Abstract:

Glass stars consisting of a molecular glass core and multiple short polymer arms were synthesized. The etch resistance of the samples were measured and demonstrated to be dependent on the architectural parameters \( f \) and \( n \).

Summary of Research:

In the search for next generation photoresists, there are many critical performance benchmarks that must be met, including sufficiently slow etch rates to achieve efficient pattern transfer from the resist to the substrate. Linear polymers have been the traditional material utilized as photoresists. However, there has been recent interest in using a molecular glass architecture as the basis for photoresist design [1]. In order to better understand the role of these two architectures on etch resistance, we investigated a novel glass star architecture that combines features of both.

The glass star consists of three or more polymer arms initiated from a molecular glass core. Similar to star polymers, the glass star can be parameterized as having \( f \) arms, each containing a chain of \( n \) mers in length. Unlike star polymers \( n \) and \( f \) are restricted such that the overall size of the molecule is no larger than that of a standard linear polymer photoresist. In this regime, as \( f \) decreases and \( n \) increases, the architecture of the glass star begins to resemble that of a linear photoresist. Oppositely, as one increases \( f \) and decreases \( n \), the glass star begins to take on the architecture of a molecular glass photoresist. Therefore, one can examine the etch resistance of glass stars while varying \( n \) and \( f \) in order to better understand the role of architecture on etch resistance.

Three glass star samples were synthesized using a sucrose core such that \( f = 8 \) in the case of 100% initiator efficiency. The polymerization time was varied for each sample according to a kinetics study such that the samples consisted of \( n = \{5,10,20\} \) arm lengths of tert-butyl methacrylate (tBMA) mers. An additional two samples were synthesized, using the conditions for \( n = 10 \), but utilizing different initiator cores. A cholic acid derivative was utilized to achieve a glass star of \( f = 3 \) while a glucose derivative was utilized to achieve a glass star of \( f = 5 \), again assuming 100% initiator efficiency.

In this manner two sets of samples, one with a constant \( f = 8 \) but \( n = \{5,10,20\} \) and another with a constant \( n = 10 \) but \( f = \{3,5,8\} \), were obtained. A sixth sample, \( \{f = 3, n = 20\} \), was synthesized, which did not fall within either the constant \( f \) nor the constant \( n \) sample sets, to test the veracity any observed trends.

An Oxford PlasmaLab 80+ RIE was utilized to study the etch resistance of each sample with a standard CF\(_4\) nitride etch. Films of each sample were obtained through spin coating on silicon and measuring the film thickness with a Tencor P10 Profilometer before and after etching to determine the etch rate relative to a polyhydroxystyrene (PHOST) standard. The etch rate

<table>
<thead>
<tr>
<th>Sample</th>
<th>( f=8 ) n=5</th>
<th>( f=8 ) n=10</th>
<th>( f=8 ) n=20</th>
<th>( f=5 ) n=10</th>
<th>( f=5 ) n=10</th>
<th>( f=3 ) initiator</th>
<th>( f=5 ) initiator</th>
<th>( f=8 ) initiator</th>
<th>( f=3 ) n=20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etch Rate</td>
<td>2.56</td>
<td>2.49</td>
<td>2.47</td>
<td>2.31</td>
<td>1.77</td>
<td>1.46</td>
<td>3.72</td>
<td>2.36</td>
<td>2.25</td>
</tr>
</tbody>
</table>
of the initiator cores were similarly measured against a PHOST standard and the films were then examined by x-ray diffraction to confirm that the initiator core films were amorphous. The etch rates relative to PHOST are reported in Table 1.

Current etch rate models such as the Ohnishi Parameter [2] and Ring Parameter [3] are based on composition, not architecture. If etch rate were entirely compositional one would expect Eq. 1 to hold true, where $V$ is the etch resistance, $MW$ is the molecular weight and the subscripts $gs$, $mg$ and $tBMA$ refer to the glass star, molecular glass and tBMA arms respectively. Using the measured etch rates for each sample and core $V_{tBMA}$ was found to be \{2.0, 2.5, 2.7, 3.1, 3.3, 4.1\} and not a constant. Therefore, there is an important architectural component to etch rate, which was not observed by models that considered only a linear architecture.

Equation 1:

$$V_{gs} = \frac{V_{mg} * MW_{mg}}{MW_{gs}} + \frac{V_{tBMA} * MW_{tBMA}}{MW_{gs}}$$

Eq. 3 was tested using the sixth sample \{f = 3, n = 20\} yielding $V_{arms}(f = 3, n = 20) = 2.16$ and $V_{gs,calc}(f = 3, n = 20) = 2.30$. This is just over 2% from the measured value of $V_{gs}(f = 3, n = 20) = 2.25$. Therefore, one can accurately predict the etch rate for tBMA glass stars from the etch rate of the initiator core and the architectural parameters $f$ and $n$ within the range of $f = \{3-8\}$ and $n = \{5-20\}$. Additional data points should refine the equation and assist in expanding it beyond its current range.

Equation 2:

$$V_{gs} = \frac{V_{mg} * MW_{mg}}{MW_{gs}} + V_{arms}(f, n)$$

One can modify Eq. 1, replacing the compositional term for tBMA with $V_{arms}(f,n)$ as shown in Eq. 2. The data points for $V_{arms}(f,n = 10)$ show a linear relation to $f$ and the data points for $V_{arms}(f = 8,n)$ show a linear relation to $n$. One can fit both sets of data to the combined Eq. 3.

Equation 3:

$$V_{gs}(f,n) = 0.25f + 0.10n - 0.01fn + 0.01$$

References:

