Supporting Document

Experimental Procedure

Materials

ZDOL and Z-03 were purchased from Solvay Solexis Inc. and utilized as received. 2,3-dihydrodecafluoropentane, a good solvent for PFPEs, was purchased from Miller Stephenson Chemical Co. and used as received. The Si \(<100>\) wafers covered with 2nm native oxides (P/B \(<100>\) 1-10 OHM-CM; 279 ± 25μm) were purchased from Silicon Quest International, Inc. and rinsed with 2,3-dihydrodecafluoropentane thoroughly before usage. DI water was produced from a Millipore Academic A10 system in house with total organic carbon below 40 ppb. Hexadecane (anhydrous; 99%) was purchased from Sigma-Aldrich and used as received. The PTFE sheet with a thickness of 0.03” was purchased from eplastics.com and rinsed with 2,3-dihydrodecafluoropentane thoroughly before usage.

Fabrication of nanometer-thick films

All the nanometer-thick films were deposited using a KSV-DCX2 dip-coater, equipped with a Kinetic Systems vibration free platform. ZDOL and Z-03 films were coated on Si wafer by dip-coating with 2,3-dihydrodecafluoropentane as the solvent at a pullout velocity of 1 mm/s. The ZDOL solution with the concentration of 0.5 g/L and 1.5 g/L were utilized to produce the films with different thicknesses on the Si wafer. The Z-03 solution with the concentration of 2.0 g/L was used to
produce the film on the Si wafer. For ZDOL coated PTFE sheet, the solution with the concentration of 1.5 g/L was used.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Solution concentration (g/L)</th>
<th>Ra (nm)</th>
<th>PFPE Total Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-03 1.7 nm</td>
<td>2.0</td>
<td>0.18</td>
<td>1.7</td>
</tr>
<tr>
<td>ZDOL 0.9 nm</td>
<td>0.5</td>
<td>0.19</td>
<td>0.9</td>
</tr>
<tr>
<td>ZDOL 1.8 nm</td>
<td>1.5</td>
<td>0.17</td>
<td>1.8</td>
</tr>
</tbody>
</table>

1.8 nm ZDOL/Si
0.9 nm ZDOL/Si

1.7 nm Z-03/Si

Fig. S1 XPS C1s spectra and curve-fitting results
The XPS experimental procedure was described elsewhere. The XPS C1s spectra of all three PFPE samples are similar and the raw data, along with the curve-fitting results, are shown in Fig. S1. For all three samples, the peaks centered around 295 eV and 294 eV are assigned to -OCF₂O- and –OCF₂CF₂O-, respectively. The smaller peaks centered around 287 eV and 285 eV of all three samples are assigned to the contaminants, which is consistent with previous reports.

Fig. S2 TGA results of hexadecane (room temperature in air)

Fig. S3 KWW Fitting results of cosθ of hexadecane on ZDOL (0.9 nm)/Si (left) and ZDOL (1.8 nm)/Si (right)

\[
\cos \theta(t) = \cos \theta_e + (\cos \theta_0 - \cos \theta_e) \exp \left[-\left(\frac{t}{\tau}\right)^\beta\right]
\]
Here $t$ is the aging time, $\cos \theta_e$ is the equilibrium contact angle, $\cos \theta_0$ is the initial contact angle, $\tau$ is the relaxation time constant indicating how fast the system approaches equilibrium and $\beta$ is the stretch factor characterizing the nonlinearity of the relaxation process.