

Supplementary information

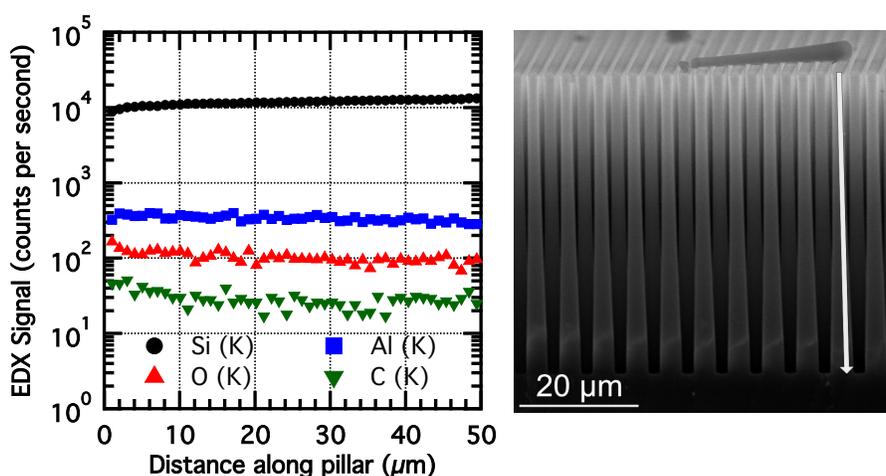


Figure S1: The Si, Al, O and C signal intensities from an EDX line scan along the edge of a 50 μm Si pillar as a function of the distance along the pillar (top to bottom). A 112 nm thick EG alucone film (500 TMA/EG cycles) was deposited on top of a Si pillar array (height: 50 μm , width: 2 μm , spacing: 2 μm). The white arrow indicates the scan direction.

The conformality of the deposition was verified on a silicon pillar array sample. The pillars were 50 μm high with a diameter of 2 μm and an interspacing of 2 μm . In order to reach saturated exposures, the exposure times had to be tripled for both TMA and the organic reactants: 15 s for TMA; 60 s for EG and GL. An EDX line scan along the edge of a pillar was measured to confirm that the hybrid coating is present and equally thick from the top to the bottom of the pillar.

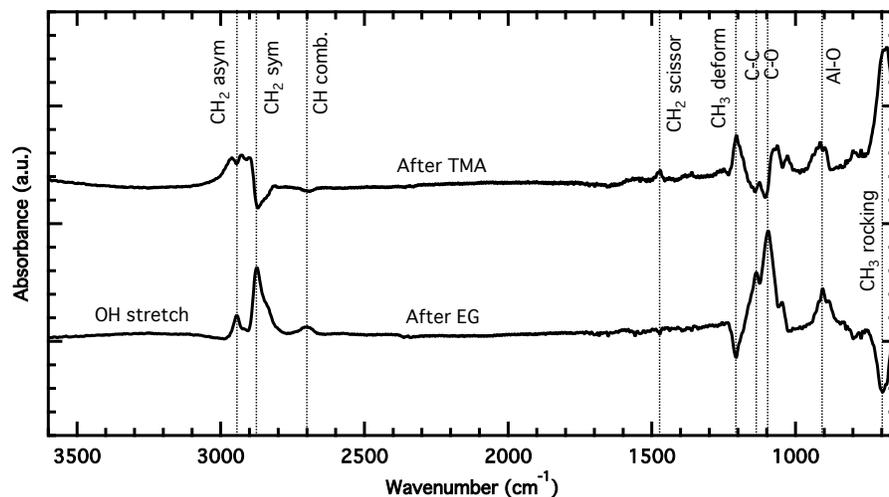


Figure S2: Difference spectra measured after TMA and EG exposures with in situ FTIR.

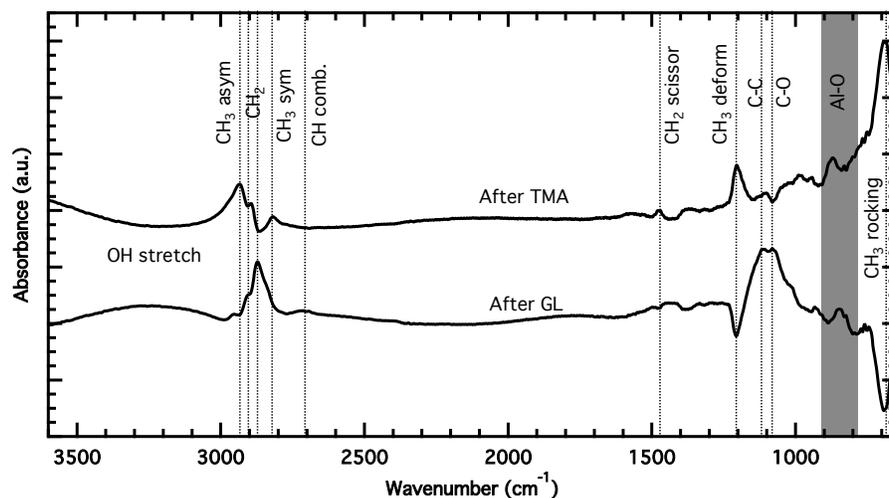


Figure S3: Difference spectra measured after TMA and GL exposures with in situ FTIR.

In figures S2 and S3 difference infrared spectra illustrating the chemical changes after each precursor and reactant exposure are shown. These difference spectra are obtained by subtracting the spectrum measured after the previous exposure from the spectrum measured after the current one. “After TMA” represents the spectrum measured after TMA exposure subtracted from the spec-

trum measured after the previous EG or GL exposure. The difference spectra shown in S2 and S3 were averaged over 200 deposition cycles in order to improve the signal-to-noise ratio. This averaging is possible due to the repetitive and reproducible nature of the MLD process.

Both spectra share many common features due to the fact that for both processes TMA was used as the precursor, and that EG and GL are chemically relatively similar. A broad band ranging from 3000 to 3500 cm^{-1} is visible and is associated to the addition and removal of OH groups, which originate from the organic reactants. In the 2700 to 3000 cm^{-1} range, multiple vibrations are present and are attributed to methyl groups, which are linked to TMA, and CH/CH₂ groups from the organic reactants. In the fingerprint region, at 1205 cm^{-1} the CH₃ deformation mode is found and is attributed to TMA. After EG and GL exposure, C-C and C-O modes are present at respectively 1135 cm^{-1} and 1084 cm^{-1} . In the 850 to 920 cm^{-1} wavenumber range, the Al-O phonon vibration mode appears in the spectra. Finally, at 693 cm^{-1} the CH₃ rocking mode, attributed to TMA, is seen.