Supplementary Information

Advancing the next generation nanolithography with infiltration synthesis of hybrid nanocomposite resists

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Table S1. E-beam dose (μC/cm²) matrix depicting the dose array exposed for patterning exposure dose matrix

<table>
<thead>
<tr>
<th></th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>350</td>
<td>400</td>
<td>450</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>700</td>
<td>800</td>
<td>900</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>1200</td>
<td>1300</td>
<td>1400</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>1750</td>
<td>2000</td>
<td>2250</td>
<td>2500</td>
<td>2750</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>4000</td>
<td>5000</td>
<td>6000</td>
<td>7000</td>
<td></td>
</tr>
</tbody>
</table>
Table S2. Summary of ICP-RIE conditions used in the study

<table>
<thead>
<tr>
<th>Process</th>
<th>Temp. (°C)</th>
<th>Pressure (mTorr)</th>
<th>RF Power (W)</th>
<th>ICP Power (W)</th>
<th>Gas flow rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ Etch</td>
<td>20</td>
<td>30</td>
<td>200</td>
<td>0</td>
<td>O₂: 50</td>
</tr>
<tr>
<td>SiO₂ Etch</td>
<td>25</td>
<td>15</td>
<td>40</td>
<td>700</td>
<td>O₂: 1.5 CHF₃: 50</td>
</tr>
<tr>
<td>Cryogenic Si Etch (etch rate)</td>
<td>-100</td>
<td>15</td>
<td>15</td>
<td>800</td>
<td>O₂: 12 SF₆: 40</td>
</tr>
<tr>
<td>Cryogenic Si Etch (nanopatterns)</td>
<td>-100</td>
<td>15</td>
<td>15</td>
<td>800</td>
<td>O₂: 16 SF₆: 40</td>
</tr>
</tbody>
</table>
Figure S1. Dark-field optical microscopy images of as developed exposure dose test array of samples subjected to different infiltration cycles showing consistency of dose-to-clear across samples.
Figure S2. AFM height maps of exposure dose matrix patterned as per the dose array illustrated in Table S1. With increasing infiltration cycles, the dose-to-clear can be seen to increase.
Figure S3. As acquired QCM measurement showing temporal change in mass gain per area, ALD chamber temperature, and pressure against the measurement time for 12 infiltration cycles. In the pressure variation plot, the larger pulse corresponds to TMA half cycle, whereas the smaller pulse depicts water half cycle and the dip in pressure signifies chamber purge step.
Section S1. Estimation of elemental composition of infiltrated hybrid resists

The mass gain data (Fig. S3) measured by in-situ QCM experiments can be used to estimate the elemental composition of AlOx-infiltrated PMMA by assuming that the infiltrated precursors form stoichiometric Al2O3, which is homogeneously distributed within the PMMA matrix. Specifically, we can convert the mass gain per area value to the number of Al and O atoms added for the given number of infiltration cycles by using following expressions:

\[
\text{[no. of Al atoms gained/area]} = \frac{\text{[wt. gain/area]} \times 2 \times N_A}{(2 \times \text{[Atomic wt. of Al]} + 3 \times \text{[Atomic wt. of O]})}
\]

\[
\text{[no. of O atoms gained/area]} = \frac{\text{[wt. gain/area]} \times 3}{(2 \times \text{[Atomic wt. of Al]} + 3 \times \text{[Atomic wt. of O]})}
\]

, where \(N_A\) is Avogadro number, atomic wt. of Al is 26.98 g/mol and atomic wt. of O is 15.99 g/mol. Furthermore, the wt. % of Al gained for the given number of infiltration cycles can be estimated as:

\[
\text{[Al wt. gain/area]} = \text{[no. of Al atoms gained/area]} \times \text{[Atomic wt. of Al]}
\]

Meanwhile, using the PMMA density \(\sim 1.18 \text{ g/cm}^3\) and the film thickness \(\sim 60 \text{ nm}\), the wt. of the PMMA thin film can be estimated as,

\[
\text{[PMMA thin film wt./area]} = \text{[Density of PMMA]} \times \text{[Thickness of PMMA thin film]}
\]

, which calculates to \(7.08 \mu\text{g/cm}^2\). Additionally, assuming that the atomic composition in PMMA is the same as that in its monomer methyl methacrylate(MMA or \(\text{C}_5\text{H}_8\text{O}_2\)), the no. of C and O atoms per area can be estimated as,

\[
\text{[no. of C atoms in PMMA film/area]} = \frac{\text{[PMMA thin film wt./area]} \times 5}{\text{[Molecular wt. of MMA]}}
\]

\[
\text{[no. of O atoms in PMMA film/area]} = \frac{\text{[PMMA thin film wt./area]} \times 2}{\text{[Molecular wt. of MMA]}}
\]

, where molecular wt. of MMA is 100.121 g/mol. The total no. of O atoms for the given number of infiltration cycles would then be the sum of no. of O atoms in PMMA and no. of O atoms gained by infiltration of AlOx (Al2O3). Based on these estimations the evolution of no. of atoms of Al and O as well as atomic ratio of Al to C are illustrated in Fig. S4.
Figure S 4 Evolution of estimated no. of Al and O atoms with increasing number of infiltration cycles (left axis) and atomic ratio or Al to C within the synthesized hybrid resist (right axis).