

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; $279 \pm 25\mu\text{m}$) 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 use 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.

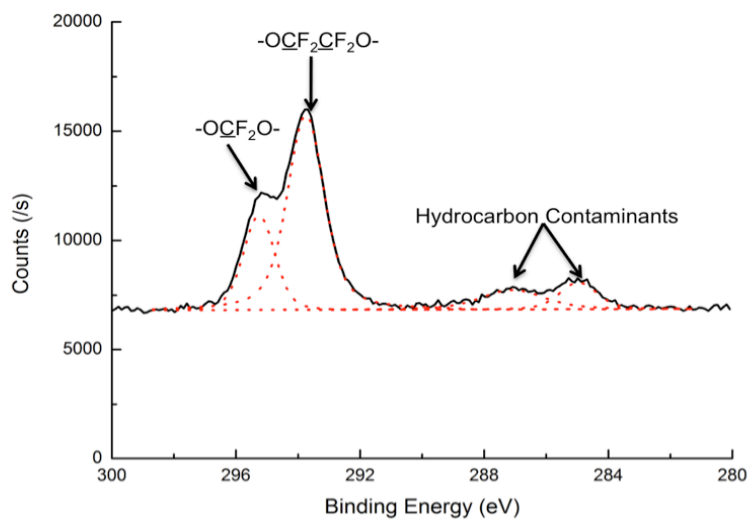
- Fabrication of nanometer-thick films

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

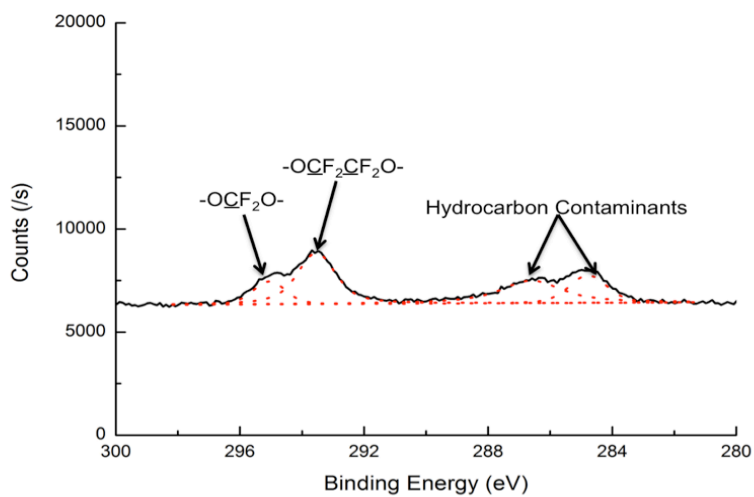
produce the film on the Si wafer. For ZDOL coated PTFE sheet, the solution with the concentration of 1.5 g/L was used.

Table S1 Roughness (Ra) and PFPE thickness on Si Wafers

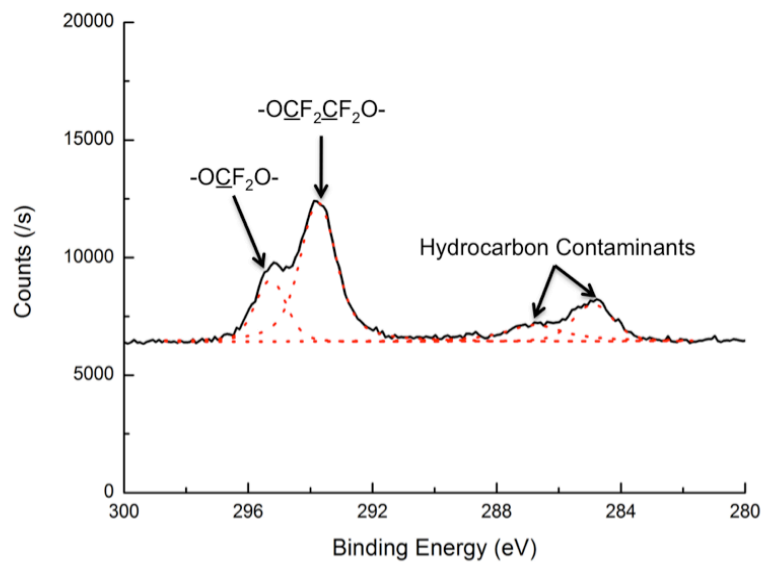
Sample Name	Solution concentration (g/L)	Ra (nm)	PFPE Total Thickness (nm)
Z-03 1.7 nm	2.0	0.18	1.7
ZDOL 0.9 nm	0.5	0.19	0.9
ZDOL 1.8 nm	1.5	0.17	1.8



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.¹⁵ 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 $-\text{OCF}_2\text{O}-$ and $-\text{OCF}_2\text{CF}_2\text{O}-$, respectively.¹⁶ 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.¹⁶

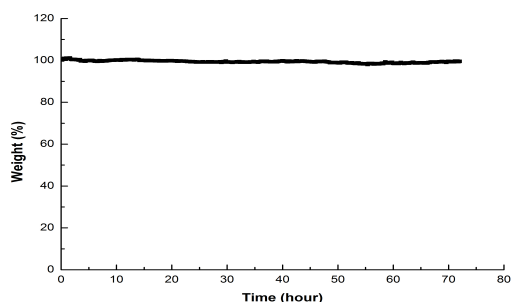


Fig. S2 TGA results of hexadecane (room temperature in air)

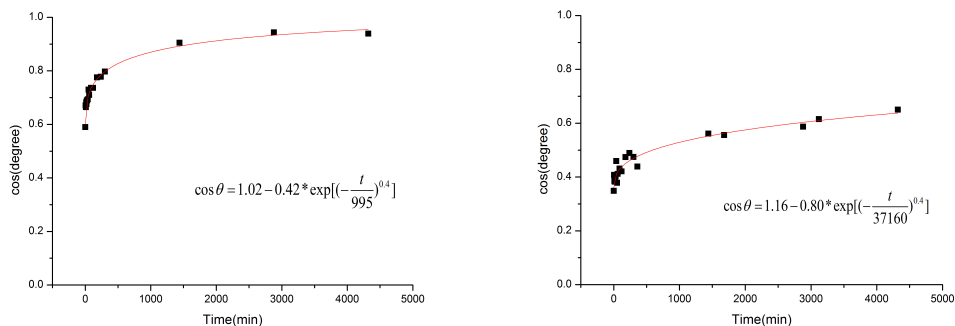


Fig. S3 KWW Fitting results of $\cos\theta$ of hexadecane on ZDOL (0.9 nm)/Si (left)
and ZDOL (1.8 nm)/Si (right)

$$\cos\theta(t) = \cos\theta_e + (\cos\theta_0 - \cos\theta_e) \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

Here t is the aging time, $\cos\theta_e$ is the equilibrium contact angle, $\cos\theta_0$ is the initial contact angle, τ is the relaxation time constant indicating how fast the system approaches equilibrium and β is the stretch factor characterizing the nonlinearity of the relaxation process.