Electronic Supplementary Material (ESI) for Chemical Communications.

Atmospheric pressure atomic layer deposition to increase organic solvent resistance of PDMS†

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1 Supplementary Information

PDMS sample preparation: The samples used for the organic resistance testing were prepared by depositing a droplet of degassed PDMS (elastomer and curing agent in a 10:1 weight ratio) on top of the surface of a silicon wafer, which was diced in pieces of 2 cm $\times$ 2 cm. The resulting spherical cap had a diameter of 1.5 cm and a thickness of 1 mm. The reason to deposit PDMS on top of a silicon wafer is that the full surface of PDMS is then treated in the ALD reactor. This is not the case when simply treating a slab of PDMS in the ALD reactor as the bottom is then left untreated. PDMS was cured at 200°C and 70°C for at least 10 hours for samples reported in Figures **??** and S1, respectively.

Thermal and plasma-enhanced atomic layer deposition: Th-ALD and PE-ALD experiments were carried out in a commercial ALD reactor (Veeco Fiji G2) at 10^{-5} mbar and 100°C. The Ti precursor (tetrakis(dimethylamino)titanium, TDMAT) was stored in a stainless-steel bubbler and kept at 70°C. For Th-ALD, water was used as the co-reactant and kept in a stainless-steel bubbler at room temperature. For PE-ALD, oxygen was flown through a plasma coil. Both reactants were introduced into the ALD chamber at 20 sccm for 60 ms alternately, with a purging step with argon introduced in the ALD chamber at 60 sccm for 5 s (PE-ALD) and 45 s (Th-ALD). The pulse and purge time of the PE-ALD and Th-ALD have been established by the previous researchers and the suppliers.

Atmospheric pressure atomic layer deposition: AP-ALD experiments were carried out in a custom-built tubular flat-substrate reactor, equipped with a reaction chamber consisting of a metal cylinder (100 mm in internal diameter and 300 mm in length) with a substrate holder (70 mm $\times$ 100 mm). Experiments were carried out at atmospheric pressure and 100°C. The gas flowed parallel to the surface of the substrate. A heating cable with isolation bands was wrapped on the reactor, with feedback control to maintain constant temperature during AP-ALD. The Ti precursor (TDMAT) was stored in a stainless-steel bubbler and kept at 70°C. The Ti precursor was carried to the reactor column with nitrogen gas flow of 0.5 L min^{-1}. The other reactant, ozone, was produced by flowing in oxygen at flowrate of 0.5 L min^{-1} into an ozoniser (Sander Certizon). One ALD process cycle consisted of exposures of the PDMS substrate to 10 s of Ti precursor and 10 s of ozone, with 150 s of nitrogen purging step (1.7 L min^{-1}). Please note that at higher flow rate of purging, and/or longer purge time, the obtained layer thickness at similar number of cycles was comparable.

Sample storage: To prevent contamination of the ALD treated PDMS samples prior to XPS analysis, the samples were transferred to a closed and clean container directly after ALD treatment.

Organic solvent resistance evaluation: Bare and treated PDMS samples were weighed before fully immersing in a beaker glass containing cyclohexane. At certain period of time (10, 60, 180, 300, 420, 1440, and 14400 minutes), the sample was taken out, blown dry and weighed directly. The sample was then put back to the beaker glass to continue the exposure. The mass at the measuring time and the mass difference were noted down. The fractional mass increase was calculated by comparing the mass difference with the initial mass. In Figures S2 and S4, the fractional mass increase was measured after 24 hours of immersion. After this time, the system was considered in equilibrium and we use the commonly used symbol Q (equilibrium swelling ratio).

Remarks on determination of film thickness: We approximated the etch rate of TiO_x layer on PDMS by placing a Si wafer next to the PDMS sample during the ALD process, and calculated the etch rate of TiO_x layer on silicon wafer. The etch rate was then fixed although it depends on the material etched; a harder or denser material would etch slower than a softer one. Despite the etch depth measured from XPS cannot be considered as the conclusive film thickness, we can still use these values to compare the depth profiles between the different PDMS samples.

Transmittance test: The transmittance test is conducted using UV-Vis spectrophotometer VWR®using glass cuvette holder as reference for 100% transmittance. Measurement is conducted from 200 to 1000 nm with increment of 1 nm, and conducted 3 times).

Spectroscopy ellipsometry Woolam: The thickness of metal oxide layer on silicon wafer is approximated using spectroscopy ellipsometry Woolam M-2000 at 50°,60°, and 70° inspection angle. Cauchy is used as a model to approximate the psi and delta, with mean squared error lower than 1.

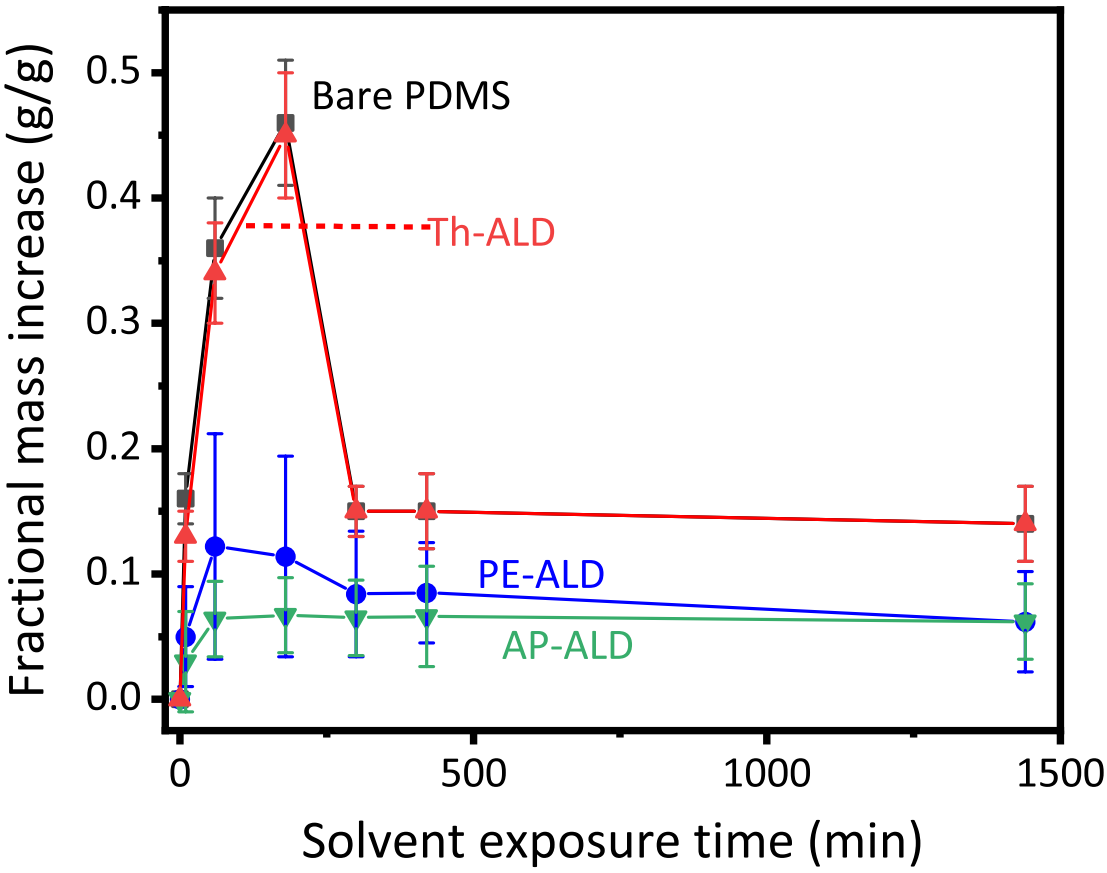


Fig. S1 Fractional mass increase of bare and ALD-treated PDMS, cured at 70°C. Error bars of bare PDMS were calculated as the standard deviation of 20 samples per time point, while error bars of ALD treated PDMS were based on 3 samples.

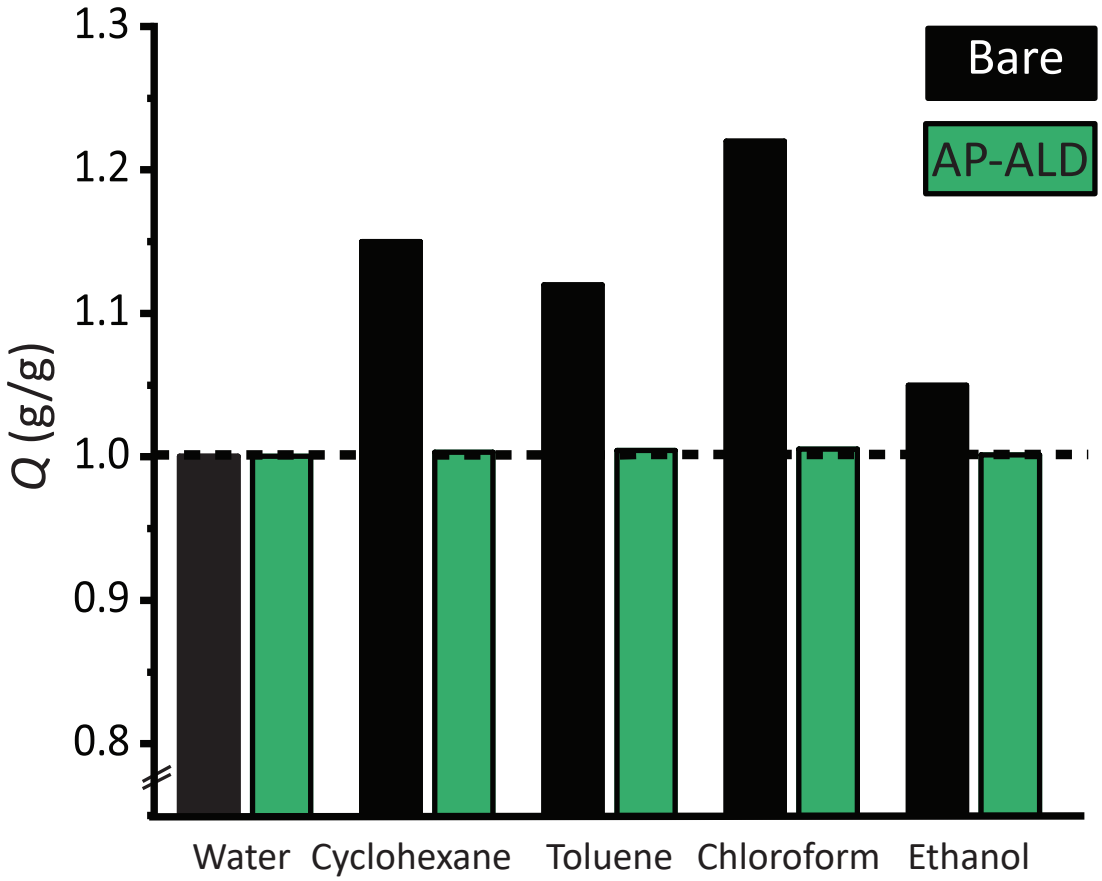


Fig. S2 Equilibrium solvent coefficient (Q, in g/g) of bare and AP-ALD treated PDMS (cured at 200°C) after 24 h of immersion in different common solvents.

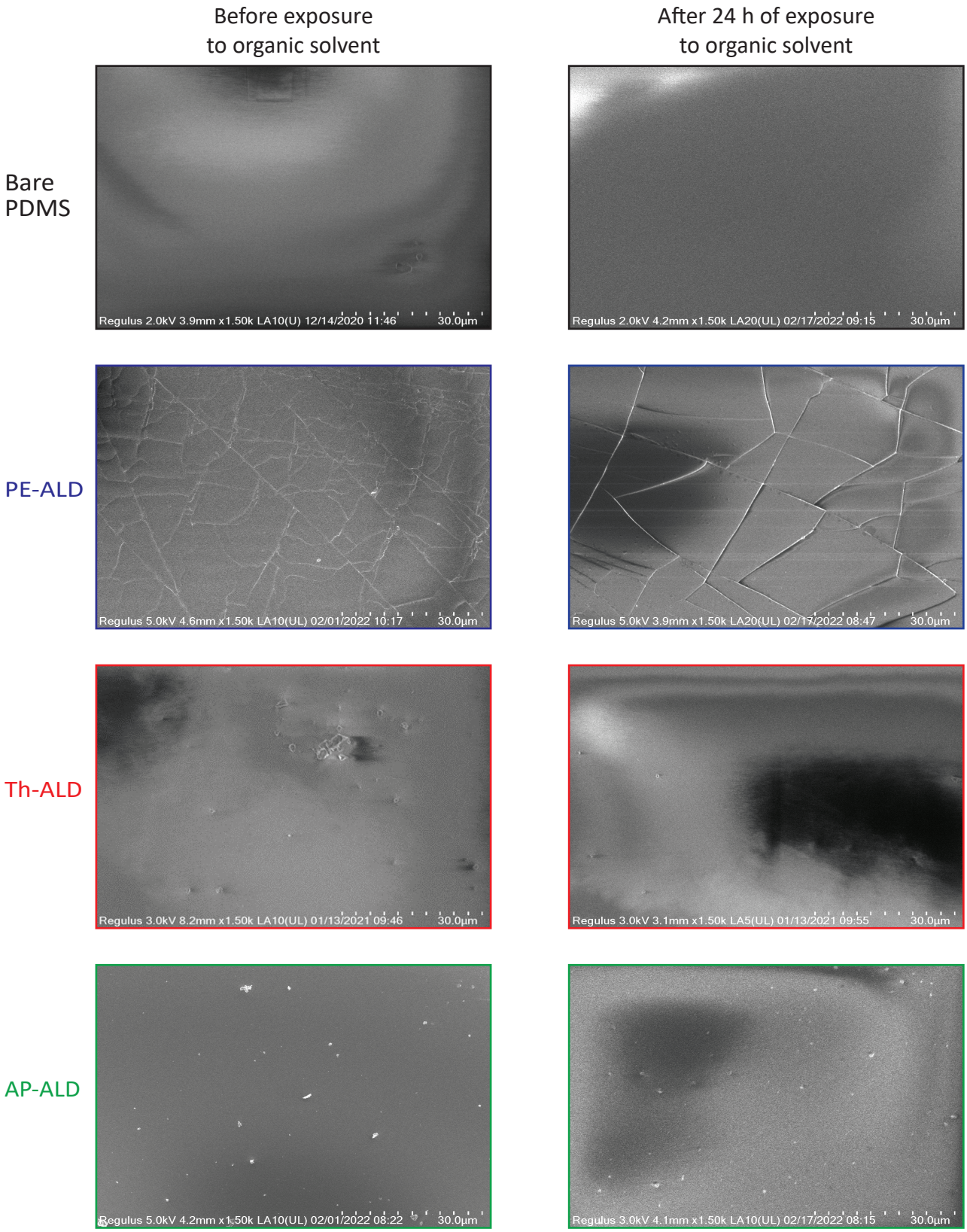


Fig. S3 Scanning electron microscopy pictures of bare and ALD-treated PDMS samples (cured at 200°C) before and after being immersed in cyclohexane for 24 hours.

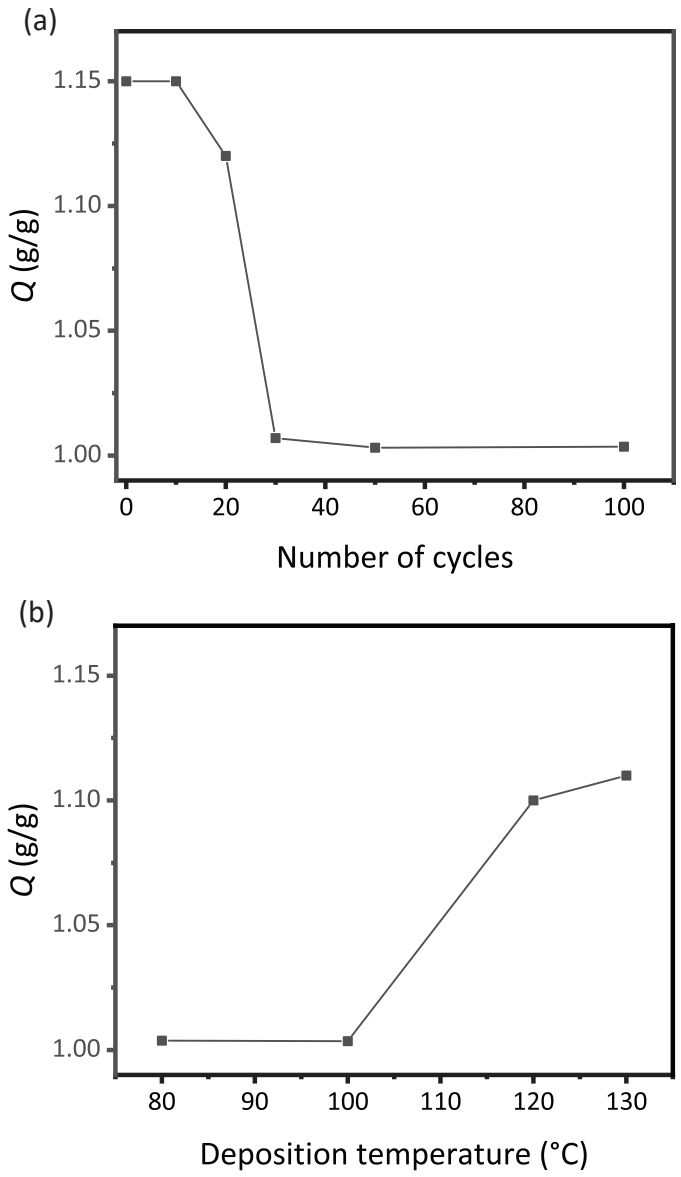


Fig. S4 Equilibrium solvent coefficient (Q) of AP-ALD treated PDMS (cured at 200°C) after 24 hours of exposure to cyclohexane for (a) different numbers of ALD cycles at 100°C and (b) different deposition temperatures at 100 cycle. These graphs show range of operating parameter where comparable low swelling is found.

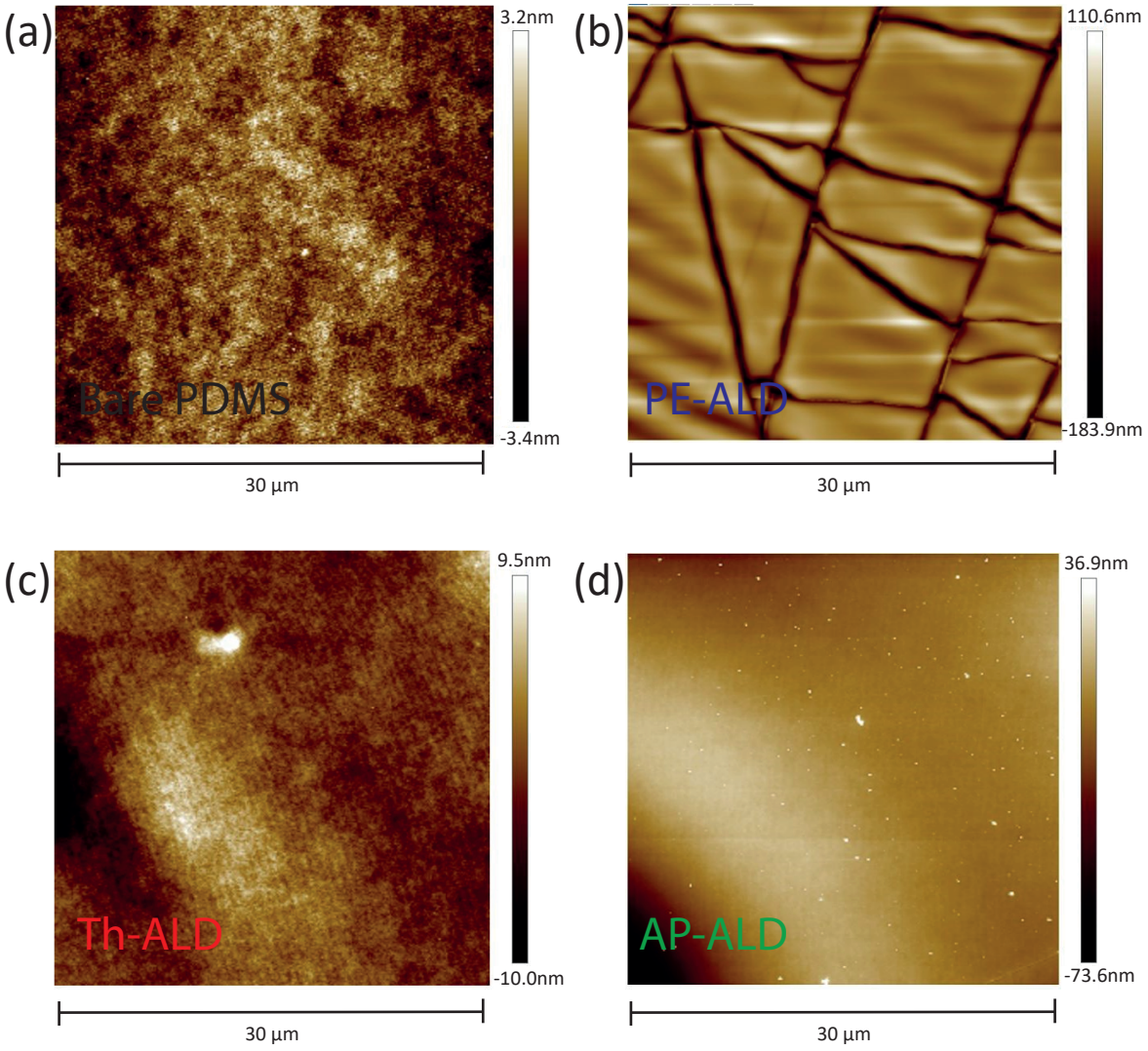


Fig. S5 Atomic force microscopy surface height profile of (a) bare PDMS, (b) PE-ALD treated sample, (c) Th-ALD treated sample and (d) AP-ALD treated sample. All samples are treated at 100°C for 100 cycles. Cracks on PE-ALD sample extends up to hundreds of nm, deeper than the expected metal oxide thickness in the range of tens of nm

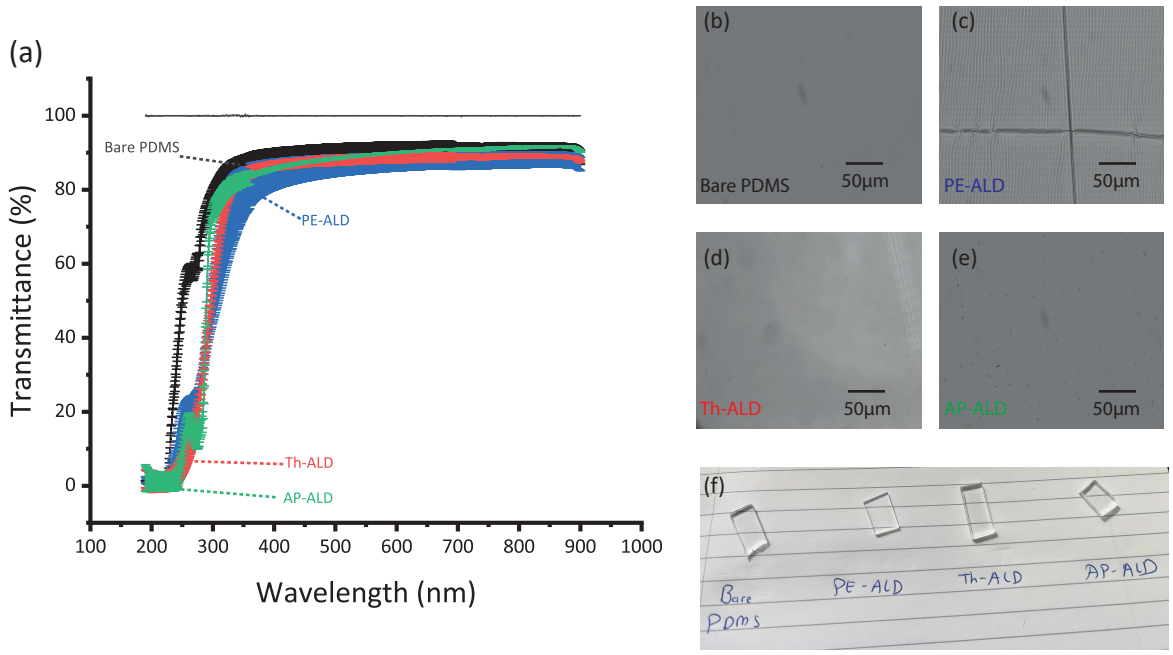
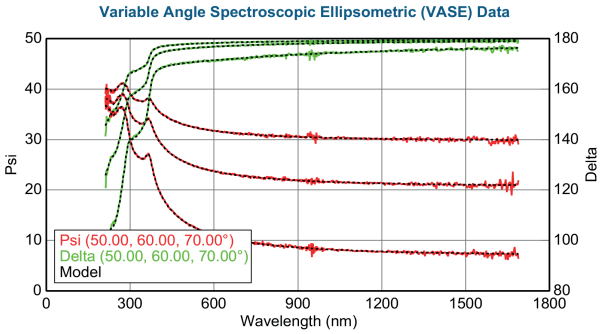
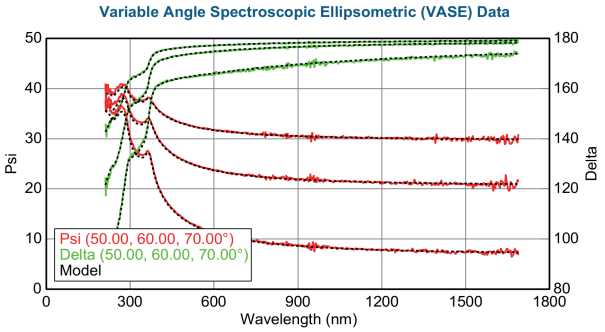


Fig. S6 (a)Transmittance spectra of bare PDMS and ALD treated samples from 100nm to 1000nm range obtained using UV-Vis spectrophotometer; (b-e) Surface profile obtained by optical microscopy of bare PDMS and treated PDMS; and (f) comparative visual photo of bare PDMS and treated samples. All samples are cured at 200°C, and treated at 100°C for 100 cycles

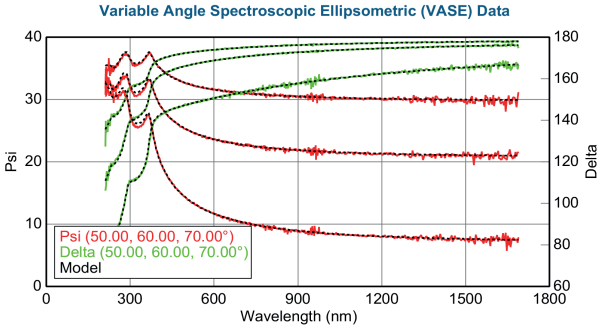
a. Bare silicon wafer



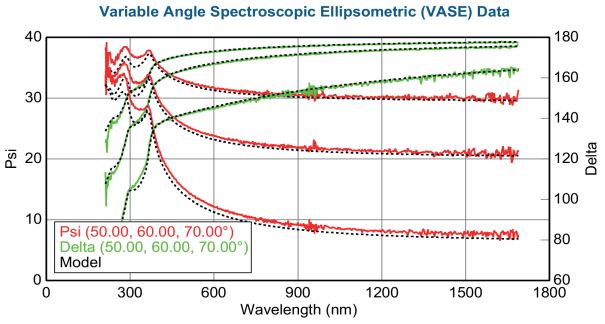
c. Silicon with Th-ALD TiOx



b. Silicon with PE-ALD TiOx



d. Silicon with AP-ALD TiOx



e. Table containing ellipsometry results and estimated XPS etch rate

Sample	Ellipsometry			XPS	Estimated etch rate (nm/s)
	Thickness (nm)	Error bar	MSE	Etch time (s)	
Bare silicon	0	0.007	0.330	0	0
PE-ALD treated Si	6.21	0.016	0.478	36	0.173
Th-ALD treated Si	1.53	0.011	0.436	9	0.171
AP-ALD treated Si	6.82	0.033	0.980	34	0.200

Fig. S7 (a-d) Psi and delta spectroscopy ellipsometric profile of bare and treated silicon wafer. The measurement is conducted at 50°, 60°, and 70° with Cauchy model to approximate the thickness and mean squared error lower than 1. The table shows the summary of approximated thickness obtained from spectroscopy ellipsometry fitted with Cauchy, XPS etch time where the plateau of Titanium atom starts going down and estimated XPS etch rate.