SENSITIVITY ENHANCEMENT OF t-BOC BASED CHEMICALLY AMPLIFIED RESISTS THROUGH OPTIMIZATION OF PROCESS PREBAKE CONDITIONS

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Partial deprotection of copolymers of 4-t-butoxycarbonyloxystyrene (TBS) and sulfur dioxide (SO2) during the process prebake step is used to improve the x-ray lithographic performance of this resist. For a 2.6:1 TBS:SO2 single component chemically amplified resist, removal of >50 but <90% of tert-butoxycarbonyl protecting group during prebake improves the x-ray (14 Å) sensitivity from a value of 50 to 15 mJ/cm². Partial deprotection during prebake is shown to minimize the film loss observed after the postexposure baking step. At 50% deprotection, the percent film loss in the exposed resist film areas is reduced from 33 to 12%. Greater percentages of resist deprotection are possible but at a consequence of reduced process control.

1. Introduction

Resist materials which derive their sensitivity through amplification of the initial photo event are viewed to meet the requirements for use with advanced deep-UV and x-ray lithographic processes. Numerous reports [1-4] have highlighted the use of chemically amplified resists in the manufacture of sub-0.5 µm devices. These resists, however, present processing issues relating to weight loss after postexposure bake and sensitivity towards basic air borne contaminants which did not have to be addressed when using standard novolac-diazonaphthoquinone resist based materials [5]. Recent studies investigating the performance of single component chemically amplified resists based on 4-t-butoxycarbonyloxystyrene (TBS) and sulfur dioxide (SO2) have provided a
means of minimizing the above deleterious processing issues while simultaneously improving the resist exposure response [6,7]. This paper will describe a process in which the prebake step is given a new function. Conditions for this step are set so that partial removal of the t-butoxycarbonyl group (t-BOC) of the resist occurs. The affects of partial deprotection on resist x-ray sensitivity, and film loss will be discussed. Considerations such as maintaining differential solubility in the exposed vs nonexposed regions as a function of prebake and postexposure bake (PEB) conditions will be presented.

Experimental

Poly (4-t-butoxycarbonyloxystyrene-co-sulfur dioxide) (PTBSS) was prepared and characterized as described in the literature [8]. The percentage weight loss of PTBSS as a function of a set temperature in N₂ was determined using a Perkin-Elmer TGS-7 thermogravimetric analyzer. The temperature scan rate for the TGA experiments was 10⁰C/min and the N₂ (99.99% purity) flow rate was 20 cm³/min.

The percentage of t-BOC group removal in PTBSS as a function of prebake, x-ray exposure and PEB conditions was determined by recording FT-IR spectra of processed PTBSS films spun onto silicon wafers. FT-IR spectra were obtained using a Mattson Instruments Inc. Galaxy Series Model 8020 Spectrometer in the single-beam mode.

X-ray lithographic response of PTBSS was obtained by spinning 0.5 to 1.0 µm thick films onto 5" silicon substrates which were then vacuum hot-plate baked for 2 min at temperatures ranging from 105-160⁰C. X-ray (λ = 8-22 Å centered @14 Å) exposures in helium were performed using a Hampshire Instruments Series 5000 point source proximity print stepper. The laser pulse rate was set at 1.0 Hz and the flux was measured to be 0.8-1.2 mJ/cm²/pulse. Resist films were immediately PEB on a vacuum hot plate at temperatures ranging from 120-140⁰C for 2.5 to 4.0 min. Film thickness loss resulting from pre and postexposure baking, and x-ray exposure was measured using a profilometer.

The exposed and baked films were immersion developed in a 0.17 N tetramethylammonium hydroxide (TMAH) solution for 30-60 seconds and rinsed for 45-60 seconds in de-ionized water. The minimum dose (Dₚ) necessary to completely develop
a large x-ray exposed area of the film was used as the reported PTBSS sensitivity.

Results and Discussion

Previous reports have shown that PTBSS functions as a single component aqueous base soluble chemically amplified x-ray ($\lambda = 14 \text{ Å}$) resist [6]. PTBSS x-ray sensitivity increased with increasing SO$_2$ content in the resist and was independent of molecular weight. Using standard pre and postexposure vacuum hot-plate baking conditions of 105°C for 2.0 min and 140°C for 2.5 min, respectively, x-ray sensitivities in range of 30-50 mJ/cm$^2$ was achieved for materials having a TBS:SO$_2$ compositional range of 2.0-3.0:1.0. FT-IR spectra of the nonexposed regions of films processed using the baking conditions listed above indicated that no removal of the t-BOC protecting group occurred. The FT-IR spectra of the nonexposed areas and x-ray exposed film regions of a resist having approximately a 2.5:1 TBS:SO$_2$ composition is shown in Figure 1.

![Figure 1. FT-IR spectra of nonexposed and x-ray exposed followed by PEB (140°C for 2.5 min) regions of a 0.5 µm thick PTBSS film](image)

From Figure 1, the extent of PTBSS deprotection is calculated by integration of the
peak area of the carbonyl absorption band (1676-1876 cm\(^{-1}\)) of the exposed and baked film regions, and normalizing it to that region of the absorption spectrum corresponding to the nonexposed portions of the film. A decrease in carbonyl absorption with increasing dose is accompanied by an increase in the band at \(-3500\) cm\(^{-1}\) which corresponds to the formation of poly(4-hydroxystyrene co-sulfur dioxide) PHSS.

Table 1 lists the percentage of t-BOC groups removed as a function of x-ray dose, and indicates whether those exposed regions dissolved in the 0.17 N TMAH developer.

TABLE 1. X-ray exposure results and aqueous base dissolution characteristics of a ~2.5:1 TBS:SO\(_2\) resist

<table>
<thead>
<tr>
<th>X-ray Exposure Dose (mJ/cm(^2))</th>
<th>% t-BOC Groups Removed</th>
<th>Dissolution* (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>26.5</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>80.8</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>96.5</td>
<td>+</td>
</tr>
</tbody>
</table>

* + = aqueous base soluble

Correlation of aqueous base dissolution to the extent of PTBSS deprotection indicates that for dissolution to occur, approximately 90% of t-BOC groups must be removed. These results suggest that partial deprotection (<90%) of PTBSS prior to exposure and no further deprotection in the nonexposed film regions after PEB will decrease the overall weight loss in the exposed regions of the film. Weight loss as recorded by the percent film thickness difference between the exposed and nonexposed regions of the film after PEB contributes to a reduction in pattern quality and image resolution when using a fully protected PTBSS resist [9]. A reduction in the amount of t-BOC groups removed after exposure and PEB should also lead to a reduction in the dose required to achieve aqueous base solubility in the exposed regions of the film.

Partial deprotection of PTBSS can be achieved without the need of introducing an additional synthetic or processing step in the overall PTBSS imaging scheme. This is realized by defining a new function for the process prebake step. During prebake PTBSS t-BOC group removal is made possible by adjusting the bake temperature. Determination of the allowed temperature range is simplified in that only the thermal properties of PTBSS need be addressed since we are dealing with a single component
chemically amplified resist. The extent of PTBSS deprotection as a function of temperature for a material having a 2.6:1 TBS:SO2 ratio is summarized in Figure 2. This figure depicts isothermal TGA traces over a prebake temperature range of 140 to 155°C.

![Figure 2. Isothermal TGA traces for a 2.6:1 TBS:SO2 resist](image)

For a period extending to 10 min, little weight loss is observed at 140 to 145°C. Above 145°C, appreciable weight loss corresponding to PTBSS deprotection is seen. The affect of varying the prebake temperature on $D_\alpha$, and the % film thickness difference (FTD) in the exposed vs nonexposed regions is summarized in Table II. The prebake time was 2.0 min, and a PEB of 140°C for 2.5 min was used for each prebake (PB) condition investigated.

**TABLE 2. Affect of varying PB temperature on PTBSS lithographic performance**

<table>
<thead>
<tr>
<th>PB Temp. °C</th>
<th>% t-BOC Groups removed</th>
<th>$D_\alpha$ (mJ/cm²)</th>
<th>% FTD After PEB</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>0</td>
<td>50</td>
<td>33</td>
</tr>
<tr>
<td>150</td>
<td>12.1</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>155</td>
<td>17.4</td>
<td>25</td>
<td>21</td>
</tr>
<tr>
<td>160</td>
<td>48.6</td>
<td>15</td>
<td>12</td>
</tr>
</tbody>
</table>
The standard PB condition of 105°C yields the nonexposed film regions remaining fully protected. Complete conversion of PTBSS to PHSS after PEB, in this case, results in a 33% film thickness difference between the exposed and nonexposed film regions. Increasing the PB temperature to ≥160°C leads to effectively removing ~50% of the t-BOC groups, and is well below what is needed for the film to be rendered aqueous base soluble.

The affect of partial deprotection is seen to improve the x-ray sensitivity from 50 to 15 mJ/cm² and reduces the total film thickness difference to ~12% when a PB of 160°C is used. Further improvements in sensitivity can be achieved at higher PB temperatures but at the expense of process control. Therefore, a compromise must be made between enhancing the resist lithographic performance and controlling the processing variables leading to the enhancement.

Conclusions

The x-ray (λ = 14 Å) lithographic performance of PTBSS has been shown to improve by optimizing the process prebake conditions. Partial deprotection of the resist during prebaking improves the sensitivity threefold, and reduces the percentage of film loss in the exposed film areas by ~21%. Partial deprotection during prebake is constrained only by the facts that the prebake temperature chosen is not appreciably above the onset temperature for decomposition (deprotection) for PTBSS at a given TBS:SO₂ composition, and the nonexposed regions of the film remain <90% deprotected after completion of the postexposure baking step. The single component nature of the chemically amplified PTBSS resist greatly simplifies the variables which must be addressed for differential solubility of exposed vs nonexposed regions of the film to be maintained. Partial deprotection during prebake additionally removes the need of introducing another step in either the preparation of a partially deprotected resist or during the processing of the resist.

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References


