Phenolic Based Molecular Glass Resists for Next Generation Lithography

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Principal Investigator: Prof. Christopher K. Ober
Users: Anuja De Silva, Nelson M. Felix

Affiliation: 1. Department of Materials Science & Engineering, 2. Department of Chemistry and Chemical Biology, 3. Department of Chemical and Biomolecular Engineering; Cornell University
Primary Funding: Semiconductor Research Cooperation (SRC)
Contact: cober@ccmr.cornell.edu, ead35@cornell.edu, nmf3@cornell.edu

Abstract
The idea of using small molecules instead of polymers for next generation lithography has enabled improved resolution and line edge roughness (LER). Rather than using polymeric materials, we are focusing on a new class of materials known as molecular glasses. These are low molecular weight organic materials that demonstrate high glass transition temperatures despite their modest size. Unlike polymeric resists, these molecules have the added advantages of distinct size and uniformity. We have synthesized a series of molecular resists containing rigid aromatic backbones and phenolic moieties. An increase in glass transition temperature is observed with increasing size and rigidity. Glass transition temperatures (Tgs) between 80-130°C have been observed for resists with molecular weights within the range of 500-900g/mol. These phenolic based resists also show the high sensitivity and sub-50 nm contrast required of candidates for next generation lithography.

Introduction
As the semiconductor industry moves to the 32 nm node and below, obtaining smaller feature sizes with reduced fluctuations on the resist pattern known as line edge roughness (LER) is a main focus [1]. As extreme ultra violet (EUV) lithography gains credibility as the next generation lithographic technology LER, sensitivity and outgassing remain crucial factors. The patterning target for the 32 nm node in 2009 is reported to be LER < 2 nm and sensitivity 2-5 mJ/cm². Hence, novel resist architecture and design strategies need to be introduced to successfully meet these requirements.

A recent advance in resist design has been the introduction a new type of molecular glass (MG) photoresist [2]. These materials combine the beneficial aspects of small molecules along with the favorable aspects of polymers. Like most organic molecules, molecular glasses have a well defined structure and purity. But unlike most small molecules they have a low tendency towards crystallization. These molecules are trapped in a kinetically stable amorphous state. Like polymers, they too demonstrate glass transitions (Tgs) significantly above room temperature.

This report sheds light on the challenges of designing a molecular glass photoresist for EUV lithography. When choosing a robust glass forming core, the molecular architecture is a very important parameter. This defines molecular flexibility as well as the packing ability of various molecular systems. Branched and star shaped molecules are well known glass forming molecules due to their topology. This paper introduces a new family of phenolic based bulky molecular systems with branched architecture. The phenolic component provides rigidity, etch resistance and base solubility due to the presence of the hydroxyl groups that can be modified with a solubility switching functionality.

Experimental Section
The synthesis of polyphenols was performed by the condensation of phenol with a ketone or aldehyde in the presence of hydrochloric and ascetic acid [3]. By varying the aromatic core, several compounds were synthesized with increasing mass and phenolic content. The compounds were obtained in relatively moderate yields after column chromatography. These compounds were protected with tert-butoxy carbonyl (t-BOC) to varying degrees (50%-100%) by a standard base catalyzed reaction in the presence of 4-dimethyl amino pyridine (DMAP).

Results and Discussion
Our initial efforts on patterning of MGs were based on commercially available phenolic compounds such as alpha, alpha’,alpha’-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene (CR 1) [4]. Patterns of 70 nm lines were obtained with EUV lithography. When compared with the calix[4]resorcinarene resists that have produced 30 nm resolution, the sub 100°C glass transition was identified as a limiting factor for these phenolic resist to attain sub 50 nm features [5]. Hence the structures (CR2-6) are based on a systematic increase of size and phenolic content around a planar benzene core.
Chemistry

Figure 1: The phenolic MG resist structures.

![Image of phenolic MG resist structures]

Table 1: Thermal properties of t-BOC protected phenolic MGs.

<table>
<thead>
<tr>
<th>MG Compound</th>
<th>% of t-BOC Protection</th>
<th>Phenolic Function</th>
<th>Mw (g/mol)</th>
<th>Tg (°C)</th>
<th>C/O Ratio</th>
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<tbody>
<tr>
<td>CR1-66</td>
<td>66</td>
<td>2</td>
<td>624.8</td>
<td>65</td>
<td>4.18</td>
</tr>
<tr>
<td>CR2-50</td>
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<td>2</td>
<td>702.9</td>
<td>No Tg</td>
<td>4.13</td>
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<tr>
<td>CR3-50</td>
<td>50</td>
<td>2</td>
<td>702.9</td>
<td>80</td>
<td>4.13</td>
</tr>
<tr>
<td>CR4-50</td>
<td>50</td>
<td>2</td>
<td>778.9</td>
<td>83</td>
<td>4.69</td>
</tr>
<tr>
<td>CR8-50</td>
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<td>2</td>
<td>792.9</td>
<td>81</td>
<td>4.79</td>
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<tr>
<td>CR6-50</td>
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<td>1015.2</td>
<td>94</td>
<td>3.94</td>
</tr>
<tr>
<td>CR1-100</td>
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<td>724.9</td>
<td>53</td>
<td>3.67</td>
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<tr>
<td>CR2-100</td>
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<td>0</td>
<td>903.1</td>
<td>No Tg</td>
<td>3.38</td>
</tr>
<tr>
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<td>100</td>
<td>0</td>
<td>903.1</td>
<td>74</td>
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<td>979.2</td>
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<td>993.2</td>
<td>73</td>
<td>3.82</td>
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<tr>
<td>CR6-100</td>
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<td>0</td>
<td>1315.5</td>
<td>83</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Lithographic Evaluation

Phenolic MG resists were evaluated through EUV exposure at Albany Sematech RTC and Lawrence Berkeley National Laboratory (LBNL). The contrast curve was obtained for CR 6-50.

The EUV microexposure tool at LBNL is capable of fabricating fine features below 30 nm. For the compounds tested, the films were baked (PEB) at 75, 80, 85 and 90°C for 30s. The best result was obtained using a post-exposure bake of 80°C, developed in 0.26N TMAH solution. Although the PEB temperature was around the Tg of this resist material for CR3-50 sub 50 nm resolution was achieved. The LER was calculated using SuMMIT image analysis software.

References


Figure 2: Contrast curve of CR6-50 obtained at Albany Sematech RTC. PEB = 80°C, 30s, Developed in 0.26N TMAH. Sensitivity = ~ 10 mJcm².

![Image of contrast curve with sensitivity data]

Figure 3: SEM images of EUV exposed resist CR2-50, dose 18.5 mJcm², LER (3σ) 7.3 nm.