Development Of Non-chemically Amplified Photoresists for Extreme Ultraviolet (EUV) Lithography

Kirsten Lawrie,1 Idriss Blakey,1,2 James Blinco,1 Roel Gronheid,3 Kevin Jack,4 Ivan Pollentier,3 Michael J. Leeson,5 Todd R. Younkin5 and Andrew K. Whittaker,1,2*

1Australian Institute for Bioengineering and Nanotechnology,
2Centre for Magnetic Resonance,
3IMEC, Leuven, Belgium
4Center for Microscopy and Microanalysis, University of Queensland, St Lucia, Queensland, 4072, Australia.
5Intel Corporation, Hillsboro, Oregon, USA.

INTRODUCTION

Current photoresist technologies rely heavily on the use of photoacid generators (PAG) to chemically amplify the response of the resist formulation to the incident radiation. However, the diffusive path length of the photons (and counter-ion) generated by the PAG is significant compared with the target dimensions of EUV lithography. Additionally, the problem of low sensitivity, and hence increased production costs, is encountered when alternatives to photo-acid generation are used to produce chemical changes. Thus, the objective of this investigation is to develop new polymeric non-chemically amplified materials having higher sensitivity, for use as photoresists in EUV lithography.

Poly(olefin sulfones) Poly(olefin sulfones)
- Polymers formed by the reaction of sulfur dioxide (SO\textsubscript{2}) and olefins which are highly sensitive to degradation by EUV radiation\textsuperscript{1}
- Exhibit low ceiling temperatures (T\textsubscript{c}) and have propensity to ‘unzip’ to parent monomers following scission of C-S backbone bonds
- Main-chain scission unzipping mechanism removes the need for chemical amplification
- Possible to terpolymers terpolymers third macromonomer to tailor desired attributes to resist material e.g. adhesion promotion, etch resistance, high T\textsubscript{c}

SYNTHETIC METHODOLOGIES AND RESULTS

Table 1 – Results of poly(1-pentene-co-PMMA sulfone) synthesis (4)

<table>
<thead>
<tr>
<th>PMMA macromonomer M\textsubscript{m} (Da)</th>
<th>No. % PMMA in product\textsuperscript{a}</th>
<th>Wt. % PMMA in product</th>
<th>M\textsubscript{n} (Da)</th>
<th>PDI</th>
<th>T\textsubscript{c} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.7k (1)</td>
<td>0.16</td>
<td>1.0</td>
<td>83k</td>
<td>2.2</td>
<td>84.5</td>
</tr>
<tr>
<td>2.7k (1)</td>
<td>0.43</td>
<td>7.0</td>
<td>90k</td>
<td>2.1</td>
<td>84.5</td>
</tr>
<tr>
<td>2.7k (1)</td>
<td>0.87</td>
<td>23</td>
<td>130k</td>
<td>1.7</td>
<td>84</td>
</tr>
<tr>
<td>4.8k (2)</td>
<td>1.0</td>
<td>42</td>
<td>47k</td>
<td>3.4</td>
<td>85</td>
</tr>
<tr>
<td>7.6k (3)</td>
<td>0.60</td>
<td>29</td>
<td>39k</td>
<td>2.6</td>
<td>84</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Obtained using triple detection on a DMAC GPC system. *Found using 'H NMR.

EUV Outgassing - Witness Plate Contamination

- High levels of outgassing
- Witness plate contamination found to be low compared to some CAR materials and independent of outgassing rate

Table 2 – Outgassing and contamination properties

<table>
<thead>
<tr>
<th>Resist</th>
<th>Outgassing Rate (mol cm\textsuperscript{-2} s\textsuperscript{-1})</th>
<th>Total Outgassing (mol cm\textsuperscript{-2})</th>
<th>Witness Plate Contamination (a.u.)\textsuperscript{**}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(1-pentene sulfone)</td>
<td>4.67x10\textsuperscript{-10}</td>
<td>1.94x10\textsuperscript{-10}</td>
<td>2.96</td>
</tr>
<tr>
<td>Poly(1-pentene-co-PMMA sulfone)</td>
<td>3.52x10\textsuperscript{-10}</td>
<td>1.52x10\textsuperscript{-10}</td>
<td>not tested</td>
</tr>
<tr>
<td>Poly(1-pentene-co-PMMA sulfone)</td>
<td>3.52x10\textsuperscript{-10}</td>
<td>1.52x10\textsuperscript{-10}</td>
<td>not tested</td>
</tr>
<tr>
<td>Resist B</td>
<td>3.07x10\textsuperscript{-10}</td>
<td>4.68x10\textsuperscript{-10}</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\textsuperscript{**}Dose 80 x E\textsubscript{0}. \textsuperscript{**}Dose 10 x E\textsubscript{0}. Based on thickness (nm) difference measured by ellipsometry between background and resist exposure sites on witness plate, and normalised to exposed resist area. NIST approved material.

Figure 1 - Outgassing species from poly(1-pentene sulfone) and poly(1-pentene-co-PMMA sulfone) containing 23 wt% 2.7k PMMA

EUV Patterning

- Initial patterning studies show 35nm patterning in poly(1-pentene sulfone) possible
- E\textsubscript{lim} = 70mJ/cm\textsuperscript{2} for 50nm hp and 90mJ/cm\textsuperscript{2} for 35nm hp
- Optimisation of patterning parameters expected to lower achievable cd

Figure 2 - Example of thickness measurement by ellipsometry over background (top) and poly(1-pentene sulfone) resist (bottom) contaminated areas of the witness plate.

Figure 3 - Lines patterned into poly(1-pentene sulfone) at 50nm and 35nm half pitches using EUV interference lithography.

CONCLUSIONS

- Synthesis of a range of poly(1-pentene-co-PMMA) terpolymers achieved
- Incorporation of PMMA macromonomer shown to reduce outgassing
- Despite high levels of outgassing, witness plate contamination comparable to some commercial materials
- Patterning of 35 nm hp lines achieved

REFERENCES


ACKNOWLEDGEMENTS

The authors would like to thank Intel Corporation, the Australian Research Council (Project ID LE0775684, LP0667941) and the Smart State Innovation Building Fund for funding. The authors would also like to thank Greg Denbeaux and Alin Antohe for helpful discussions and the Paul Scherrer Institut for EUV interference patterning exposures and KJL would like to thank IMEC, the University of Queensland, the Australian Institute of Bioengineering and Nanotechnology and Intel for funding.