The Thermal Deprotection Process in an E-beam Exposed, Phenolic-Based Polymer

by

Treva Long, S. Kay Obendorf, and Ferdinand Rodriguez

Prepared for presentation at the Ninth Int. Conference on Photopolymers
The Society of Plastics Engineers
October 28-30, 1991
Ellenville, NY

Olin Hall, Cornell University
School of Chemical Engineering
Ithaca, NY 14853

September 18, 1991

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited
The Thermal Deprotection Process in an E-Beam Exposed, Phenolic-Based Polymer.

Treva Long, S. Kay Obendorf, and Ferdinand Rodriguez


An alkali soluble latent image can be generated in pure PBOCST (poly(tert-butoxycarbonoxy styrene)) by e-beam exposure followed by a post-exposure bake (PEB) at relatively high temperatures (140°-150°C). Pattern wet development operates on the same basis as a PBOCST/acid generator two component system. Deprotection (heating), accelerated by the exposure, yields alkali soluble areas while unexposed areas remain insoluble. Sensitivities of 5-10 L/mC/cm² and contrasts of 6-10 have been measured. Complete TBOC deprotection results in a film thickness loss of 35-40% as CO₂ and isobutene are evolved. A laser interferometer/hotplate setup was used to track film thickness with time during the thermal deprotection process. IR analysis confirmed the correlation between conversion and thickness. It was found that a slow initial conversion rate was followed by an exponentially steep rise in rate after the 50% conversion point. Activation energies were on the order of 30 kcal/mol. It is apparent that thermolysis in both exposed and unexposed resist occurs during the PEB but that the difference in extent of conversion on exposure is sufficient to generate a pattern.
The Thermal Deprotection Process in an E-beam Exposed Phenolic-Based Polymer

Treva Long¹, S. Kay Obendorf¹, and Ferdinand Rodriguez²,
¹ Fiber Science Program, MVR Hall, ² School of Chemical Engineering, Olin Hall
Cornell University, Ithaca, New York 14853

Abstract

In our current work, we have examined the e-beam sensitivity and thermal processing behavior of pure PBOCST (poly(tert-butoxycarbonoxystyrene)). An alkali soluble latent image can be generated in the PBOCST by e-beam exposure followed by a post-exposure bake (PEB) at relatively high temperatures (140-150°C). Pattern wet development operates on the same basis as a PBOCST/acid generator two component system. Deprotection, accelerated by the exposure, yields alkali soluble areas while unexposed areas remain insoluble. Sensitivities of 5-10 μC/cm² and contrasts of 6-10 have been measured. Complete TBOC deprotection results in a film thickness loss of 35-40% as CO₂ and isobutene are evolved. A laser interferometer/hotplate setup was used to track film thickness with time during the thermal deprotection process. IR analysis confirmed the correlation between conversion and thickness. It was found that a slow initial conversion rate was followed by an exponentially steep rise in rate after the 50% conversion point. Activation energies were on the order of 30 kcal/mol. It was concluded that thermolysis in both exposed and unexposed resist occurred during the PEB but that the difference in extent of conversion on exposure was sufficient to generate a pattern.

1 Introduction

Wafer throughput in microlithography is dependent on the radiation sensitivity of the resist film. The lower the dose needed to produce a latent image in the resist, the higher the throughput. One route to higher sensitivity is through chemical amplification (CAMP). A single radiation event generates a moiety which catalyzes numerous reactions before being consumed. One of the most successful CAMP resists is PBOCST, the tert-butoxycarbonate (tBOC) protected form of poly(para-hydroxystyrene) (PPHS). When in the tBOC protected form, the polymer is only soluble in nonpolar solvents. Removal of the tBOC group by acidolysis or thermolysis yields PPHS, an alkali soluble polymer.

\[
\begin{align*}
\text{PBOCST} & \xrightarrow{\Delta} \text{PPHS} + \text{CO}_2 \\
\text{OCOOC(CH}_3)_3 & \xrightarrow{H^+} \text{CH}_3 = C(CH_3)_2 \\
\end{align*}
\]
In microlithography applications, an acid generating species (AG) is blended with the PBOCST. Upon exposure, the AG produces a strong acid. A short post-exposure bake (PEB) step at low temperatures activates the acid in the exposed areas to convert the PBOCST to PPHS leaving unexposed areas unaffected [1]. The latent image is then wet-developed using aqueous alkali. Two major advantages of the PBOCST/AG resist are elimination of toxic organic solvents in development and absence of swelling during development. Swelling does not occur since the alkali selectively wet-etches the hydrophilic PPHS without interacting with the hydrophobic PBOCST.

The two component PBOCST/AG system has been shown to produce submicron images using deep UV (DUV), e-beam or X-rays. Umbach, et al. [2] used PBOCST with an unspecified acid catalyst to fabricate structures with 18 nm linewidths at an e-beam dose of 50 μC/cm². Ito, et al. [3] have evaluated PBOCST sensitized with 5-15 wt% onium salts as a negative-working resist. E-beam exposed films were post-baked at 100 or 130°C for 2 min and developed with anisole. Sensitivities of 1-3 μC/cm² and contrasts of 2.3 were reported. DUV sensitivities are typically 20 mJ/cm² or less, again with PEB temperatures around 100°C [4].

Onium salts, the common AG component of the PBOCST system, are hard to synthesize and often toxic. Less efficient acid generators, such as the nitrobenzyl tosylate compounds, have been tested as onium salt substitutes. Unfortunately they can reduce the sensitivity of the CAMP system by almost an order of magnitude [4]. A more radiation sensitive CAMP polymer can compensate for this reduced sensitivity. Copolymers of PBOCST and SO₂ (poly(tBOC/hydroxystyrene-sulfur dioxide), TBSS) incorporate a C-S bond into the backbone that will easily scission upon exposure [5]. In a positive-working scheme, the acid catalyzed deprotection reaction acts together with chain scissioning to yield a resist with increased alkali solubility in the exposed area. TBSS/tosylate DUV sensitivities are in the range of 50 mJ/cm² while the contrast achieved with TBSS/tosylate exceeds that of the original TBOCST/onium salt [4]. Two-component systems can be more complex to characterize and control than simple one component resists. Novembre, et al. [6] have shown that TBSS alone can function as a chemically amplified X-ray or electron beam resist. Its sensitivity depends on the TBOCST-sulfur dioxide ratio. For a 2:1 TBSS:SO₂ copolymer, a dose of 90 μC/cm² resolved 0.25 μm l/s patterns [7]. Radicals produced by the exposure were proposed as being responsible for acid formation and the CAMP-like performance. As with the two component systems, heat treatment after exposure was critical in developing the latent image.

This work investigates the thermal deprotection behavior of PBOCST films as monitored with a laser interferometer/hotplate apparatus. Deprotection of PBOCST films results in a significant loss of thickness as volatile products are evolved. Laser interferometry is an effective method for tracking thickness losses and hence for measuring the deprotection rate under various conditions. We have found that pure PBOCST has potential as an electron-beam sensitive, CAMP-like resist when coupled with the proper thermal processing conditions. Thermal deprotection approximates autocatalytic behavior with the reaction half-life dependent on electron-beam dose. Differences in extent of conversion between exposed and unexposed regions are sufficient to yield submicron features in the PBOCST resist.
2 Experimental

2.1 PBOCST Synthesis

Three Hoechst Celanese PPHS's, manufacturer's MWs of 6500, 17500 and 56200, were used as the starting materials. Hoechst Celanese produced these by suspension polymerization of acetoxy styrene monomer and subsequent hydrolysis of the acetoxy group to the hydroxy group. Conversion of the hydroxy group to the tBOC group to obtain PBOCST proceeded via the method described by Houlihan, et. al. [8]. IR spectra confirmed that the conversion of the hydroxy groups was complete.

2.2 GPC Evaluation

Molecular size determinations of the PBOCST polymers were made using a Waters gel permeation chromatograph (GPC) system equipped with duPont Zorbax columns. Tetrahydrofuran was used as the eluting solvent in all cases. Polystyrene calibration standards were used for MW correlations. The PBOCST MW distributions are listed in Table 1. The molecular weights reported by the manufacturer were obtained by GPC of the acetoxy precursor polymers followed by adjustment for the change in mass on hydrolysis to PPHS. Conversion of PPHS to PBOCST should increase $M_w$ only by a factor of $1.83 (220/120)$. The fact that $M_w$ is larger than predicted for the PBOCST may be due to a difference in interaction of the polymer with column packing vis a vis the acetoxy precursors.

2.3 Laser Interferometer and Thermal Processing

Thermal processing behavior of PBOCST (6500 MW) was evaluated using a laser interferometer/hotplate setup. Films of approximately 1.5 μm thickness were spin-cast from chlorobenzene onto 3" diameter silicon wafers and prebaked at 105°C for 1/2 hr. A beam from an unpolarized He-Ne laser (2 mW, 632.8 nm) was reflected at an angle of about 10° from the surface of a coated wafer placed on the hotplate. The reflected light beam was collected by a photocell coupled through an amplifier to a chart recorder. An aluminum hotplate equipped with an Omega programmable temperature controller provided uniform temperatures at the wafer's surface to within ± 2°C . Input to the temperature controller was from a surface thermocouple bonded to the top of the coated Si wafer. Rates of conversion were measured from 130 to 155°C.

Conversion of PBOCST films to PPHS results in a 35-40% thickness decrease [10] as volatile products are lost. As the film thickness changes, thin film interference effects cause a sinusoidal oscillation in intensity. Each oscillation or fringe can be translated into an equivalent thickness loss, $d_p$ [9], using:

$$d_p = \frac{\lambda}{2(n_2^2 - n_1^2 \sin^2 \alpha)^{1/2}}$$

where:

- $\lambda$ = light wavelength
- $n_2$ = polymer refractive index
- $n_1$ = air refractive index
- $\alpha$ = incident angle

Analysis of interferometer data for a film with time-varying composition must take into account the changing refractive index in eqn 1. Refractive indices of PBOCST and PPHS
are 1.53 and 1.61, respectively, as measured by ellipsometry. Given that \( d_p \) will differ by only 5% for these polymers, the interferometer traces were interpreted based on an average of 203 nm/fringe. The effect of electron beam exposure on the thermal processing behavior was also tested on the interferometer/hotplate by flood exposing PBOCST films at 20 \( \mu \text{C/cm}^2 \) prior to the bake step. Films were exposed to a wide beam of electrons with a modified JEOL JEM7A transmission electron microscope (50 kV). Incident electron doses were determined from the exposure time and the electron charge density, which was measured with a Faraday cup.

2.4 IR Evaluation

To correlate the film thickness during thermolysis with composition, PBOCST films at various bake stages were analyzed by IR. Films were spun onto Si wafers from chlorobenzene and baked at 140 or 150\(^\circ\)C at times ranging from 0 to 50 mins. IR spectra for these samples were recorded on a Perkin Elmer 683 infrared spectrophotometer. Extent of conversion as reflected by the carbonyl peak intensity at 1755 cm\(^{-1}\) agreed well with fractional conversion based on film thickness changes.

2.5 Lithographic Evaluation

Films for lithographic evaluation were spin-cast at 1500 rpm from 15-25 wt% solutions in chlorobenzene onto 3” silicon wafers. The films were prebaked at 105\(^\circ\)C for 30 min. Film thicknesses were 1300, 1500 and 1100 nm for polymers A, B and C (Table 1) respectively, as measured with a Leitz Film Thickness Interferometer. Test patterns (for sensitometry and evaluation of contrast) were exposed using a Cambridge EBMF 10.5 at Cornell’s National Nanofabrication Facility (NNF). All patterns were exposed using an accelerating voltage of 20 kV. The exposed patterns were post-baked for 38-39 min at 150\(^\circ\)C in a forced air oven. Patterns were dip-developed in Shipley MF319 (a TMAOH aqueous base formulation) at 23\(^\circ\)C, followed by a deionized water rinse. Resolution of the patterns was evaluated using a Cambridge S200 SEM.

3 Results and Discussion

3.1 Laser Interferometer/Hotplate

Figure 1 is an actual interferometer trace for the conversion of a PBOCST film to PPIIS at 140\(^\circ\)C. Over a 51 min bake time approximately 3.5 fringes or an equivalent film loss of 710 nm occurs. The conversion is initially slow but accelerates rapidly after 40 mins such that the bulk of the film loss is in the last 10 min bake segment. All interferometer traces for bake temperatures of 130 through 155\(^\circ\)C and for unexposed and exposed films follow this same pattern.

The interferometer data can be translated into fractional film thickness loss vs time by defining

\[
f = \frac{\Delta d}{\Delta d_{\text{total}}} \tag{2}
\]

where \( \Delta d \) is the thickness loss at time \( t \) and \( \Delta d_{\text{total}} \) is the total thickness loss observed. Plots of \( f \) vs time for bake temperatures of 140 and 150\(^\circ\)C are sigmoidal but with very different
time scales (Figure 2). Included in Figure 2 for comparison with the interferometer data is the IR analysis of the PBOCST films. The absorbance of the C=O peak at 1755 cm\(^{-1}\) was chosen as a measure of the extent of deprotection. Good agreement between IR and interferometer data allows the fractional film thickness loss to be interpreted as an extent of conversion for the reaction.

The half-life \(t_{1/2}\) of a reactant is defined as the time at which its concentration is halfway between its initial and final values. For the PBOCST films \(t_{1/2}\) is the time corresponding to \(f = 1/2\). If \(f\) is plotted against a reduced time \(\theta = t/t_{1/2}\), the interferometer curves all collapse onto one master curve regardless of bake temperature or e-beam exposure dose (see Figure 3). Table 2 lists \(t_{1/2}\) measured for interferometer runs at temperatures from 130 to 155°C and for e-beam exposures of 0 and 20 \(\mu\)C/cm\(^2\). As an approximation, the half-life is inversely related to the reaction rate constant. Plotting \(t_{1/2}\) vs 1000/T (Figure 4) yields straight lines with a slope of \(Ea/R\) where \(Ea\) is an activation energy. Both unexposed and exposed films have activation energies of 31 kcal/mol. The constant offset between the lines indicates that the half-life of the unexposed films is approximately 20% higher than the half-life of the exposed films.

Ito. et al. [11] have shown that the thermolysis of PBOCST is autocatalytic: a small amount of phenol, a weak acid, present in the PBOCST is enough to catalyze the tBOC loss. Phenol groups thus formed by an initially slow thermolysis could catalyze tBOC conversion at a much more rapid pace during the later stages of the film deprotection. The standard model for autoaccelerated reactions is based on two reactions taking place [12]. The first is a very slow residual reaction of the reactant (A) to a product (B). The second is a very fast reaction of A to B catalyzed by the presence of B.

\[
\begin{align*}
A & \rightarrow B & \quad k_1 \text{ small} \\
A + B & \rightarrow 2B & \quad k_2 \gg k_1
\end{align*}
\]

The net result is that the conversion, \(f\), goes from 0 to 1 in terms of a reduced time \(\theta = t/t_{1/2}\) according to

\[
\frac{f}{1-f} = \frac{r}{1-r}(r^{-\theta} - 1)
\]

where \(r = k_1/k_2A_o \ll 1\) and \(A_o\) is the initial concentration of A. In Figure 3 is a plot of Eqn 3 for \(r = 0.001\). The shape is sigmoidal but does not rise as steeply after \(f = 0.5\) as does the PBOCST conversion data plotted with it. The fact that the measured data diverges from the model at high conversion is understandable since the system is a solid undergoing a change in mass rather than an idealized solution. A rough fit of the experimental data from \(f = 0\) to 0.5 using equation 3 yields activation energies of 46 and 26 kcal/mol for rate constants \(k_1\) and \(k_2\) respectively. The relative values of these activation energies is reasonable. The slow initial conversion of A to B is highly temperature dependent while the autocatalyzed reaction is less temperature sensitive.

3.2 Patterning characteristics

Exposure to radiation followed by an appropriate PEB makes exposed portions of the film soluble in base and leaves the unexposed areas insoluble. PBOCST films were line-exposed
at dosages of 4-10 $\mu$C/cm$^2$ and postbaked at 150°C for 36-39 min. Increasing or decreasing the bake time by as little as 3-4 min yielded over- or under-developed line profiles. Dip-development of the patterns for 10-20 sec in MF319 gave good line profiles with minimal lift-off problems. Development using KOH or NaOH solutions produced severe undercutting and lift-off. Figure 5 shows photos of 1 $\mu$m features for each resist MW. The profile photomicrographs show that the resist features are significantly undercut with the PBOCST A but not with higher molecular weights. Figure 6 shows photos of 0.5 $\mu$m line features for B. Very little swelling was observed during development as one might expect when the differential dissolution is controlled by a change in polymer polarity.

### 3.3 Sensitivity and Contrast

Resist performance is reflected by sensitivity and contrast. Determining contrast requires measurement of the thickness of the resist remaining as function of exposure dose. The contrast, $\gamma$, is defined as

$$\gamma = \left[ \log \frac{D_1}{D_0} \right]^{-1}$$

where $D_0$ and $D_1$, the dose at which the dissolution begins and the dose at complete development, are determined by drawing a tangent line through the inflection point of the exposure curve. Gamma curves for the PBOCST resists are shown in Figure 7. Contrast values of 10, 4 and 6 were computed for A, B and C respectively. In addition, the sensitivity (electron dose at which half the film thickness remains) ranged from a low of 4.8 $\mu$C/cm$^2$ for C to 8.3 $\mu$C/cm$^2$ for B.

### 3.4 Lithographic Mechanism

Image formation in PBOCST is controlled by the extent of conversion of the tBOC group to the hydroxy functionality. Two component PBOCST/AG systems operate on the basis of an acid-catalyzed deprotection of tBOC in the exposed areas while unexposed areas remain in the PHOST form. Exposure to radiation produces an acid from the acid-generating component. Low PEB temperatures then yield complete deprotection within a few minutes. In the pure PBOCST system the mechanism for producing the latent image is less apparent. Changes in the film induced by the electron-beam exposure require higher PEB temperatures for long times to produce a developable image. Thermolysis rather than acidolysis of the tBOC groups predominates in the deprotection process. The electron-beam induced change between the exposed and unexposed film is magnified during this thermolysis. Results from the laser interferometer emphasize the non-linear nature of the deprotection reaction in the pure PBOCST system. A slow initial conversion stage is followed by a period of extremely rapid conversion. If even only a small quantity of acidic phenols are generated in the exposed film, those regions may reach and go through the second phase of rapid conversion while the unexposed regions lag behind in the slow conversion phase. Stopping the thermal treatment before unexposed regions can achieve high conversion levels leaves a sufficient percentage of nonpolar tBOC groups to prevent dissolution in alkali. At what extent of tBOC conversion does the polymer film become base soluble? Nalamasu et al. [5] have noted an almost step-function-like dependence of TBSS alkali development on the tBOC concentration. When tBOC content is less than 5% the film becomes alkali
soluble. Laser interferometer results indicate that tBOC conversion of unexposed areas is only from 40 to 80% complete when the 20 μC/cm² areas have achieved 100% conversion.

4 Conclusions

When an acid generator is present in a CAMP resist formulation, the mechanism for producing a lithographic pattern is straightforward. The strong acid generated causes deprotection at a relatively low temperature with an activation energy of about 11 to 14 kcal/mol. We have found that PBOCST alone can function as a CAMP e-beam resist. The e-beam exposure may cause the production of acidic phenolic groups in the film resulting in an autoaccelerated deprotection of exposed regions during the PEB. Thermolysis in both exposed and unexposed resist occurs in the PEB but the difference in extent of conversion is sufficient to generate a pattern that can be developed with aqueous alkali. The energy of activation (31 kcal/mol) is much higher for this autocatalyzed reaction than for the strong acid case.

Acknowledgements

This work was partially supported by the Office of Naval Research. We are grateful for the cooperation of the National Nanofabrication Facility (supported by NSF). Thanks also to M. Sheehan of Hoechst Celanese for monomer and polymer samples.

References


Table 1: Molecular weight (polystyrene equivalent) of PBOCST

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Polydispersity</th>
<th>Manufacturer's $M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4900</td>
<td>10000</td>
<td>2.0</td>
<td>6500</td>
</tr>
<tr>
<td>B</td>
<td>17900</td>
<td>62000</td>
<td>3.5</td>
<td>17500</td>
</tr>
<tr>
<td>C</td>
<td>57800</td>
<td>168000</td>
<td>2.9</td>
<td>56200</td>
</tr>
</tbody>
</table>

Table 2: Half-life PBOCST films at exposures of 0 and 20 $\mu$C/cm$^2$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Half-life for 0 $\mu$C/cm$^2$ (min)</th>
<th>Half-life for 20 $\mu$C/cm$^2$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>109.2</td>
<td>97.6</td>
</tr>
<tr>
<td>135</td>
<td>68.8</td>
<td>58.1</td>
</tr>
<tr>
<td>140</td>
<td>43.0</td>
<td>36.2</td>
</tr>
<tr>
<td>145</td>
<td>26.8</td>
<td>22.8</td>
</tr>
<tr>
<td>150</td>
<td>16.7</td>
<td>14.1</td>
</tr>
<tr>
<td>155</td>
<td>11.8</td>
<td>10.1</td>
</tr>
</tbody>
</table>
Figure 1  Laser interferometer trace for PBOCST film baked at 140°C on hotplate.

Figure 2  Fraction conversion vs bake time for 140°C and 150°C. Solid lines represent interferometer data and filled and open circles represent infrared data.

Figure 3  Fraction conversion vs reduced bake time. Dashed line represents autocatalytic model (Eqn 3).

Figure 4  Half-life vs 1000/T for depretexion of PBOCST film.
Figure 5  1 μm line features in Polymer A. Exposure dose 8 μC/cm².

Figure 6  0.5 μm line features in Polymer B. Exposure dose 29 μC/cm².

Figure 7  Lithographic response of Polymers A, B and C.

- Polymer A
- Polymer B
- Polymer C

PEB 150°C in air oven
Developer Shipley MF319

Normalized film thickness vs. incident E-beam dose (μC/cm²)
Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia  22217-5000

Dr. Richard W. Drisko  (1)
Naval Civil Engineering Laboratory
Code L52
Port Hueneme, CA  93043

Dr. James S. Murday  (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C.  20375-5000

Dr. Harold H. Singerman  (1)
David Taylor Research Center
Code 283
Annapolis, MD  21402-5067

Dr. Robert Green, Director  (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA  93555-6001

Chief of Naval Research  (1)
Special Assistant for Marine Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA  22217-5000

Dr. Eugene C. Fischer  (1)
Code 2840
David Taylor Research Center
Annapolis, MD  21402-5067

Defense Technical Information Center  (2)
Building 5, Cameron Station
Alexandria, VA  22314

Dr. Elek Lindner  (1)
Naval Ocean Systems Center
Code 52
San Diego, CA  92152-5000

Commanding Officer  (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana  47522-5050

* Number of copies to forward