

Supporting information

Distribution of fluoroalkylsilanes in hydrophobic hybrid sol-gel coatings obtained by co-condensation

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Contents

S 1. ¹H NMR of FAS-R, FAS-U and FAS-E

FAS-R was provided from Evonik and was used without any further purifications. The ¹H NMR spectrum of the corresponding commercial reference can be seen in Figure S1. ¹H NMR spectra of FAS-U and FAS-E are presented respectively in Figure S2 and S3.

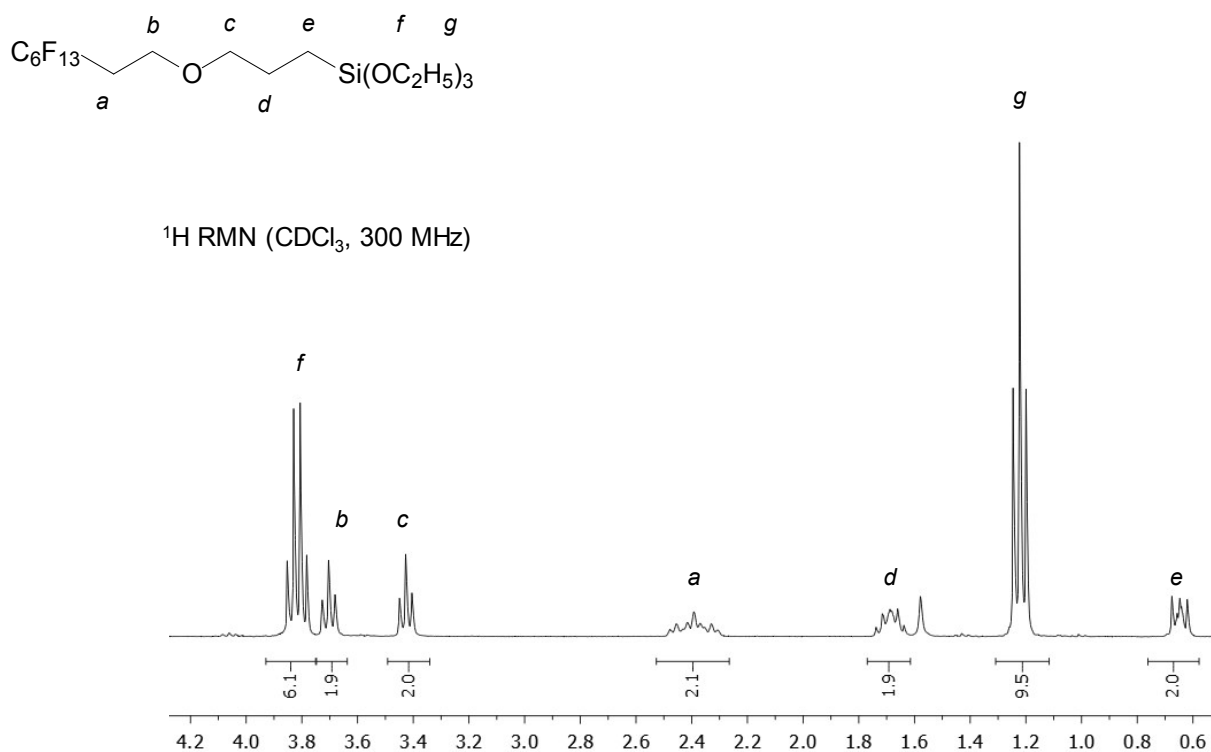


Figure S3. ^1H NMR of FAS-E

S 2. Surface topography of the Co-SG thin films

Morphology of the Co-SG sample surfaces were analyzed by Atomic Force Microscopy (AFM) (PSIA XE-100 AFM) in order to evaluate the surface roughness of the developed hybrid thin films (Figure S4). An average root-mean square roughness of 0.2 nm was obtained which is comparable to the surface roughness of an untreated Si substrate.¹

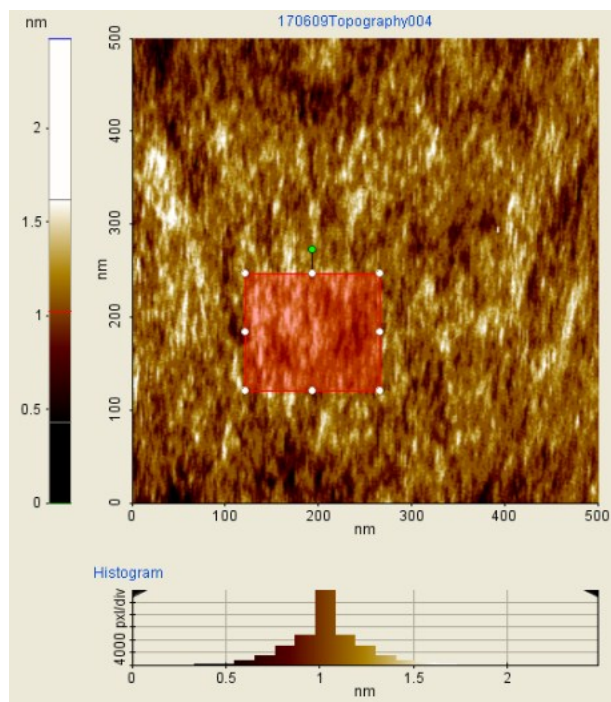


Figure S4. AFM image of Co-SGU surface

S 3. Thermal behavior of the FAS molecules

To have a better understanding of the degradation phenomenon involved with FAS, Thermal Gravimetric Analysis (TGA) were also performed on the molecules themselves. TGA profiles of FAS-R, FAS-U and FAS-E are presented in Figure S5. Degradation onset and percentage of residue after 200°C were evaluated for each molecule.

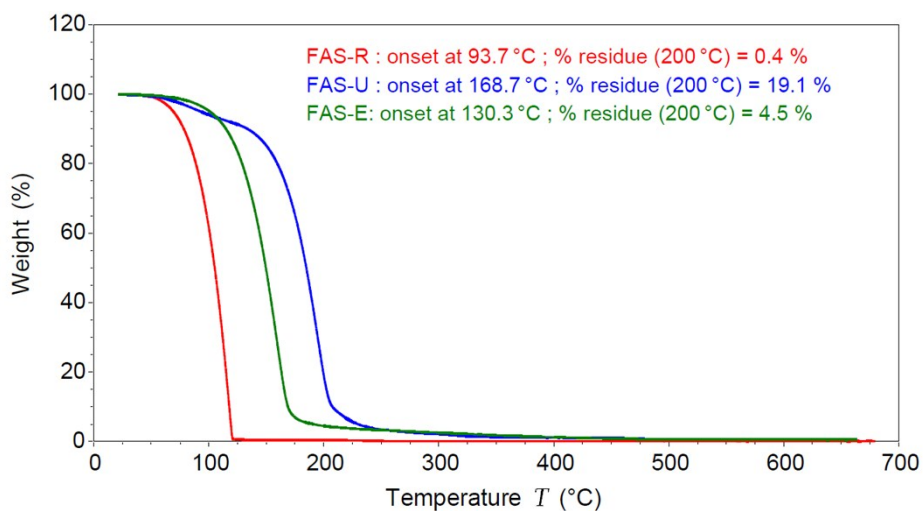


Figure S5. TGA of the FAS-R, FAS-U and FAS-E, showing their respective degradation temperature and percentage of residue at 200°C

Interestingly, it can be observed that the degradation of FAS-R starts at 93°C while FAS-U and FAS-E get degraded only after 130°C. Moreover, the percentage of residue at 200°C is much higher for FAS-U (19.4 wt%) than for FAS-E and FAS-R (4.5 wt% and 0.4 wt%) whereas only a decrease of the contact angle of Co-SGU was observed at this temperature. One possible explanation of the late degradation of the FAS-U observed here and the concomitant decrease of hydrophobicity might be related to the formation of trimethyl isocyanurates after cleavage of the urethane bond and loss of the fluorinated moiety. Indeed, these compounds are known to exhibit high thermal stability, starting to degrade above 270°C.² This hypothesis is consistent with the observation of two different slopes on the FAS-U curve in Figure S5., the first one corresponding to a partial liberation of the fluorinated part and the second one to the degradation of the trimethyl isocyanurates. The study of these molecules by TGA give important information on their thermal resistance. However, these results are not representative of their behavior when integrated into a sol-gel network.

Therefore, in-situ thermal ellipsometry analysis were carried out to investigate the thermal evolution of these three Co-SG layers. For in-situ thermal ellipsometric analysis, the ellipsometer was fitted with a home-built covered heating unit connected to a programmable temperature regulator. Small holes were present to allow a thermocouple and beam access to the sample as well as gas flow. The calcination environment was adjusted by flowing 0.1 L min⁻¹ of dry air through the sample stage at controlled RH with a continuous ramp rate of 5°C/min. Ellipsometric data were fitted using the optical properties of the silicon substrate at 20 and 300°C.³ The thin sol-gel layers were prepared as described in the Experimental Section of the manuscript but were only aged for 5 minutes at room temperature. Figure S6. displays

the refractive index and the relative thicknesses of the three Co-SG films as a function of the temperature. From 0 to 100°C, the refractive index and the relative thickness decrease which correspond respectively to the evaporation of the solvent and the densification of the inorganic matrix. Above 100°C, the densities of the film continue to increase while the refractive indexes decrease, attesting of the formation of microporosity. The refractive index varied from 1.43 to 1.41 for Co-SGR, 1.44 to 1.43 for Co-SGU and 1.44 to 1.42 for Co-SGE. After 200°C, the thickness decreases to a lesser extent indicating that the condensation of the network is almost complete. The decline of the refractive index cannot be this time only related to the creation of porosity. Therefore, another mechanism is at stake which could correspond to the degradation of the FAS. Despite the slight difference of refractive index variation of FAS-U between 100 and 200°C, thermal curves can be considered similar for the three FAS-based materials.

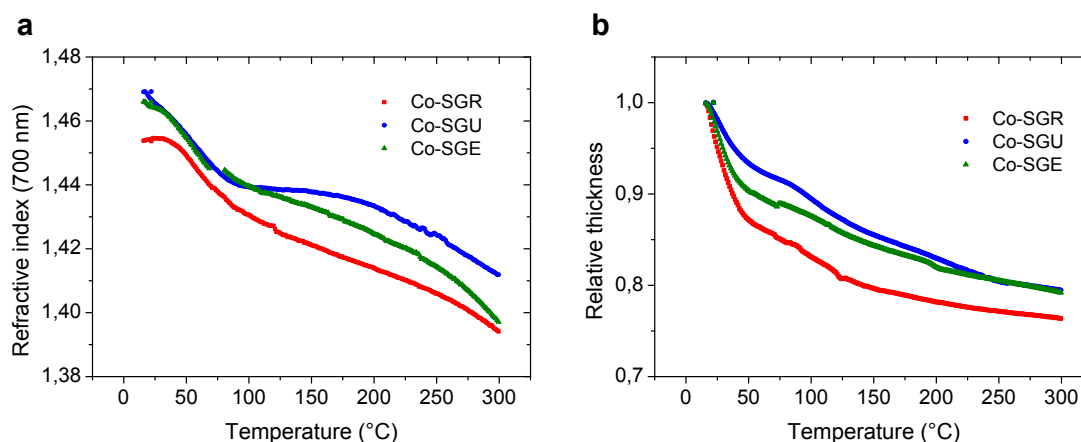


Figure S6. (a) Refractive index and (b) relative thickness of the Co-SGR, Co-SGU and Co-SGE thin films as a function of the temperature

S 4. Fitting of the XPS C 1s region

The hypothesis that one ethoxy function remained per silane after condensation of the species into the network was made. Therefore, the proportions of each carbon were equal to 10%.

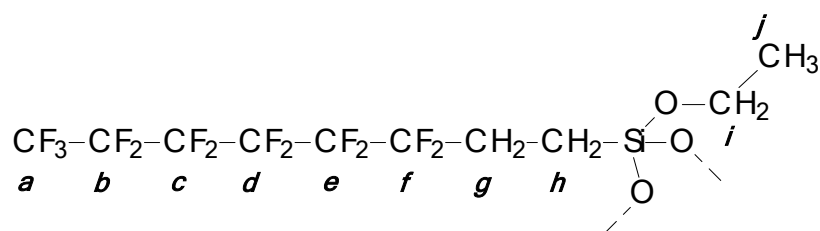


Figure S7. Attribution of the carbons constituting FAS-R when co-condensated in a sol-gel network

The area percentages of each component of the XPS C 1s region (see Figure S8.) were obtained from CasaXPS software and are presented in the following table (second column). The carbons of FAS-R were ascribed to the different components 'region as a function of their binding energies. It can be seen that the area percentages of each component are consistent with the proportions of carbon attributed. The small variations can be related to the approximation of the hypothesis made at first.

Regions	Area percentages	Ascribed carbons of the FAS-R	Proportions of the ascribed carbons per area
I	25.0 %	i,j	20 %
II	23.4 %	g,h	20 %
III	8.2 %	f	10%
IV	35.2 %	b,c,d,e	40 %
V	8.2 %	a	10 %

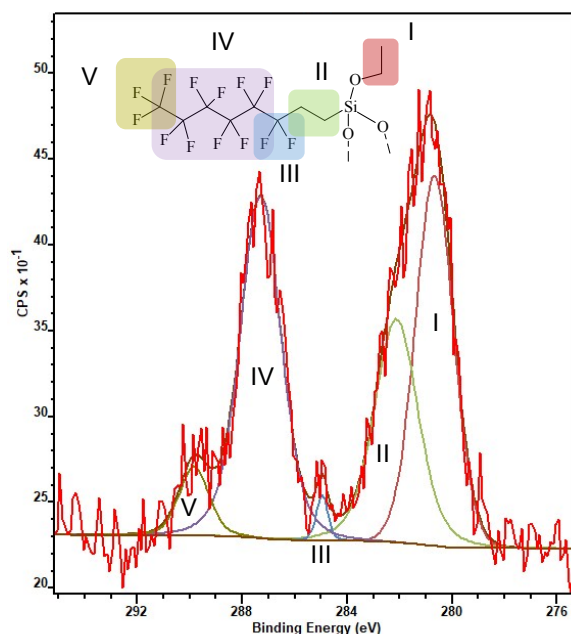


Figure S8. XPS C 1s region (bold line) fitted with five components (normal lines)

References

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2. D. K. Chattopadhyay and D. C. Webster, *Prog Polym Sci*, 2009, **34**, 1068-1133.
3. J. D. Bass, D. Grosso, C. Boissiere and C. Sanchez, *Journal of the American Chemical Society*, 2008, **130**, 7882-7897.