P(SI-CMS) have be optimized for specific resist thicknesses. This allows for optimal resist films for use in an oxygen RIE bi-layer pattern transfer process and introduces potential for P(SI-CMS) in single layer application.

2. EXPERIMENTAL

2.1. Polymer synthesis and characterization

Poly(trimethylsilylmethyl methacrylate) [P(SI)] and various compositions of P(SI-CMS) were synthesized for 193 nm exposure evaluation. Trimethylsilylmethyl methacrylate and chloromethylstyrene were obtained from Hüls America, Inc. and Dow Chemical Company respectively. Both monomers were purified by distillation at reduced pressure prior to use. Polymers were prepared by free-radical solution polymerization at 95 °C in toluene. Reactions were initiated using Vazo® 67 (DuPont). Reactions were carried out to a monomer conversion of ~60%, and copolymer compositions were adjusted using reactivity ratios for SI and CMS of 0.49 and 0.54 respectively.
Polymer was recovered from the reaction solution by precipitation in a mixture of methanol and propylene glycol (3:2 volume ratio) at 8 °C. The polymer was then purified by dissolving in acetone and precipitating in a mixture of methanol and water (2:1 volume ratio). The product was then vacuum dried at ambient temperature.

Copolymer compositions were determined through combustion analysis for elemental chlorine and are accurate to ±0.5 mole %. Molecular weights were measured using high pressure size exclusion chromatography. Resist films were spin coated from degassed ethyl 3-ethoxypropionate (EEP). Scission yield \( G_x \) of P(SI) was carried out by 193 nm exposure of coated resist material to a dose of 1 J/cm\(^2\) and measuring the induced molecular weight change \( (M_n - M_p) \). UV absorption measurements of films coated onto fused silica substrates and baked at 140 °C for one hour in a convection oven were obtained on a Perkin Elmer Model 552 UV-Vis spectrometer, using a deuterium lamp for measurement in the wavelength range of 190 to 225 nm.

2.2. Evaluation of lithographic properties

A 20X small field refractive projection system, operating at a numerical aperture of 0.38 and a partial coherence of 0.6 was used for lithographic exposures. A Lumonics EX700 ArF laser, spectrally narrowed with dual Fabry Perot etalons, was used to deliver the spectral bandwidth required at the specified numerical aperture. Exposure energies delivered to the wafer plane were approximately 0.8 mJ/cm\(^2\) per pulse. Resist materials were coated over a 0.5 to 1.0 μm thick film of a hard-baked novolac-based resist (Shipley 812, 200°C/ 30 minutes, convection oven), and prebaked at 90°C for 30 minutes in a convection oven. Resist development was performed in an APT915 spray processor using ethanol, followed by a two step rinse in methanol and isopropanol/water (7:3 volume ratio). Characteristic exposure response curves were generated for each formulation by coating the copolymers directly onto 4" fused silica wafers and bulk image exposing through the substrate. Thickness measurements were carried out using an Alpha Step surface profilometer. A Phillips 501 SEM was used to evaluate patterned image quality and resolution. A PlasmaTherm parallel plate reactive ion etch system operating at 100 W power, 8 mTorr pressure, and 25 sccm O\(_2\) was used to evaluate copolymer etch rate and selectivity to hard-baked novolac.

3. RESULTS

3.1. Polymer synthesis and properties

Figure 1 shows the chemical structure of the repeat unit in P(SI) and P(SI-CMS). While the SI:CMS mole ratio in the copolymer has been varied to obtain optimum absorbance, \( M_n \) has been maintained at values near 40 x 10\(^3\) g/mole for each material to achieve highest resolution. Preliminary absorption measurements were made for a copolymer sample having a 90:10 SI:CMS mole ratio and a \( M_n \) of 40 x 10\(^3\) g/mole. Absorption measurement of the 90:10 mole ratio P(SI-CMS) yielded an absorbance value of 1.81/μm, which corresponds to a required film thickness of 2400 Å for an ideal absorbance of 0.434. From these results, copolymer compositions were targeted to allow for a range of resist thicknesses up to 6000 Å. Copolymers with compositions of 95:5 and 98:2 SI:CMS were targeted to produce estimated absorbance values of 1.13/μm and 0.74/μm respectively, corresponding to optimal thicknesses of 3800 Å and 5900 Å.

Table 1 lists the resulting weight percent chlorine, mole ratio SI:CMS, and molecular properties of the copolymers investigated. Molecular weights for all formulations were held near 40 x 10\(^3\) g/mole. The corresponding number average degree of polymerization (\( \bar{X}_n \)) for formulations have been calculated based on their composition and molecular weight. The variation in number average degree of polymerization for the 90:10, 95:5, and 98:2 materials is within 6%.

Absorption measurements were also made for a sample of poly(trimethylsilvylmethy] methacrylate) cast from EEP. The absorption spectrum for this polymer is shown in Figure 2. Absorbance of the poly(trimethylsilvmethyl methacrylate) measured 0.40/μm at 193 nm.

To evaluate the extent of backbone scissioning in the P(SI) polymer, the scission yield, \( G_x \), was determined through measurement of the molecular weight change from 193 nm irradiation. To account for both crosslinking and scissioning of the polymer upon irradiation, both scission yield and crosslinking yield, \( G_x \) and \( G_p \), were determined by measuring \( M_n \) and \( M_p \) of irradiated and unirradiated samples. Simultaneous solutions of equations relating \( M_n \) and \( M_p \) values result in \( G_x \) and \( G_p \) values:\n

\[ \text{SPIE Vol. 2438 / 505} \]
where $D$ is exposure dose, expressed in electron volt per gram and $N_a$ is Avagadro's number. Resist films were coated on 2" wafers, at a thickness of 14600 Å, which yielded approximately 1.3 mg of polymer per wafer. Initial $M_N^0$ for the polymer was $42 \times 10^5$ g/mole and $M_W^0$ was $71 \times 10^5$ g/mole. The exposure dose of 1 J/cm$^2$ given to the films is equivalent to $4.84 \times 10^{21}$ eV/g, resulting in a molecular weight change to $20 \times 10^5$ g/mole for $M_N$ and $48 \times 10^5$ g/mole for $M_W$. Resulting $G_s$ and $G_x$ values are 0.41 and 0.08, respectively. Although chain scissioning is dominant ($G_s = 5.12 G_x$), the magnitude of the scission yield is low. It can be expected, therefore, that chain degradation in the P(SI-CMS) at 193 nm is low.

The UV absorption spectra for copolymers are shown in Figure 3. Although absorption at 193 nm is due to a large extent to the CMS moiety, absorbance of the SI moiety is 0.40/µm. Based on the measured absorption properties of the P(SI-CMS) formulations prepared, optimum thicknesses to produce an optical absorbance of 0.434 have been determined and are shown in Table 2.

### 3.2. 193 nm exposure response

P(SI-CMS) films were coated onto fused silica substrates by spin casting resists dissolved in EEP at concentrations ranging from 8-20 wt./vol. %. Characteristic exposure response curves for formulations are shown in Figure 4. Values for incipient gel dose ($D_g$), sensitivity ($D_s^{0.5}$, dose required for 50% film retention), % film loss, and contrast ($\gamma$) are given in Table 3. Absorption via the CMS moiety is responsible for crosslinking, and is extremely efficient at 193 nm. Neglecting competing chain degradation, the effective quantum yield of crosslink formation can be estimated from $D_g$ values obtained via exposure through a transparent support as $\Phi = t d/(A M W d)$ where $t$ is resist thickness, $d$ is specific gravity [1.19 for P(SI-CMS)], and $A$ is absorption (1-T). Calculated values for effective quantum yield are included in Table 3.

A contrast ($\gamma$) value near 2 for all three materials is relatively high. However, when compared to values reported previously for 248 nm exposure ($\gamma_{248} \approx 3$), there is a significant decrease. Since the absorption of the trimethylsilylmethyl methacrylate is very low at 248 nm (absorbance is $\sim 0.01/\mu m$), this is likely an indication of the presence of radiation induced scissioning effects in the P(SI-CMS) at 193 nm exposure. The measured contrast at 193 is closer to that reported for electron beam exposure ($\gamma \sim 1.5$), indicating that the scissioning events are similar to those occurring for electron beam irradiation.

A function which relates the gel fraction $W$ with exposure $E$ can be determined from the Flory function if the molecular weight distribution of a polymer is known. This function depends on the dispersity of the polymer and is characterized by a single parameter $\beta$, the width of the lognormal molecular weight distribution. Using a measured dispersion value of 1.42 for the 90:10 SI:CMS copolymer sample, a $\beta$ value of 0.59 results. To extend measured material parameters to resist films coated over a non-reflecting support and exposed from the front side, calculations for $D_g^{0.50}$ were made based on a generalized Flory function and a fundamental exposure relationship for crosslinking resists:

$$D_g^{0.50} = 1.7 \frac{D_g}{T} = 1.7 \frac{t d}{A M W \Phi T}$$

where $T$ is transmission through the resist film.

Exposure values required for $D_g^{0.5}$ were calculated and plotted for film thicknesses ranging from 2000 Å to 10000 Å and are shown in Figure 5. Additionally, ideal exposure values required for materials with film absorbance of exactly 0.434 for any thickness are plotted. As seen from this plot, required exposure values increase substantially as films increase beyond ideal thicknesses of 2400, 3700 and 5500 Å for the 90:10, 95:5 and 98:2 materials respectively. Additionally, two relationships are evident. At film thicknesses near 2000 Å, quantum
efficiency dominates as exposures required for higher Φ materials are less than those required for lower Φ materials. As thickness increases, however, optical effects dominate and exposures required for lower absorption materials are less. It can be expected that as film absorption forces high levels of exposure, the ability of resist films to be imaged through an entire coating thickness will be reduced.

3.3. Lithographic performance

P(SI-CMS) materials were spin coated at thicknesses of 2000, 3000, 4000, and 5000 Å. All films were coated over 6000 Å of hard-baked novolac resist, which allowed for control of reflection effects at the resist/substrate boundary. A line and space grating mask with patterns from 0.10 μm to 1.0 μm was used to expose materials in 0.8 mJ/cm² per pulse increments up to 50 mJ/cm². Exposure dose values required to print 0.4 μm line and space pairs were determined for each material over the range of thicknesses and are shown in Table 4. As expected, the 90:10 SI:CMS material coated beyond 2000 Å is not capable of imaging to the resist/substrate interface without complete crosslinking at the resist surface. SEM results from exposure trials are shown in Figure 6. Swelling effects from the ethanol/methanol development and rinse are evident as film thickness increases, which is significant with the higher mole ratio SI:CMS materials.

3.4. Reactive ion etching results

The high silicon content of P(SI-CMS) has been shown to provide substantial O₂ plasma etch resistance for anisotropic pattern transfer in RIE. For the materials under investigation, pressure and O₂ flow rates were chosen to maximize etch selectivity between the P(SI-CMS) copolymer and hard-baked novolac resist. Optimal etch conditions were 10 W power, 8 mTorr pressure, and 25 sccm O₂. Within the range of materials evaluated, silicon content is high enough to produce an effective etch stop at oxygen pressures which readily remove novolac. Silicon content, etch rates in O₂ RIE, and selectivity values over Shipley 812 are shown in Table 5 for each material.

Figure 7 shows the results obtained from O₂ RIE transfer of 2000 Å P(SI₀.₉₈-CMS₀.₀₂) images as an etch mask over 6000 Å Shipley 812. Vertical 0.35 μm line and space features have been transferred through to the wafer surface, indicating a high degree of anisotropy.

4. CONCLUSIONS

The random copolymer of trimethylsilylmethyl methacrylate and chloromethyl styrene has been shown to be a potential photoresist candidate for 193 nm exposure. Through control of mole ratios of SI and CMS monomers, optical properties of the copolymer have been tailored to maximize material performance. Resist sensitivities on the order of 4-20 mJ/cm² and high O₂ RIE resistance have been achieved in films from 2000 Å to 5000 Å thick. Resolution to 0.4 μm has been demonstrated in P(SI₀.₉₅-CMS₀.₀₅) and P(SI₀.₉₈-CMS₀.₀₂) films with thicknesses up to 5000 Å. Through O₂ RIE pattern transfer into a hard baked novolac, resolution to 0.35 μm has been shown. Film loss at CMS concentrations less than 5 mole % may be attributed to insufficient distribution of crosslinking sites within the copolymer. Through use of higher molecular weight materials, improvements in crosslinking performance may be expected.

5. REFERENCES

Figure 1. Structure of repeat unit in P(SI) (left) and P(SI-CMS) (right).

Figure 2. Absorption spectrum of poly(trimethylsilylmethyl methacrylate).

<table>
<thead>
<tr>
<th>Targeted Composition</th>
<th>wt.% Cl</th>
<th>Composition</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>Polydispersity Index</th>
<th>$X_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(SI₈₉₉-CMS₈₂₀)</td>
<td>2.17</td>
<td>89.6:10.4</td>
<td>39800</td>
<td>1.42</td>
<td>128</td>
</tr>
<tr>
<td>P(SI₀₉₅-CMS₈₅₅)</td>
<td>0.97</td>
<td>95.3:4.7</td>
<td>38300</td>
<td>1.56</td>
<td>123</td>
</tr>
<tr>
<td>P(SI₀₉₀-CMS₉₇₇)</td>
<td>0.45</td>
<td>97.8:2.2</td>
<td>40900</td>
<td>1.83</td>
<td>131</td>
</tr>
</tbody>
</table>

Table 1. Properties of P(SI-CMS) formulations.
Figure 3. UV absorption spectra for P(SI-CMS) formulations.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Absorbance/μm</th>
<th>Optimum thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(SI&lt;sub&gt;1090&lt;/sub&gt;-CMS&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>1.81</td>
<td>2400Å</td>
</tr>
<tr>
<td>P(SI&lt;sub&gt;1095&lt;/sub&gt;-CMS&lt;sub&gt;0.5&lt;/sub&gt;)</td>
<td>1.16</td>
<td>3700Å</td>
</tr>
<tr>
<td>P(SI&lt;sub&gt;0.5&lt;/sub&gt;-CMS&lt;sub&gt;2.5&lt;/sub&gt;)</td>
<td>0.79</td>
<td>5500Å</td>
</tr>
</tbody>
</table>

Table 2. Absorption properties of P(SI-CMS) formulations.

Figure 4. Characteristic 193 nm exposure response curves for P(SI-CMS) formulations.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$D_{\text{f}}^1$</th>
<th>$D_{\text{f}}^{0.5}$</th>
<th>Film loss (%)</th>
<th>Contrast ($\gamma$)</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(S1090-CMS0.10)</td>
<td>1.5</td>
<td>3.0</td>
<td>2.7%</td>
<td>1.8</td>
<td>0.56</td>
</tr>
<tr>
<td>P(S1095-CMS0.05)</td>
<td>2.0</td>
<td>3.4</td>
<td>3.2%</td>
<td>2.0</td>
<td>0.38</td>
</tr>
<tr>
<td>P(S1098-CMS0.02)</td>
<td>3.7</td>
<td>6.0</td>
<td>20%</td>
<td>2.2</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 3. 193 nm exposure response properties of P(SI-CMS) formulations

![Graph showing estimated $D_{\text{f}}^{0.5}$ values for P(SI-CMS) formulations coated from 2000 Å to 10000 Å.]

**Figure 5.** Estimated $D_{\text{f}}^{0.5}$ values for P(SI-CMS) formulations coated from 2000 Å to 10000 Å.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>2000 Å</th>
<th>Exposure dose required</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3000 Å</td>
</tr>
<tr>
<td>P(S1090-CMS0.10)</td>
<td>4 mJ/cm²</td>
<td>-</td>
</tr>
<tr>
<td>P(S1095-CMS0.05)</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>P(S1098-CMS0.02)</td>
<td>13</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 4. Required exposure dose values for P(SI-CMS) formulations for 0.4 µm line and space pairs.
Figure 6. SEM micrographs of 0.4 μm line and space pairs in P(SI-CMS). Coating thicknesses are from top 2000 Å, 3000 Å, 4000 Å, and 5000 Å.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>wt. % silicon</th>
<th>Etch rate (Å/min)</th>
<th>Selectivity Novolac/P(SI:CMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(SI$<em>{1.09}$-CMS$</em>{0.10}$)</td>
<td>14.6</td>
<td>98</td>
<td>12</td>
</tr>
<tr>
<td>P(SI$<em>{1.05}$-CMS$</em>{0.02}$)</td>
<td>15.5</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>P(SI$<em>{1.98}$-CMS$</em>{0.02}$)</td>
<td>16.0</td>
<td>35</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 5. Summary of etching characteristics of P(SI-CMS) formulations. Etch conditions: 100 Watt, 25 sccm O$_2$, 8 mTorr.

Figure 7. O$_2$ RIE pattern transfer of 0.35 µm line and space pairs in P(SI$_{1.98}$-CMS$_{0.02}$) through 6000 Å Shipley 812.