Supporting Information

Deposition of Dense Siloxane Monolayers from Water and Trimethoxyorganosilane Vapor

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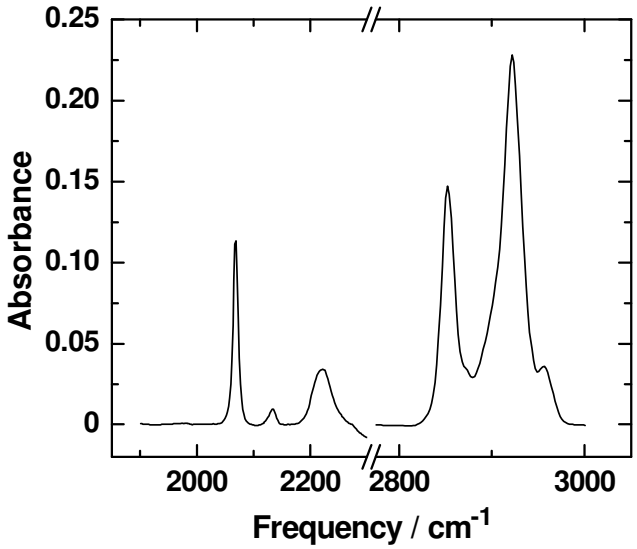

Figure S1. Attenuated total reflectance (ATR) FTIR spectrum of the bulk, liquid tetradecyl-tri(deuteromethoxy)silane used for siloxane monolayer vapor depositions.

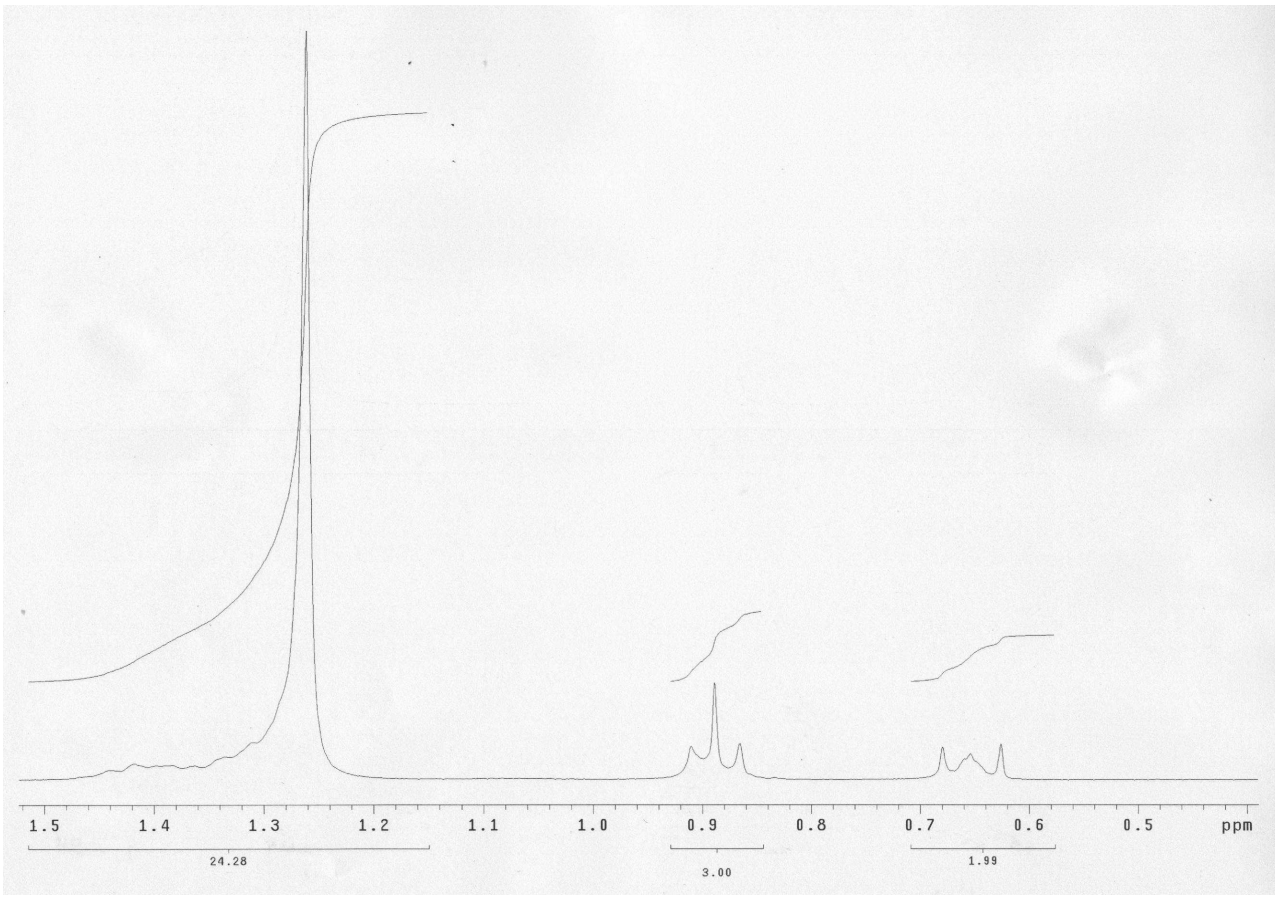

Figure S2. NMR spectrum of tetradecyl-tri(deuteromethoxy)silane that was synthesized and used for siloxane monolayer vapor depositions. The spectrum was obtained on a 300 MHz Varian Inova spectrometer in $CDCl_3$ solvent.

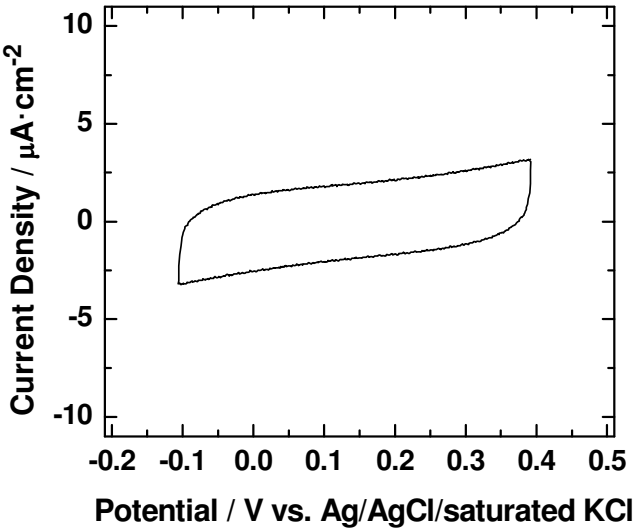

Figure S3. Plot of the current versus applied potential measured during cyclic voltammetry for a siloxane monolayer on ITO exposed to 0.1 M $NaClO_4$ in water at a scan rate of 1000 mV/s. The siloxane monolayer was formed from two repeated 12 h vapor depositions, each with 100 μL of fresh $(CD_3O)_3$-Si-$(CH_2)_{13}$-CH_3 and fresh 0.5 g $MgSO_4 \cdot 7H_2O$.

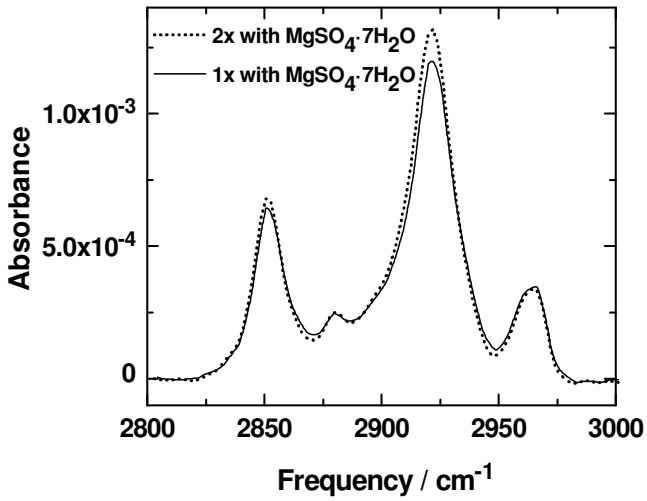

Figure S4. Carbon-hydrogen stretching region of the p-polarized Brewster's angle transmission FTIR spectra of siloxane monolayers on silicon oxide after one 12 h vapor deposition (solid line) and two repeated 12 h vapor depositions (dotted line), each with 100 μL of fresh $(CD_3O)_3$-Si-$(CH_2)_{13}$-CH_3 and fresh 0.5 g $MgSO_4 \cdot 7H_2O$.

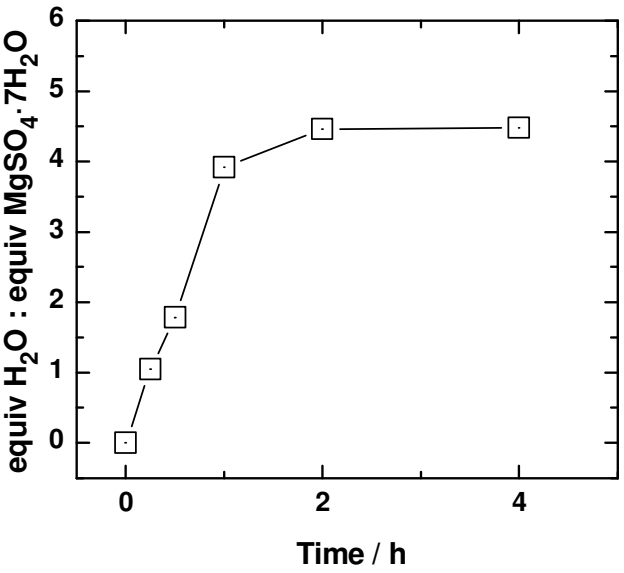

Figure S5. Time dependence of the dehydration of $MgSO_4 \cdot 7H_2O$ at 110°C under reduced pressure starting with 0.5 g $MgSO_4 \cdot 7H_2O$. The dehydration of the salt was monitored gravimetrically. The plateau at about 4.5 equivalents of water released per equivalent of initial $MgSO_4 \cdot 7H_2O$ was used for all stoichiometry calculations. The line is a guide to the eye.

Table S1. Calculated CH_3OH:H_2O Ratio in Deposition Chamber Assuming Complete Hydrolysis and Condensation

		mass $MgSO_4 \cdot 7H_2O$					
		0 g	0.005 g	0.050 g	0.25 g	0.50 g	1.0 g
volume silane	10 µL			0.092		0.0088	
	50 µL			0.56		0.045	
	100 µL	∞	∞	1.6	0.19	0.092	0.045
	300 µL			∞		0.3	

Table S1 shows the calculated CH_3OH:H_2O ratio expected at long deposition time in the silane deposition chamber assuming a water:trimethoxysilane stoichiometric ratio of 1.5:1 for conditions used in this study. Entries in the table with '∞' indicate pure methanol should remain because there was enough silane present to consume all of the water in the system. Therefore, it is not surprising that CD_3 stretching was observed after those experiments with less than stoichiometric water present. However, CD_3 stretching was still observed from experiments with water in stoichiometric excess, 100 µL silane and 0.05 g $MgSO_4 \cdot 7H_2O$, for example. A CH_3OH:H_2O ratio of 1.6 in the deposition chamber is predicted under those conditions. With the estimated equilibrium constant of 4.3 for the hydrolysis reaction, a $SiOCD_3$:SiOH ratio of ~ 0.36 is predicted. Decreasing the amount of silane to 50 µL with the same amount of water from 0.05 g $MgSO_4 \cdot 7H_2O$ still resulted in CD_3 stretching. Under these conditions, a $SiOCD_3$:SiOH ratio of ~ 0.13 is predicted. Although the amount water present under these conditions was greater than stoichiometric requirements, equilibrium predicts that a fraction of available silanols would be methoxylated as confirmed by the observation of CD_3 stretching. No CD_3 stretching was observed after lowering the amount of initial silane to 10 µL with 0.05 g $MgSO_4 \cdot 7H_2O$. Less driving force for reversing the hydrolysis would be expected with a calculated CH_3OH:H_2O ratio

of 0.092 and a $SiOCD_3$:SiOH ratio of 0.021. This same ratio is expected for experiments using 100 μL silane with 0.5 g $MgSO_4 \cdot 7H_2O$ which resulted in dense, completely hydrolyzed monolayers. Dense, completely hydrolyzed monolayers were also obtained from experiments using 300 μL silane with 0.5 g $MgSO_4 \cdot 7H_2O$ with higher calculated CH_3OH:H_2O and $SiOCD_3$:SiOH ratios of 0.3 and ~ 0.07, respectively.