Post-Exposure Bake Temperature Considerations for High Activation Energy Resist Systems

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Polymers based on tertiary-butyl acrylate were synthesized with different compositions and glass transition temperature (T_g) values. These polymers are formulated identically and exposed under identical optical conditions. Lithographically, these polymers responded differently to different post exposure bake temperature (T_{PEB}) conditions. In general, resist contrast, photosensitivity and PED-sensitivity improved at T_{PEB} above polymer-T_g. The resist resolving power improved as T_{PEB} approaches polymer-T_g. However, loss of resolution is observed at T_{PEB} above polymer-T_g. Also, high T_g polymers show greater PEB sensitivity than the corresponding low T_g polymers.

Key words: DUV lithography, chemical amplification, Energy of activation, deprotection reaction, post exposure bake, acid diffusion

1. INTRODUCTION

The current generation of chemically-amplified resists has demonstrated capability of printing sub-130 nm features [1] utilizing both low- and high activation energy (E_a) chemistries for deprotection. Both classes of resist rely upon photogenerated acid to catalyze deprotection. High-E_a resists typically require a high post-exposure bake (PEB) temperature (>100°C) to effect complete deprotection under acceptable processing conditions. Migration (diffusion) of the photogenerated acid also takes place at these temperatures enabling the acid to catalyze deprotection at multiple reaction sites thereby amplifying the effect of a single molecule of acid.

The rate of acid-diffusion through the polymer matrix depends not only on the size of the acid, but also on the bake temperature relative to the polymer glass transition temperature (T_g) [2-5]. Free volume generated during deprotection reaction may further enhance local diffusion of the acid. The diffusivity of acid is an exponential function of the free volume created by the deprotection reaction. [6]. The resist film begins to densify as the PEB temperature approaches polymer-T_g, creating a barrier between acid-rich and acid-depleted zones [7]. This boundary begins to move as temperature continues to increase. Croffe et al. [8] described this phenomenon by a moving boundary transport model of acid diffusion.

While resist sensitivity increases with increasing PEB temperature (T_{PEB}), lithographic process latitudes can be compromised if diffusion is excessive. The acid diffusion coefficient changes drastically at T_{PEB} of 10-20°C above polymer-T_g [4]. Hence, the PEB temperature can significantly impact important lithographic properties such as isolated to dense line (I-D) bias and resolution. The effect of acid diffusion on the final photoresist image has been studied extensively by simulation [6-10]. Mortini et al. [11, 12] studied the effect of diffusion contrast between exposed and unexposed areas for different types of resists. They emphasized the importance of maintaining a high diffusion contrast to minimize I-D bias for high-E_a resists. However, post-exposure baking the resist at 50°C above the polymer T_g was detrimental to resolution and depth-of-focus (DOF).

There is a wide difference in reported values of optimum PEB temperature relative to the polymer T_g. Petersen et al. reported that the optimal PEB temperature for minimum I-D bias in a commercial photoresist was near or slightly below the polymer-T_g [7]. However, Mortini et al. [11] found the minimum I-D bias at PEB=T_g+50°C for a high E_a-
resist. These results imply that the optimum PEB temperature depends on the physical properties of the polymer backbone and chemistry of the blocking group.

In this paper, we report the effect of PEB temperature on lithographic properties of a variety of t-butyl acrylate containing polymers. The \( T_g \) values of these polymers varied between 115 and 160 °C, allowing us to study the lithographic properties over a broad temperature range relative to the typical PEB temperatures (130-140°C) employed for such ESCAP-type resists. Our results indicate that significant improvement in photosensitivity, PEB- and PED-sensitivity can be achieved for PEB temperatures approaching the polymer-\( T_g \). The resolving power of the resist is also improved. However, post-exposure baking at temperatures >\( T_g \) results in the loss of resolution. Hence, optimal lithographic performance for a given set of processing conditions requires tailoring the thermal properties of the polymer.

2 EXPERIMENTAL

2.1. Materials.

Hydroxy styrene and tertiary-butyl acrylate based polymers were either purchased or synthesized in the lab, following typical free radical polymerization procedures.

2.2. Characterization:

Molecular weights of the polymers were determined by GPC against polystyrene standards using a RI detector and a set of 4 Styragel columns. \( M_w \) was computed using the Millenium™ (v2.15) software package from Waters Corporation.

Thermal behavior of the polymers was studied using a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter. A rate of heating of 10°C / minute was used for all the measurements.

Polymer compositions were determined by \( ^{13}C \) and \( ^1H\)-NMR spectroscopy using a Bruker spectrometer Model AC250 operating at 250MHz.

2.3 Lithographic properties:

Photoresist formulations were prepared by blending the acid-sensitive polymers with standardized amounts of a photo acid generator (PAG) and an organic amine in propylene glycol monomethyl ether acetate (PGMEA). Films were deposited on six-inch silicon wafers by spin coating to a soft film thickness of 4900 Å. The films were soft-baked at 140 °C for 60 seconds and exposed to 248 nm wave length using an IS1 XLS 7800/3153 stepper (NA=0.53 ; \( \sigma_i=0.74; \) 4X reduction optics). The films were subjected to a post-exposure bake at the specified temperature for 60 seconds. The images were stream or puddle developed for 60 seconds using an aqueous 0.262 N tetramethyl ammonium hydroxide solution (OPD 262).

Dissolution rate data were generated by static immersion development in 0.26 N TMAH using a Perkin Elmer, multiple channel Development Rate Monitor (DRM). Sixteen separate open frame exposures (zones) ranging from unexposed to 60 mJ/cm² were printed. The 256 channel raw data were reduced to 16 zones using DREAMS PC software. A custom software was used to produce the dissolution rate-exposure dose curves.

3. Results and Discussion

3.1. Choice of Materials:

3.1.1 Synthesis of High-Ea-Polymers:

Polymers containing tertiary-butyl acrylate and hydroxy styrene along with additional monomers were synthesized. These polymers can be represented by the general structure:

\[
\text{I}
\]

Where R can be phenethyl (PE) or isobornyl (iB)

The detailed description of the polymers and their physical characteristics are given in Table 1:
The tertiary-butyl acrylate content of all four polymers was nearly constant at 25-mole%. The glass-transition temperature \( T_g \) of these polymers was varied by choosing appropriate \( R \) functionality and by adjusting the relative proportions between \( a \) and \( c \) in Structure I. The composition of the polymers was determined by \(^1\text{H}-\) and \(^{13}\text{C}-\text{NMR.}\)

### Table 1

<table>
<thead>
<tr>
<th>Polymer ID</th>
<th>R</th>
<th>Mw, (Daltons)</th>
<th>% tBA</th>
<th>( T_g ) (°C)</th>
<th>Absorbance @248 nm (A/g/L THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>iB</td>
<td>13,471</td>
<td>25</td>
<td>157</td>
<td>0.51</td>
</tr>
<tr>
<td>B</td>
<td>iB</td>
<td>14,355</td>
<td>26</td>
<td>144</td>
<td>0.49</td>
</tr>
<tr>
<td>C</td>
<td>iB/PE</td>
<td>12,880</td>
<td>27</td>
<td>124</td>
<td>0.55</td>
</tr>
<tr>
<td>D</td>
<td>PE</td>
<td>13,090</td>
<td>25</td>
<td>115</td>
<td>0.57</td>
</tr>
</tbody>
</table>

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#### 3.1.2 Photoresist Formulations:

The polymers listed in Table 1 were formulated using a triphenyl sulfonium PAG and an organic amine as the acid-quencher. The PAG generated an aromatic sulfonic acid upon photolysis. The amount of PAG and acid-quencher were the same in all formulations.

#### 3.2 Polymer \( T_g \) - Post-Exposure Bake - Dose to Clear Relationship:

The resist property, \( E_0 \) is defined, as the exposure energy required to clear a large area of the resist in a given time. \( E_0 \) is plotted in Figure 1 as \( \log E_0 \) against \( AT = (T_{\text{PEB}} - T_g) \) for the resist systems based on Polymers A through D. The plot shows that in all cases, \( E_0 \) decreases with increasing PEB temperature up to a temperature approximately 20°C above the polymer-\( T_g \) but thereafter shows essentially no further decrease.

These polymers each contain about 25 mole-percent of t-butyl acrylate. They have similar absorbance values at 248-nm wavelength and are formulated identically. Given their structural similarity, the activation energy for deprotection of t-butyl acrylate (ca. 12 Kcal/mole) should not be very different for each polymer. Hence the extent of deprotection of t-butyl acrylate for Polymers A through D might be expected to be the same at a given exposure dose and PEB temperature, i.e., assuming the deprotection reaction is kinetically controlled. Further, since the development rate (DR) of a resist is proportional to the concentration of carboxylic acid, we would also expect comparable dissolution rates under the same conditions. Stated another way, we would expect each resist to exhibit the same \( E_0 \). However, the results in Figure 1 show that \( E_0 \) values are comparable, not at the same PEB temperature, but at the same normalized value of \((T_{\text{PEB}} - T_g)\). Polymer D, for example, with \( T_g \) of 115°C deblocks very rapidly (low \( E_0 \)) when baked at 115°C (\( \Delta T = 0 \)) whereas Polymer A exhibits a very high \( E_0 \) value at this temperature (\( \Delta T = 47°C \)).

These results indicate that both diffusion and kinetic considerations must be taken into account. At low PEB temperatures relative to the polymer \( T_g \) \((T_{\text{PEB}} < < T_g)\), the reaction is diffusion controlled. Very high doses are required to effect deprotection. This region is labeled I in Figure 1. As \( T_{\text{PEB}} \) approaches \( T_g \), a point is reached (at \( \Delta T = -30°C \)) where the molecular mobility of the matrix begins to facilitate acid diffusion enabling more efficient deprotection. In this region (Region II in Figure 1), \( E_0 \) decreases with increasing temperature reflecting the transition from diffusion to kinetic control. At temperatures \( \approx 20°C \) above \( T_g \), there is no further decrease in \( E_0 \) which is comparable for all 4 resist formulations suggesting complete kinetic control of deprotection (Region III).

In addition to temperature, free volume is another important factor that can alter the rate of acid diffusion and hence the rate of deprotection reaction [6]. Poor annealing and residual trapped solvent contribute to free volume when a resist film is pre-baked at temperatures below its polymer \( T_g \).
All resist films of this study were soft-baked for 60 seconds at 140°C. Hence, the residual free volume in resists formulated from polymers C and D ($T_g << 140°C$) is probably lower than that for resists formulated from polymers A and B. Such differences may explain the variations in $E_0$ for a given value of $\Delta T$ in the diffusion-controlled region. In the following sections we will show how this relationship between PEB and rate of deprotection reaction can potentially affect a number of lithographic properties.

3.3. Effect of PEB Temperature on Dissolution Rate ($R_{max}$) and Dissolution Rate Contrast ($\tan \phi$)

For the purpose of this discussion we will define $R_{max}$ as the maximum development rate achievable at 80mJ/cm$^2$ (the highest exposure dose used in this study) at a given PEB temperature. $\tan \phi$ is a measure of the DR contrast between exposed and unexposed areas of resist and is given by the slope of a plot of log DR versus log-exposure energy.

The development rates of resists formulated from polymers A through D increased as the $T_{PEB}$ was increased from 120 °C to 150°C (see Figure 2). Although polymers A through D contain identical amounts of t-butyl acrylate, they show marked differences in their $R_{max}$ values. It is apparent that the high-$T_g$ polymers (A and B) undergo only partial deblocking even at $T_{PEB}$ of 150°C compared to the polymers C and D, although again, comparable dissolution rates for the latter are seen at comparable values of $\Delta T$. The results suggest that in the transition region (Region II in Figure 1), the decline in $E_0$ does correlate with an increased level of deblocking as evidenced in the increasing value of $R_{max}$. The significant increase in DR for resists formulated from polymers C and D which occurs at temperatures above 120-130°C presumably reflects the more efficient degree of deblocking that can be attained in the kinetic controlled region (Region III).

The dependence of DR on exposure dose as a function of PEB temperature is seen in Figure 3. Both DR and $\tan \phi$ increase with increasing PEB temperature becoming a maximum for $T_{PEB} >> T_g$ where the reaction is kinetically controlled. At lower temperatures where diffusion considerations impact the overall rate of polymer deprotection, contrast is lowered.
Resist contrast plays a key role in determining several important lithographic properties such as ultimate resolution, shape of profile and linewidth control. Hence, understanding the tan δ-PEB relationship with respect to polymer-Tg is fundamental to the design of CA-resists.

3.4. PEB Temperature and Resolution:

In Figure 5 we compare the resolution of resists A through D as a function of PEB temperature. The resolving power of an individual resist was determined by measuring the smallest nested feature that could be printed in a 0.49-µm thick film at the exposure energy required to size 0.15-µm nested lines.

An improvement in resolution is observed for all the polymer systems as TPEB approaches Tg. The key here is to optimize the degree of diffusion so as to permit clearing of the resist features within the appropriate development time. Too low a degree of diffusion and the features won’t clear thereby limiting the resolution of a given polymer system. Too high a degree of diffusion can also limit resolution by eroding neighboring lines as was observed for the resists formulated from polymer D. The results in Figure 5 suggest that optimum resolution occurs near Tg within Region II (Figure 1) where the deprotection rate is still diffusion and kinetically controlled. The loss of resolution in the resist formulated from polymer D occurs above AT=10°C corresponds to the transition to full kinetic control which is clearly detrimental to lithographic resolution. Significant line erosion was also observed for Polymer C at TPEB > polymer-Tg.

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3.5. Effect of PEB on Post Exposure Delay (PED) Sensitivity:

PED sensitivity was determined by measuring the change in CD (ΔCD) for 0.21-µm nested line between zero-time (no delay between exposure and PEB) and 20 minutes delay. The results of ΔCD are plotted against PEB temperature for polymer systems B, C and D (see Figure 6).

Polymers B and C show large PED sensitivities at TPEB < Tg. TPEB for Polymer D, on the other hand, was always above its Tg of 115°C. Hence, it does not show any significant PED sensitivity in the range of TPEB studied here.

PED sensitivity is known to be caused by the quenching of the photogenerated acid by adventitious amines or bases, resulting in slower deprotection reaction. Given the time delay between exposure and PEB, the free volume in the resist film can allow limited diffusion of acid and base causing quenching of the acid by acid-base reaction. The reduction in acid concentration results in reduced rate of deprotection reaction. The slower deprotection reaction is further exacerbated by the lack of sufficient acid diffusion in the exposed areas of the glassy resist matrix (TPEB < Tg). The issue of PED sensitivity at TPEB > Tg is mitigated as the loss of acid due to base-neutralization is compensated by acid diffusing from acid-rich zones to acid-depleted zones. The increased rate of deprotection reaction at higher temperatures will have the same effect on the PED stability.
3.6. Polymer-\(T_g\) and PEB Sensitivity:

PEB sensitivity of polymers A through D was studied by measuring CD for 0.15-µm nested line over a temperature range of 130 to 140 °C. The slope of the plot gave \(\Delta CD (\text{nm})/\circ\text{C}\).

These results indicate that PEB sensitivity increases with the increase in polymer-\(T_g\).

The differences in PEB-sensitivity for these polymer systems can also be rationalized on the basis of acid-diffusion relative to polymer-\(T_g\) as explained in Section 3.2.

4. Conclusions:

High \(E_a\)-polymers containing about 25 mole-percent of tertiary-butyl acrylate were synthesized with \(T_g\) values ranging between 115-157 °C. The rate of deprotection was found to be significantly different at different PEB temperatures relative to polymer-\(T_g\). The relationship between PEB and rate of deprotection was found to have a profound effect on several important resist properties. Resist contrast, photosensitivity and PED-sensitivity improved at PEB temperatures above polymer-\(T_g\). The resolving power of the resist improved as \(T_{PEB}\) approached polymer-\(T_g\). Due to high film erosion, loss of resolution was observed at PEB temperature higher than polymer-\(T_g\). Also, high \(T_g\)-polymers showed greater PEB sensitivity than the corresponding low \(T_g\) polymers.

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References: