

*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 65th anniversary*

PREPARATION OF HYDROPHOBIC AND ANTIREFLECTIVE HYBRID FILMS BY SOL-GEL PROCESS USING PERFLUOROALKYLSILANE AND TETRAETHOXYLSILANE

Violeta PURCAR,^{a,b} Simona CAPRARESCU,^c Catalin Ilie SPATARU,^{a,*}
Marius GHIUREA,^a Valentin RADITOIU,^a Cristian PETCU,^a
Raluca SOMOGHI,^a Mihai Cosmin COROBEA^a and Dan DONESCU^a

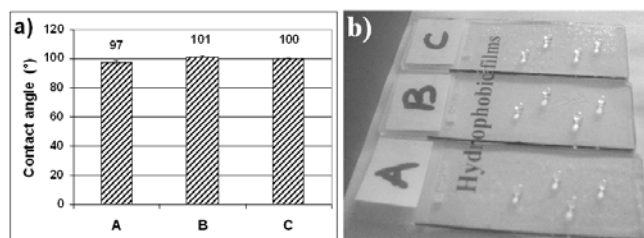
^aNational Research&Development Institute for Chemistry and Petrochemistry ICECHIM,
202 Splaiul Independentei, 6th district, P.O. 35-174, 060021, Bucharest, Roumania

^bUniversity of Bucharest, Faculty of Physics, 3Nano-SAE Research Centre, P.O.Box MG-38, 077125 Magurele, Roumania

^cUniversity Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science,
1-7 Polizu St., 011061, Bucharest, Roumania

Received February 6, 2012

Coatings films on glass substrate were fabricated by sol-gel process at room temperature (25°C), using tetraethylorthosilicate (TEOS) and 1H, 1H, 2H, 2H -perfluorooctyltriethoxysilane (FAS13), in acidic conditions with ethanol and HCl 0.1M. The molar ratios between the TEOS and FAS13 were 1:1, 1:5 and 5:1, respectively. All hybrid films were cross-linked with titanium(IV) isopropoxide (TIP) as cross-linking agent. The physical properties of the coatings films were characterized by ESEM, FT-IR, and UV-VIS-NIR. The surface properties were investigated by measuring contact angles.



INTRODUCTION

In the past decade, the wettability of solid surface has attracted great interests both in academic and in industry.¹⁻⁷ Water-repellent coatings have important applications in all aspects of use: optical systems, glasses, eyeglasses, medicine, military products, laser safety eye protective lenses, mirrors, solar cells, IR diodes, architectural and automotive glasses and any kind of display solar energy conversion systems.⁸⁻¹⁰

Various methods such as sol-gel, chemical vapor deposition, plasma etching, lithographic

patterning, electrodeposition, etc. can be used to create hydrophobic surfaces.¹¹⁻²²

Among the methods of obtaining hydrophobic thin films on glass surface, the sol-gel process is one of the most versatile methods used for continuous production.²³⁻²⁸ This process basically consists of (1) improvement of processing and properties of conventional materials and (2) creation of materials with new properties.²⁹ A variety of surface modifying agents have been used for forming hydrophobic water-repellent films on the glass surface, such as organosilanes,^{30,31} fluorosilane,³² perfluorinated

* Corresponding author: catalin_spataru2004@yahoo.com

compounds,³³ polymer,^{4,34} etc. Several groups reported the fabrication of the hydrophobic thin films using fluorinated alkoxy silane and silane (such as: 3-glycidoxypropyltrimethoxysilane, tetraethylorthosilicate (TEOS)).^{35,36} Orozco-Teran *et al.* reported the triethoxyfluorosilane films modification by silylation for the enhancement of hydrophobicity.³² Jeong *et al.* varied the perfluoroalkylsilane (PFAS)/TEOS molar ratios and reported the fabrication of coating films on glass substrate under acidic conditions, with water contact angles between 110°-118° interval.³⁷

In this paper, we report a study on the formation of hydrophobic hybrid films by sol-gel processing, using the mixtures of perfluoroalkylsilane (FAS13) and tetraethylorthosilicate (TEOS), with addition of titanium(IV) isopropoxide (TIP). The relationship between surface roughness, contact angle, and surface modification was investigated and discussed.

RESULTS AND DISCUSSION

FT-IR studies

FT-IR spectra of hybrid materials (placed into plastic vials and dried at room temperature)

containing TEOS and FAS13 at different molar ratios (1:1, 1:5, and 5:1, respectively) are shown in Fig. 1. In all samples, the bands between 1100-1050 and 840-800 cm^{-1} are observed and are assigned to Si-O-C stretching and deformation vibrations.³⁷ The peaks at 1000-1100 cm^{-1} interval, $\sim 810 \text{ cm}^{-1}$ and $\sim 455 \text{ cm}^{-1}$, respectively, are assigned to the Si-O-Si symmetric and asymmetric stretching vibration which indicates the successful hydrolysis and polycondensation reactions of TEOS and FAS13 in all samples.^{37,38} Weaker band located at ~ 650 has been attributed to Si-O-Si stretching vibrations.³⁹ The peak at about 700 cm^{-1} was located in all samples and corresponding to Si-C stretching motion.⁴⁰ The intense bands at 1138 cm^{-1} and 1190 cm^{-1} , respectively correspond to C-F stretching of $-\text{CF}_3$ and $-\text{CF}_2$.^{37,41,42} The peaks with smaller intensity between 640-620 cm^{-1} interval are attributed to the chain stretching and wagging modes of CF_2 bond, while the peak at $\sim 560 \text{ cm}^{-1}$ is assigned to bending and rocking modes.^{43,44} The presence of additional new peaks arising from the fluorinated functional groups confirms that the coating films on glass substrate were successfully made from the solution of alkoxides of TEOS and FAS13.

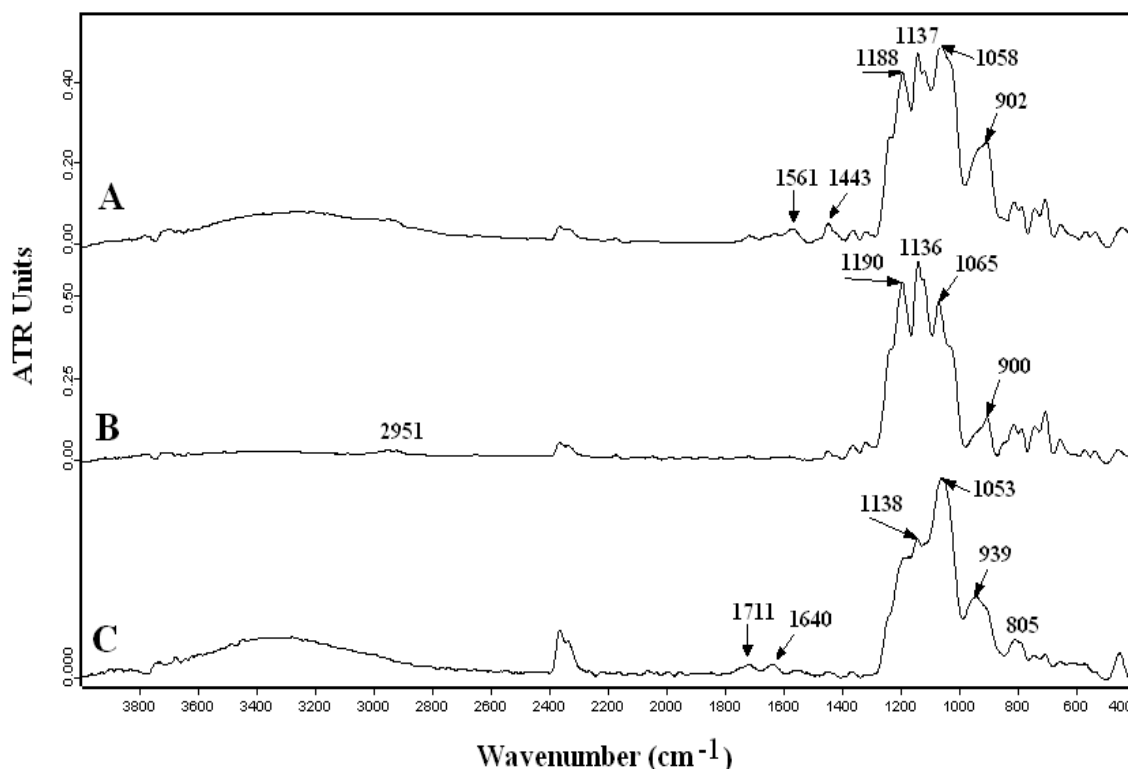


Fig. 1 – FTIR spectra of the hybrid materials (placed into plastic vials and dried at room temperature) containing TEOS and FAS13 at different molar ratios: (A) 1:1, (B) 1:5, and (C) 5:1, respectively.

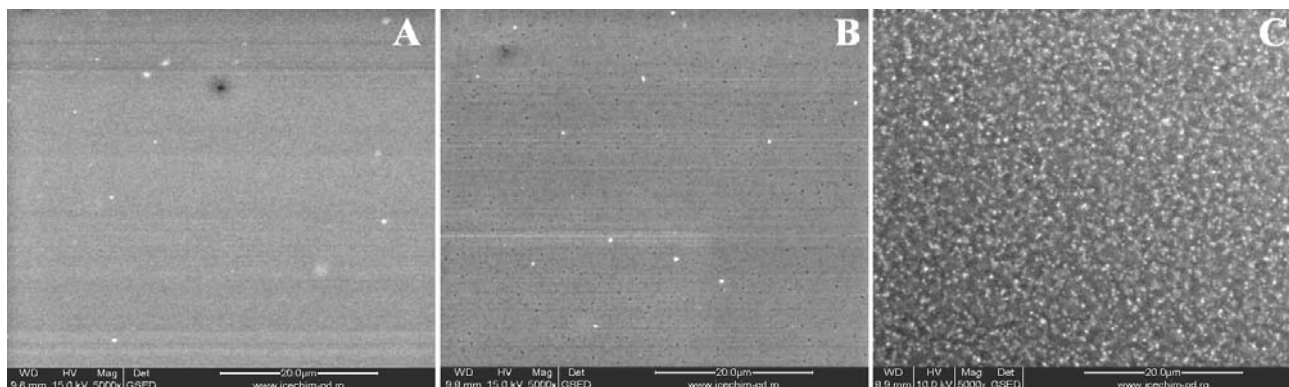


Fig. 2 – ESEM images of hybrid films containing TEOS/FAS13 at different molar ratio: (A) 1:1, (B) 1:5, (C) 5:1.

Surface morphological studies

In the present study, before the deposition of the alkoxide solutions containing TEOS and FAS13 on glass substrates, it was necessary to treat the glass substrates by placing in a fluoroalkylsilane (FAS13)/ethanol solutions to form a stable fluorosilanated layer on the silica surfaces. In this way, the compatibility between treated glass substrate and alkoxide solutions containing TEOS and FAS13 was successfully realized. From experimental point of view, this method used to obtain coating films on fluorinated glass substrates with FAS13 is reported for the first time.

The surface morphology of the hybrid films, which were deposited onto treated clean glass slides and dried at room temperature, are presented in Fig. 2. Analyzing this Fig. can be observed that the film prepared from TEOS:FAS13 molar ratio of 5:1 have rough microstructure (Fig. 3C), whereas the surfaces of the films prepared from TEOS:FAS13 molar ratios of 1:1, and 1:5, respectively, were smoother (Figures 3 A and B). It may be noted that the film surface becomes rougher with increasing of hills and valleys distributed on the film surface. In our case, hills and valleys increased in film prepared from TEOS:FAS13 molar ratio of 5:1 as compared to films prepared from TEOS:FAS13 molar ratios of 1:1, and 1:5, respectively. This phenomenon can be due to the aggregates formed by hydrogen bonding or condensation of the hydroxyl groups from TEOS at the film surface. In case of film with TEOS:FAS13 molar ratio of 5:1, the silica concentration is maximum, compared with other films, that provide higher roughness.

Static contact angle measurements

Based on Young equation, Wenzel equation, and Cassie–Baxter equation,^{45,46} many researchers

were showed that the surface energy or surface structure (roughness) can influence the contact angle of liquid droplets on solid surfaces.⁴⁷⁻⁵¹ The Wenzel equation predicts that wetting is enhanced by roughness, when contact angle is $< 90^\circ$; and the wetting is lessened by roughness, when contact angle is $> 90^\circ$. The Cassie–Baxter model assumes that the liquid forms a composite surface made of solid, liquid, and air, and the liquid does not fill the grooves on the rough surface.

Fig. 3 shows the values of water contact angle obtained for the hybrid films. The hydrophobic character of the film surface was observed for all hybrid film. In previous study, it was demonstrated that the silica film surface containing only TEOS, present hydrophilic properties.¹¹ The surface wettability can be changed from hydrophilic to hydrophobic, by adding precursor with hydrophobic organic group. Analyzing Fig. 3, it can be observed that the water contact angle increase from $97^\circ \pm 2$ (for film containing TEOS:FAS13 molar ratio of 1:1) to $\sim 100^\circ \pm 0.8$ (for films containing TEOS:FAS13 molar ratios of 1:5 and 5:1, respectively). This increase in water contact value may be attributed to the rough microstructure obtained on these surfaces.⁵² It can be deduced from these results that the coating films are hydrophobic, having fluorinated species present on surfaces. In case of films containing TEOS:FAS13 molar ratios of 1:5 and 5:1, respectively, the hydrophobic perfluoroalkyl groups (R_fSiO-) originating from FAS13 are mainly enriched at the coating film-air interface and two layers probably exist in the coating films.³⁷ From Fig. 3, it can be observed that the film with TEOS:FAS13 molar ratio of 1:5 have the same value of water contact angle compared with film containing TEOS:FAS13 molar ratios of 5:1. This observation can be explained by the fact that

the film with TEOS:FAS13 molar ratio of 1:5 contain more perfluoroalkyl groups which provide an filmogene and smooth surface, while the film with TEOS:FAS13 molar ratio of 5:1 contain lower perfluoroalkyl groups which leads to the formation of rough microstructure and according to Cassie-Baxter equation assure an higher contact angle. In the last case, due to the higher surface roughness, the density of the fluorinated species on the particles' surface can increase. Both effect of roughness and low surface energy molecules on the deposited films containing TEOS:FAS13 molar ratios of 1:5 and 5:1, respectively, can assure the higher water contact angles.

The higher water contact angle values of the film surfaces containing TEOS:FAS13 molar ratios 1:5 and 5:1, respectively, compared with that of the film surface containing TEOS:FAS13 molar ratio 1:1 (smooth surface) suggests that the surface texturing has an importance in the improving the surface hydrophobicity. In previous studies, it was shown that the interaction of water with a hydrophobic surface is primarily a function of van der Waals interactions and is independent of electrostatic interactions.⁵³ In our study, it can be concluded that the wettability behavior is intrinsically governed by the surface chemical modification promoted by the insertion of alkyl chains within hybrid films. Hydrophobic thin films obtained by sol-gel process using alkoxide solutions, under acidic conditions, with addition of titanium(IV) isopropoxide (TIP) are still at the beginning and from the best of our knowledge these thin films modified with

perfluorooctyltriethoxysilane (FAS13) have not been studied before. In previous study, the hydrophobic character of coatings films on untreated glass substrate (obtained by sol-gel method from solutions containing different precursors (tetraethylorthosilicate (TEOS), methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES), vinyltriethoxysilane (VTES), octyltriethoxysilane (OTES)), was shown.¹¹

Antireflection characteristics of hybrid films

Fig. 4 shows the diffuse reflectance analysis as a function of a wavelength of the visible light, indicating the anti-reflective character of the hybrid films deposited on glass slides. The reflectance of hybrid films at 550 nm was about 7% - TEOS:FAS13 = 1:1, 6.8% - TEOS:FAS13 = 1:5, and 11.2% - TEOS:FAS13 = 5:1, respectively. It can be seen in this Fig. that the samples containing TEOS:FAS13 molar ratios 1:1 and 1:5, respectively, have the lowest diffuse reflectance. The antireflection effect of these films can be responsible for further enhancement of transparency. In case of hybrid film with TEOS:FAS13 molar ratio 5:1 was observed the higher diffuse reflection effect supported by the increase of the roughness of film surface.

This result is in good agreements with ESEM measurements, which demonstrated that the hybrid film containing TEOS:FAS13 molar ratio of 5:1 have rough microstructure.

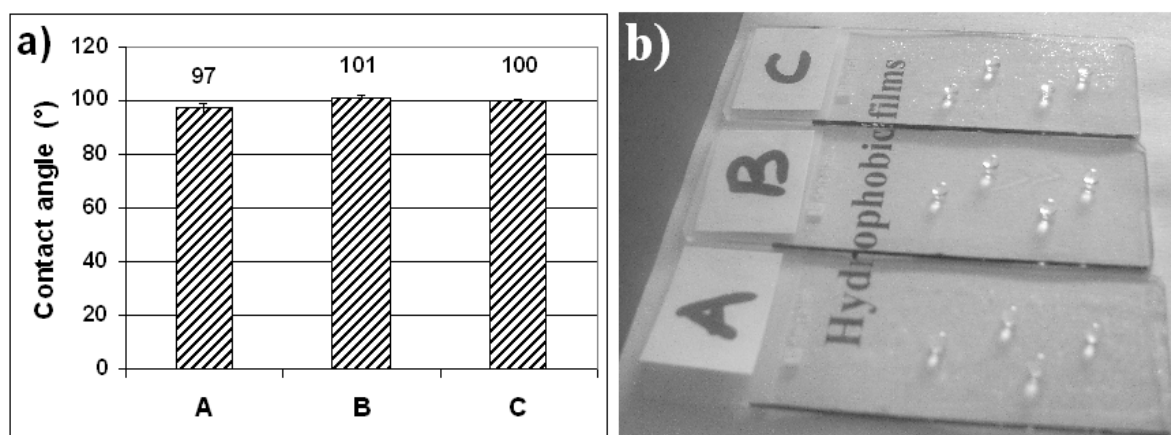


Fig. 3 – a) Water contact angle values and b) shape of the water droplets on hybrid films prepared with TEOS:FAS13 at different molar ratio: (A) 1:1, (B) 1:5, (C) 5:1, deposited on glass slides.

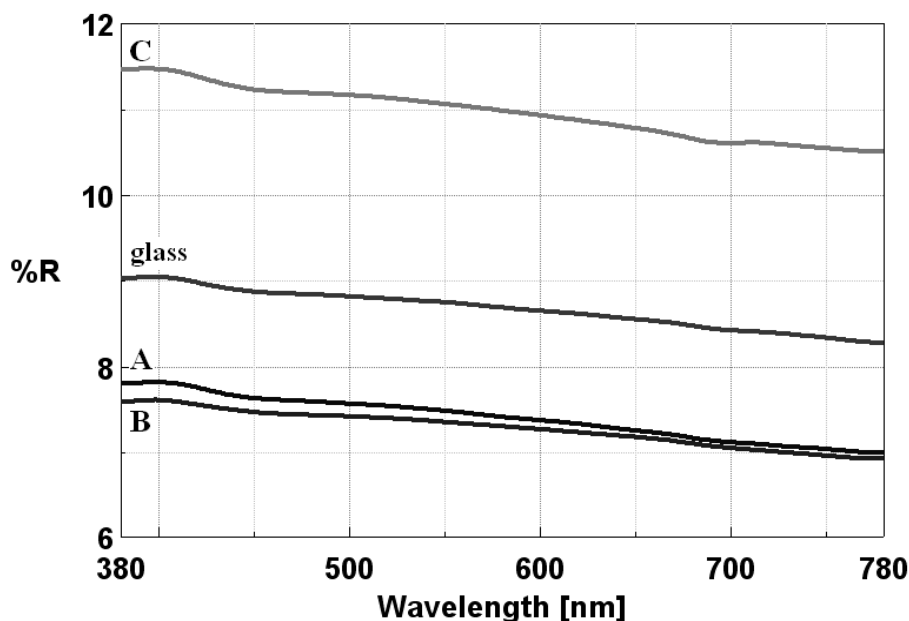


Fig. 4 – Diffuse reflectance spectra of the hybrid films deposited on glass slides containing TEOS:FAS13 at different molar ratio: (A) 1:1, (B) 1: 5, and (C) 5:1, respectively.

EXPERIMENTAL

Materials

The alkoxy silanes tetraethoxysilane (TEOS, from Merck-Schuchardt), and 1H, 1H, 2H, 2H -perfluorooctyltriethoxysilane (FAS13, from Aldrich) were used as purchased. Ethanol was obtained from Merck (99.9%). Titanium(IV) isopropoxide (TIP, Aldrich) was used as cross-linking agent under sol-gel conditions. Maleic anhydride (MA, from Fluka) was added as complexing/retardant agent in the sol-gel reaction. HCl 0.1M (from Riedel-de Haën) was used as a catalyst for rapid hydrolysis.

Preparation of the hybrid silica films

The coating solutions were prepared by sol-gel process, mixing TEOS, FAS13, and ethanol (1 mL) and reacting with HCl 0.1M (0.112 mL) for 1h, under continuous stirring at the room temperature (25°C). The molar ratio between TEOS:FAS13 was 1:1, 1:5 and 5:1, respectively. In the next stage, under continuous stirring, maleic anhydride (MA) (0.03 g) was added to the solution. After complete MA dissolution, is added in dropwise the cross-linking agent (titanium(IV) isopropoxide, TIP, 0.16 mL) with HCl 0.1M (0.24 mL) and mixed for another hour at room temperature (see Scheme 1). The compositions of the coatings solutions are summarized in Table 1. The hybrid materials were obtained by being placed into polyethylene vials (characterized by FT-IR) and deposited on a treated glass slides by draw down sample coating with the manual applicator to obtain hybrid films (characterized by ESEM, UV-VIS-NIR and contact angle measurements).

Surface fluoroalkylsilane treatment

Glass slides pretreatment, to ensure uniform wetting, was carried out by cleaning with detergent, followed by alcohol

and deionised water rinses. Then, the glass slides were placed in a fluoroalkylsilane (perfluorooctyltriethoxysilane, FAS13, 0.25 mL)/ethanol (24.75 mL) solution for two days to allow adsorption of a FAS13 layer onto the SiO₂ surface. Subsequently the glass slides were dried at room temperature for 30 min and used to obtain stable hybrid films.

Characterization

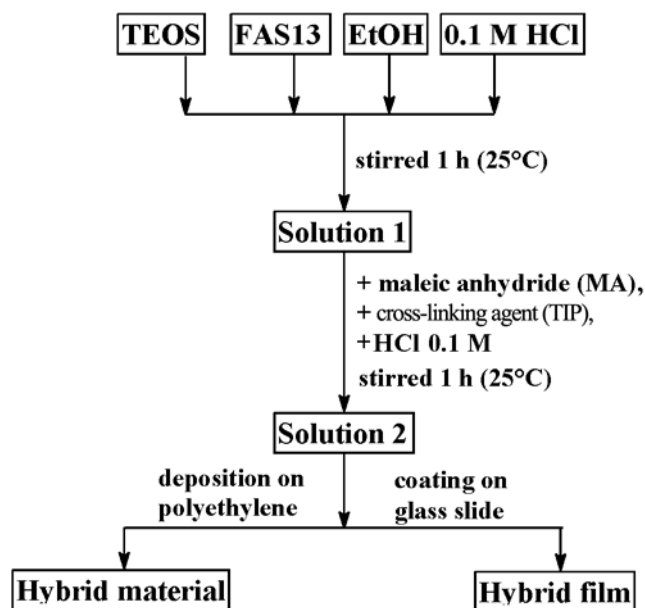
All synthesised samples were dried at the room temperature (25°) and characterized both as hybrid materials (placed into plastic vials) and as films deposited onto clean glass slides.

FT-IR spectra of hybrid materials dried at room temperature (placed into plastic vials), in the range 400-4000 cm⁻¹, using a Fourier transforms infrared spectrometer (Tensor 37 from Bruker) were measured in ATR mode using Golden Gate unite, which gave the information about the various chemical bonds such as Si-OH, Si-C, C-H, and Si-O-Si.

The surface morphology of the hybrid films deposited onto clean glass slides was visualized by Environmental Scanning Electron Microscopy (ESEM) (FEI QUANTA 200). The ESEM images were obtained in low vacuum mode.

The wetting properties of the hybrid films deposited onto clean glass slides and dried at room temperature) were performed using the contact angle measurements (KSV CAM 200). The reported values of contact angle were obtained as average of five measurements (liquid droplets (10 μ) deposited in various region of the film).

The UV-VIS-NIR reflectance spectra of the hybrid films deposited onto clean glass slides were obtained with an UV-VIS-NIR-Jasco V-570 spectrophotometer. Reflectance of coated samples was determined by diffuse reflectance analysis, in the range 380-780 nm.



Scheme 1 – Experimental procedure for preparation of hybrid materials.

Table 1

Composition of coating solution as a function of TEOS:FAS13 molar ratio

Reagent	Coating solution with TEOS:FAS13 at different molar ratio		
	A 1:1	B 1:5	C 5:1
TEOS (mL)	0.52	0.52	2.54
FAS13 (mL)	0.715	3.578	0.715
Ethanol (mL)	1	1	1
HCl 0.1M (mL)	0.112 + 0.24	0.112 + 0.24	0.112 + 0.24
Titanium(IV) isopropoxide (TIP) (mL)	0.16	0.16	0.16
Maleic anhydride (g)	0.03	0.03	0.03

CONCLUSIONS

Hydrophobic coating films on glass substrate were prepared by sol-gel method using alkoxide solutions contained TEOS and FAS13 at different molar ratios, under acidic conditions, with addition of titanium(IV) isopropoxide (TIP). In this study, the hydrophobic properties were obtained by surface modification using fluoroalkylsilane (FAS13). The water contact angle values of the coating films are high, at 97° and 100°, respectively. FT-IR spectra show the presence of C-F and Si-O bonds resulting from alkoxide solutions of TEOS and FAS13. It was observed that the hydrophobicity and optical transparency can be achieved simultaneously by controlling the surface roughness. These coatings may have numerous applications in industrial use on large scale, such as on windows and car windshields.

Acknowledgements: Violeta Purcar acknowledges the financial support of the strategic grant POSDRU/89/1.5/S/58852, Project “Postdoctoral programme for training scientific

researchers” cofinanced by the European Social Fund within the Sectoral Operational Program Human Resources Development 2007-2013; Catalin Ilie Spataru acknowledges the financial support funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Roumanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76909; Valentin Raditoiu acknowledges the financial support of the grand funded by the Roumanian National Authority for Scientific Research, CNDI-UEFISCDI, project number 3.2-1391.

REFERENCES

1. H. Yang, X. Zhang, Z.-Q. Cai, P. Pi, D. Zheng, X. Wen, J. Cheng and Z.-R. Yang, *Surf. Coat. Tech.*, **2011**, *205*, 5387-5393.
2. M. J. Liu, Y. M. Zheng, J. Zhai and L. Jiang, *Acc. Chem. Res.*, **2010**, *43*, 368-377.
3. J. H. Zhang, X. L. Sheng and L. Jiang, *Langmuir*, **2009**, *25*, 1371-1376.
4. G. Schottner, *Chem. Mater.*, **2001**, *13*, 3422-3435.
5. C. X. Wang, T. J. Yao, J. Wu, C. Ma, Z. X. Fan, Z. Y. Wang and B. Yang, *A.C.S. Appl. Mater. Interfaces*, **2009**, *1*, 2613-2617.

6. S. A. Kulinich, S. Farhadi, K. Nose and X. W. Du, *Langmuir*, **2011**, *27*, 25-29.
7. Y. Li, L. Li and J.G. Sun, *Angew. Chem. Int. Edit.*, **2010**, *49*, 6129-6133.
8. O. Duyar and H. Z. Durusoy, *Turk. J. Phys.*, **2004**, *28*, 139-144.
9. X. Liu and J. He, *J. Phys. Chem. C*, **2009**, *113*, 148-152.
10. H. Kikuta, H. Toyota and W. Yu, *Opt. Rev.*, **2003**, *10*, 63-73.
11. V. Purcar, I. Stamatina, O. Cinteza, C. Petcu, V. Raditoiu, M. Ghiurea, T. Miclaus and A. Andronie, *Surf. Coat. Tech.*, **2012**, *206*, 4449-4454.
12. R. Ianchis, M. C. Corobea, D. Donescu, I. D. Rosca, L. O. Cinteza, L. C. Nistor, E. Vasile, A. Marin and S. Preda, *J. Nanopart. Res.*, **2012**, *14*, 1-12.
13. R. Ianchis, L. O. Cinteza, D. Donescu, C. Petcu, M. C. Corobea, M. Ghiurea, R. Somoghi and C. Spataru, *Appl. Clay Sci.*, **2011**, *52*, 96-103.
14. D. K. Sarkar and N. Saleema, *Surf. Coat. Tech.*, **2010**, *204*, 2483-2486.
15. N. Saleema, D. K. Sarkar, R. W. Paynter and X. G. Chen, *A.C.S. Appl. Mater. Interfaces*, **2010**, *2*, 2500-2502.
16. G. Piret, Y. Coffinier, C. Roux, O. Melnyk and R. Boukherroub, *Langmuir*, **2008**, *24*, 1670-1672.
17. R. Fürstner, W. Barthlott, C. Neinhuis and P. Walzel, *Langmuir*, **2005**, *21*, 956-961.
18. M. H. Jin, X. J. Feng, J. M. Xi, J. Zhai, K. Cho, L. Feng and L. Jiang, *Macromol. Rapid Commun.*, **2005**, *26*, 1805-1809.
19. M. F. Wang, N. Raghunathan and B. Ziaie, *Langmuir*, **2007**, *23*, 2300-2303.
20. N. Zhao, F. Shi, Z. Wang and X. Zhang, *Langmuir*, **2005**, *21*, 4713-4716.
21. B. T. Qian and Z. Q. She, *Langmuir*, **2005**, *21*, 9007-9009.
22. X. D. Wu, L. J. Zheng and D. Wu, *Langmuir*, **2005**, *21*, 2665-2667.
23. C. J. Brinker, G. W. Scherer, "Sol-gel science. The physics and chemistry of sol-gel processing", Academic Press, San Diego, 1990, p.790-792.
24. C. F. Wang, Y. T. Wang, P. H. Tung, S. W. Kuo, C. H. Lin, Y. C. Sheen and F. C. Chang, *Langmuir*, **2006**, *22*, 8289-8292.
25. J. Bravo, L. Zhai, Z. Wu, R. E. Cohen and M. F. Rubner, *Langmuir*, **2007**, *23*, 7293-7298.
26. M. Hikita, K. Tanaka, T. Nakamura, T. Kajiyama and A. Takahara, *Langmuir*, **2005**, *21*, 7299-7302.
27. H. M. Shang, Y. Wang, K. Takahashi and G. Z. Cao, *J. Mater. Sci.*, **2005**, *40*, 3587-3591.
28. C. F. Wang, S. F. Chiou, F. H. Ko, C. T. Chou, H. C. Lin, C. F. Huang and F. C. Chang, *Macromol. Rapid Commun.*, **2006**, *27*, 333-337.
29. A. Cannavale, F. Fiorito, M. Manca, G. Tortorici, R. Cingolani and G. Gigli, *Build. Environ.*, **2010**, *45*, 1233-1243.
30. K. Y. Huang, Z. P. He and K. J. Chao, *Thin Solid Films*, **2006**, *495*, 197-204.
31. S. A. Kulkarni, S. B. Ogale and K. P. Vijayamohan, *J. Colloid Interface Sci.*, **2008**, *318*, 372-379.
32. R. A. Orozco-Teran, B. P. Gorman, D. W. Mueller, M. R. Baklanov and R. F. Reidly, *Thin Solid Films*, **2005**, *471*, 145-153.
33. H. Y. Kwong, M. H. Wong, Y. W. Wong and K. H. Wong, *Appl. Surf. Sci.*, **2007**, *253*, 8841-8845.
34. X. L. Sun, Z. P. Fan, L. D. Zhang, L. Wang, Z. J. Wei, X. Q. Wang and W. L. Liu, *Appl. Surf. Sci.*, **2011**, *257*, 2308-2312.
35. D. Frugier, P. Vaneeckhoutte, A. Robert, P. Chartier and Y. Leclaire, *European Pat. Application* 675087, Oct. 4, 1995.
36. J.-D. Brassard, D. K. Sarkar and J. Perron, *A.C.S. Appl. Mater. Interfaces*, **2011**, *3*, 3583-3588.
37. H.-J. Jeong, D.-K. Kim, S.-B. Lee, S.-H. Kwon and K. Kadono, *J. Colloid Interf. Sci.*, **2001**, *235*, 130-134.
38. S. Dirè, E. Pagani, F. Babonneau, R. Ceccato and G. Carturan, *J. Mater. Chem.*, **1997**, *7*, 67-73.
39. C. M. Müller, A. Moninelli, M. Karlowatz and A. Aleksandrov, *J. Phys. Chem. C*, **2012**, *116*, 37-43.
40. G. Gua, Z. Zhang and H. Dang, *Mater. Res. Bull.*, **2004**, *39*, 1037-1044.
41. A. Hozumi and O. Takai, *Appl. Surf. Sci.*, **1996**, *103*, 431-441.
42. Y. Han, J. Wakita, S. Kurok, X. Wang and S. Ando, *J. Photopolym. Sci. Technol.*, **2008**, *21*, 143-150.
43. S. T. Li, E. Arenholz, J. Heitz and D. Bäuerle, *Appl. Surf. Sci.*, **1998**, *125*, 17-22.
44. M. Womack, M. Vendan and P. Molian, *Appl. Surf. Sci.*, **2004**, *221*, 99-109.
45. R. N. Wenzel, *Ind. Eng. Chem.*, **1936**, *28*, 988-994.
46. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, **1944**, *40*, 0546-0550.
47. H. J. Lee and S. Michielsen, *J. Text. I.*, **2006**, *97*, 455-462.
48. H. M. Shang, Y. Wang, S. J. Limmer, T. P. Chou, K. Takahashi and G. Z. Cao, *Thin Solid Films*, **2005**, *472*, 37-43.
49. J.-Y. Shiu, C.-W. Kuo, P. Chen and C.-Y. Mou, *Chem. Mater.*, **2004**, *16*, 561-564.
50. G. Carbone and L. Mangialardi, *Eur. Phys. J. E*, **2005**, *16*, 67-76.
51. S. S. Latthe, A. B. Gurav, C. S. Maruti and R. S. Vhatkar, *J. S. E. M. A. T.*, **2012**, *2*, 76-94.
52. J.-D. Brassard, D. K. Sarkar and J. Perron, *Appl. Sci.*, **2012**, *2*, 453-464.
53. H. M. Hügel and N. Jackson, *Appl. Sci.*, **2012**, *2*, 558-565.

