

Research Article

Enhanced Mechanical Properties in Organofluorosilica Thin Films

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Fluorinated hybrid organic-inorganic silicates (ORMOSIL) thin films display exceptional mechanical properties in terms of both hardness and elastic modulus that can be finely tuned by varying the angular velocity of the spin coating process. Hence, as traditional alkyl-modified silica xerogels generally show poor mechanical behavior, these materials offer a solution to a major limitation to applicability of ORMOSIL-based films.

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1. INTRODUCTION

We recently reported that the mechanical properties of thin films of hybrid organic-inorganic silicates (ORMOSIL) can be largely tuned in a wide range by changing the degree of organic modification [1]. These findings are important since in thin functional coatings, small amount of ORMOSIL impart improved new properties to materials that are already commercialized in microelectronics as dielectric materials [2], and are about to find ubiquitous diffusion as versatile OLEDs [3]. Another structural characteristic of practical importance is that in such coatings, strong chemical adhesion between the glass substrate hydroxyls and the film occurs limiting delamination (see Figure 1) [4].

Finally, the external surface of ORMOSIL is depleted of silanol groups leading to low optical loss in the near infrared, which is an essential requirement for optical applications such as waveguides.

Returning to alkyl-modified silica thin films, we explained the drastic variation in mechanical response on the basis of the structural changes in the organosilica molecular structure [1]. In general, trifunctional alkoxy silanes and

silicon alkoxides are excellent cross-linkers and upon the sol-gel polycondensation, they lead to hybrid materials with high Young's modulus ($E > 10$ GPa) and high (or even no) glass transition temperature (T_g). A major limitation to applicability, however, often resides in their poor mechanical behavior [4] and this is partly the case also for alkyl-modified silica xerogels [1]. It is therefore of great importance that fluorinated ORMOSIL thin films display, as shown in this report, exceptionally good mechanical properties in terms of both hardness and elastic modulus. Moreover, delicate fine tuning of the mechanical properties of sol-gel coatings can easily be achieved by varying the angular velocity of the spin coating process.

2. EXPERIMENTAL SECTION

A series of thin films was obtained by spin-coating 800 μ L of precursor solution containing 3,3,3-trifluoropropyltrimethoxysilane (TFPTMS), methanol, water, and fluoride in molar ratios Si:H₂O:NaF:MeOH = 1:4:10⁻⁴:8) or 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecaoctafluoro-triethoxysilane

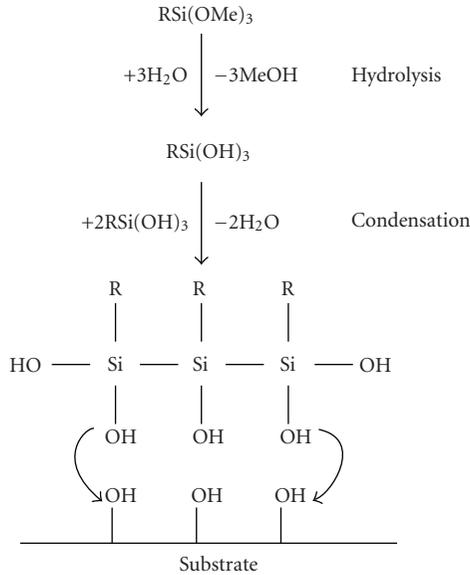


FIGURE 1: Strong chemical bonding to glass substrates in sol-gel ORMOSIL thin films ensures prevention of delamination.

(TDOFTES), using tridecafluoroethanol as cosolvent, over microscope slides, using a chemat technology KW-4A spin coater changing the spin-off speed following spin-up at equal speed (1000 rpm for 18 seconds). The preparation for the first series of samples was repeated under acid catalyzed conditions. The sol compositions and preparation conditions of the film are summarized in Table 1. A reference microscope slide (substrate) was added to the series showing that all films are actually as stiff as (and even stiffer for some of these) the slide.

All the resulting films were thus tested using a nanoindenter from CSM Instruments (Peseux, Switzerland). The instrument was equipped with a Berkovich indenter, with equivalent semiopening angle of 70.3 degrees. The tests were performed in air with the force-control mode of the machine. The loading-unloading procedure was as follows: loading to maximum load in 30 seconds, plateau at maximum load for 30 seconds, unloading in 30 seconds. The tests were repeated 15 times under a maximum load of 2 mN. The calibration procedure suggested by Oliver and Pharr [5] was used to correct the data for the load-frame compliance of the apparatus and for the imperfect shape of the indenter tip, that is, the relation between contact depth and contact area (The area function, i.e., the relation between contact depth and contact area, was calibrated performing several indentations on fused silica with penetration depth in the range 10-300 nm, with good reproducibility. The reduced elastic modulus of fused silica ($E_r = 69.6$ GPa) was used as input to evaluate the contact area at each contact depth, and the plot was fitted with the Oliver and Pharr dependence obtaining the area function). The infrared spectra of the films, in attenuated total reflection mode (ATR), were recorded using a Perkin-Elmer (Wiesbaden, Germany) 1760 X FTIR plus micro-FTIR spectrometer in the range 400–4000 cm^{-1} , at 4 cm^{-1} resolution, and are the ratio of 1000

scans for each film against the same number of scans for the clean ATR crystal.

3. RESULTS AND DISCUSSION

The thickness, hardness, modulus, and contact penetration values for all the films are given in Table 2 and plotted in Figure 2.

Hardness is the mean contact pressure, that is, the ratio of applied load and the resulting contact depth. The elastic modulus is evaluated by the Oliver and Pharr procedure, which allows one to evaluate the so-called reduced elastic modulus, E_r , by fitting the unloading curve with a power-law relation. In particular, following the equations derived by Sneddon describing the elastic contact between a rigid indenter and an elastic half-space, this is accomplished after evaluating the derivative of the latter curve at the point of maximum penetration depth through (1) [6]:

$$S = \left. \frac{dF}{dh} \right|_{h=h_{\max}} = 2\beta \cdot E_r \cdot \sqrt{\frac{A_c}{\pi}}, \quad (1)$$

where S is named contact stiffness, F is applied load, h penetration depth, A_c is the contact area. β is a pure geometric correction factor, which takes also into account that the indenter is not a perfect cone (King determined, by FEM simulations, for the Berkovich indenter a β value of 1.034) [7]. Following this approach, and taking into account also the limitations pointed out by Chaudhri on the use of the concept of reduced elastic modulus [6], the indenter was assumed to be rigid with respect to our films, so that the original Sneddon equation can be applied (see (2), in which the Poisson ratio, ν , is assumed to be equal to 0.3):

$$E_{\text{film}} = (1 - \nu^2)E_r. \quad (2)$$

As expected, contact penetration increases with the spin-coating speed, from about 76.5 ± 4.4 nm for the trifluoropropyl-modified silica sample prepared at 3000 rpm, to 83.9 ± 2.1 nm for the analogous film obtained at 5000 rpm. All films studied were mechanically stable and no time dependence of the response was observed. Similarly, the nanoindentation measurements are reproducible as shown by consecutive force curves (not displayed) giving penetration standard deviation of less than 6%.

Figure 3 shows the representative ATR of the film PFO6 in a micro-FTIR. The photograph of the sample, which has the lowest H and E_r , shows that the film is very homogeneous, both the front and the back faces. The spectrum of sample PFO6 (front in red in Figure 3) shows a band at ~ 1077 cm^{-1} , similar to that of TFA films.

As previously reported, the elastic moduli vary with nanoindentation depth, pointing to a clear substrate effect [8]. Taking therefore such effects into consideration, and thus limiting measurements at lower loads at which penetration depth is compatible with respect to the thickness of the films, intrinsic hardness, and elasticity values for both of the ORMOSIL films are given in Table 2.

Trends in Table 2 and Figure 2 reveal valuable information. The modulus values are about 80 GPa and hardness values are about and higher than 7 GPa, which compared with,

TABLE 1: Sol compositions and identification of the thin films prepared. The spin-up conditions were 18 seconds at 1000 rpm for all the films. t_2 —spin-off period in seconds; r_2 —spin-off velocity in rotations per minute TFPTMS: trifluoropropyl-trimethoxysilane, TDOFTES: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecaoctafluoro-triethoxysilane, TDF: tridecafluoroethanol.

Film designation	Sol composition volume/ μL							Total volume/ μL	Hydrolysis time	t_2/s ; r_2/rpm
	TFPT MS	TDOFTES	CH_3OH	NaF (10 mM)	H_2O	TDF	HCl (10 mM)			
TFP3 ^(a)	700	—	1151	35.6	220	—	—	2106.6	15 min	60; 3000
TFP5	700	—	1151	35.6	220	—	—	2106.6	15 min	60; 5000
PF03 ^(b)	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 3000
PF04	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 4000
PF05	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 5000
PF06	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 6000
PF07	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 7000
PF08	—	1384	1151	35.6	220	3176	—	5966.6	15 min	60; 8000
TFA3 ^(a)	700	—	1151	—	220	—	35.6	2106.6	7 h	60; 3000
TFA5	700	—	1151	—	220	—	35.6	2106.6	7 h	60; 5000
Si0Me	—	—	—	—	—	—	—	—	—	60; 3000
Si100Me	—	—	—	—	—	—	—	—	—	60; 3000

^(a) Molar ratios: $\text{Si}:\text{H}_2\text{O}:\text{NaF}:\text{MeOH} = 1:4:10^{-4}:8$

^(b) Molar ratios: $\text{Si}:\text{H}_2\text{O}:\text{NaF}:\text{MeOH}:\text{TDF} = 1:4:10^{-4}:8:4$.

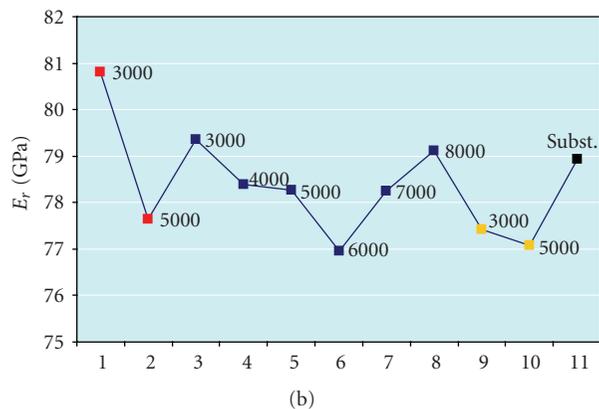
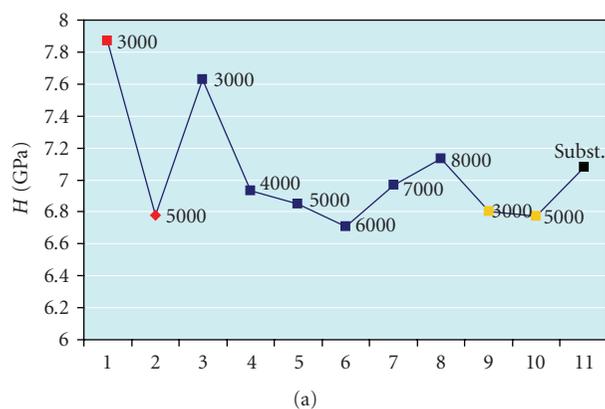


FIGURE 2: (a) Hardness and (b) elastic modulus for fluorinated organosilica thin films coated at different spin-off speed. Data for TFP- and PFO-modified samples are shown. Spin-off speed in labelled specimens is ordered as in Table 1.

respectively, 8.6 and 1.4 GPa for a 100% methyl-modified film obtained under the same spin coating conditions. Interestingly, for lower spin-off velocity (3000 rpm), the perfluorinated film has slightly worse mechanical properties than the trifluoropropyl-modified counterpart (PF3 versus TFP3). For both series, increasing the spin coating speed lowers both hardness and modulus, which is in accordance with the formation of less thick films. When the speed exceeds 6000 rpm, the substrate effect becomes predominant and eventually at 8000 rpm both values correspond to those of the glassy substrate.

Such exceptionally good mechanical properties can be explained in terms of the secondary polymeric structure of the organofluorosilica gels. Indeed, hardness and modulus of the TFP3 sample are about two and three times higher compared to the corresponding values of unmodified SiO_2

(4.2 and 33.4 GPa, resp.). We propose that the increased stiffness—the resistance of the resulting elastic structure to deflection by an applied force—is due to the presence of fluorine in the $\text{CF}_3-(\text{CH}_2)_2-[\text{Si}-\text{O}]_n$ chains, which is well known to promote orientation by lateral interactions [9]. Too high a level of fluorination, such as in the case of the perfluorinated samples, produces an adverse effect, due to the dominance of interactions within the polymer chains [10]. On the other hand, the influence of the degree of the sol-gel reactions at the moment of spinning is clear comparing films prepared at low spin velocity from sols with the same precursor but with different hydrolysis conditions (TFP3 and TFA3). The latter has lower modulus and hardness due to incomplete hydrolysis of the organosilane precursor, which under acidic conditions takes place at slower rate. On the other hand, for sufficiently high spin-

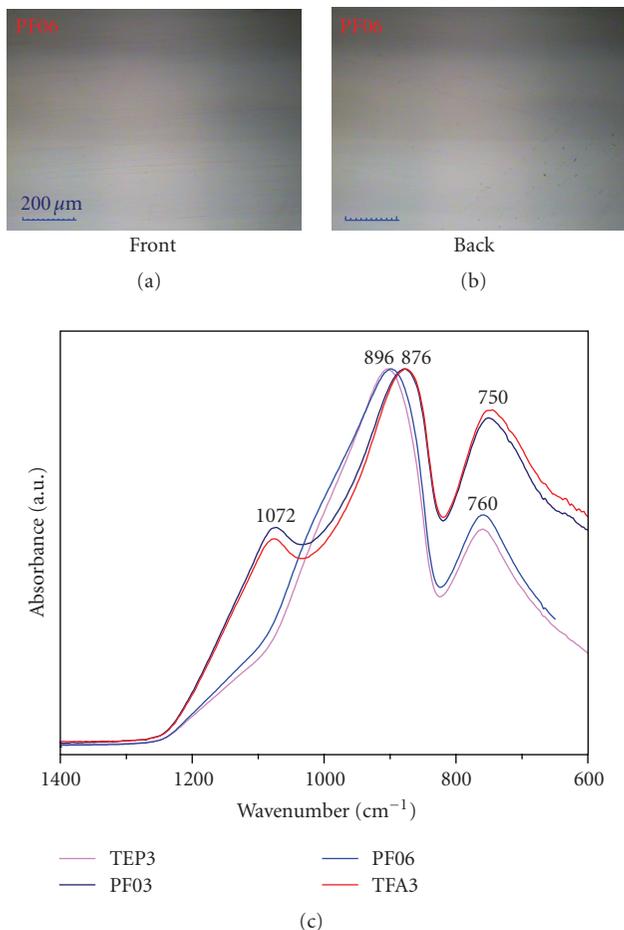


FIGURE 3: ATR spectra of films TFP3, PF03, PF06, and TFA3 in the silica fingerprint region.

TABLE 2: Hardness (H) and modulus (E_r) for the fluorinated thin films.

Film	H /GPa	E_r /GPa
TFP3	7.9	80.0
TFP5	6.8	77.6
PF03	7.6	79.3
PF04	6.9	78.4
PF05	6.8	78.3
PF06	6.7	77.0
PF07	7.0	78.2
PF08	7.1	79.1
TFA3	6.8	77.4
TFA5	6.8	77.1
Si0Me	4.2	33.4
Si100Me	1.4	8.6
Substrate	7.1	78.9

off speeds, the nature of precursors and the stage of the sol-gel process become irrelevant, yielding small differences in ORMOSILs' hardness values: indeed, all the samples

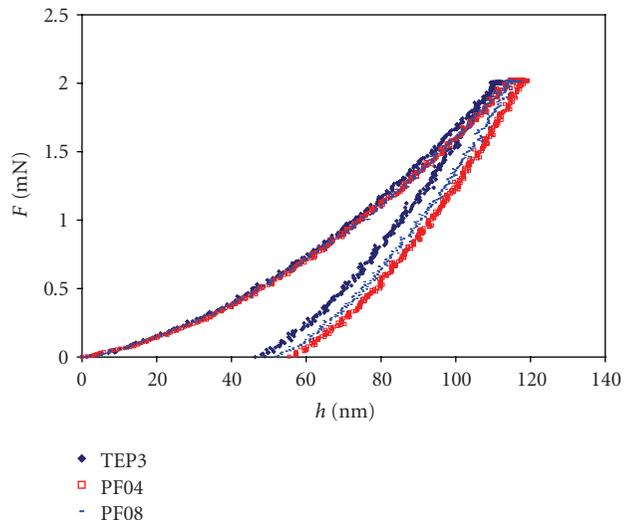


FIGURE 4: Force-penetration curve of selected fluorinated organosilica thin films coated at different spin-off speed.

prepared at 5000 rpm (TFP5, PF05, and TFA5) have almost *identical* mechanical properties.

The mechanical properties of the films correlate well with the structural information retrieved from infrared analysis. Figure 3 shows the ATR spectra of films TFP3, PF03, PF06, and TFA3 in the silica fingerprint region.

The films with better mechanical properties (TFP3 and PF03), obtained with lower spin-off velocity, have similar spectra, with two maxima at 896 and 760 cm^{-1} , assigned to the $\nu_{\text{as}}\text{Si-O-Si}$ and $\nu_{\text{s}}\text{Si-O-Si}$ modes, respectively. Those with poorer mechanical behavior (PF06 and TFA3) present the $\nu_{\text{s}}\text{Si-O-Si}$ mode much shifted (at 750 cm^{-1}), and the $\nu_{\text{as}}\text{Si-O-Si}$ band splits in two components at 876 and 1072 cm^{-1} , which can be assigned to the transverse and longitudinal optical components, respectively. This LO-TO splitting is usually observed in infrared spectra of thinner silica layers, with a higher degree of long distance order in the silica network, which points to a separation between silica rich and fluoroalkyl rich nanodomains.

Selected force-penetration curves are shown for three different films in Figure 4 with loading and unloading separated portions since the films deform plastically. The curves were obtained under the same maximum force. Under a given load however, penetration changes from one sample to the other. These changes could be analyzed in terms of hardness and modulus as extracted from unloading curve.

As previously reported, the elastic moduli vary with nanoindentation depth, pointing to a clear substrate effect [1]. Taking therefore such effects into consideration, and thus limiting measurements at lower loads at which penetration depth is compatible with respect to the thickness of the films, intrinsic hardness and elasticity values for both the ORMOSIL film series are given in Table 2.

In conclusion, we report the first case of hybrid ORMOSIL thin films displaying superior mechanical properties. The materials are organofluorosilica xerogels obtained

by sol-gel polycondensation catalyzed by fluoride. A limited amount of work has been devoted to the study of fluorinated organosilica sol-gels, despite the fact that such fluorinated materials [11] show exceptional properties in terms, for instance, of enhanced CO₂-philicity in catalysis in supercritical carbon dioxide [12] or O₂ permeability such as in the case of optical oxygen sensors [13]. As previously emphasized [1, 14], intelligent design of organosilica thin films for a number of new applications should be based on understanding the structural features governing the behavior of these materials, and thus on mastering the sol-gel process at their origin. Weak interactions amongst the fluorinated siloxane chains in the organosilica matrix likely ensure excellent stiffness and similarly good hardness and elasticity. For comparison, excellent periodic mesoporous organosilica (PMO) films obtained by surfactant template polycondensation display 0.6 GPa hardness and 10 GPa elastic modulus values [2]. The versatile chemistry of sol-gel-assembled ORMOSIL offers abundant opportunity for tailoring the mechanical properties of organosilica thin films. Hence, as organosilica sol-gel coatings are about to find a multiplicity of practical applications, these findings open the route to the preparation of silica-based films with enhanced mechanical properties.

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