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SURFACE AND COATING TECHNOLOGY

Deposition of Silicon Dioxide Antireflection Coatings on Glass by Sol-Gel Method in the Presence of Pluronic® F127 Block-Copolymer

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Abstract—Hydrolysis of tetraethoxysilane in the presence of Pluronic® F127 block-copolymer in a water-alcohol mixture was used to obtain sol-formulations from which antireflection coatings were deposited onto silicate glass by the dip-coating method and then calcined at high temperatures (200−500°C). Electron spectroscopy was used to study the dependence of the optical transmission of glass samples with a coating on the concentration of Pluronic® F127 in the starting sol, introduction of organic additives (toluene) into the sol, and calcination temperature of the glasses obtained. The refractive index and hardness of the film coatings were determined and their surface structure was assessed.

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Matrix synthesis of mesoporous silicates and aluminosilicates open up wide prospects for practical use of new nanomaterials in catalysis, microelectronics, optics, biotechnology, etc. [1−3]. Mesoporous materials are produced by the sol-gel method in the presence of surfactants, both low-molecular and macromolecular amphiphilic block-copolymers [4, 5]. Particular attention is given to studies on nonionogenic ternary amphiphilic block-copolymers of the Pluronic® type (BASF, Germany) having the chemical structure $H(OCH_2CH_2)_m(OCH(CH_3)CH_2)_n(OCH_2CH_2)_mOH$, where m and *n* are various numbers. In the pioneering studies by Mobil Oil Corp. [1, 3], mesoporous silicates and aluminosilicates were obtained only in the form of powders because the authors were primarily interested in practical application of new nanomaterials as catalysts in oil processing. A procedure has been developed for obtaining nanoporous silicon dioxide film coatings with low dielectric constant [6]. The role of the surfactant in the sol-gel process was played by Pluronic® P123 ($m = 20$, $n = 70$). It should be noted that no systematic studies of the optical and physical properties of antireflection coatings produced from silicon dioxide sols containing various block polymers of the Pluronic® type were carried out.

The goal of the present study was to examine the optical transmission of a silicate glass with a coating and the refractive index, hardness, and surface profile of the coating produced from silicon dioxide sols containing Pluronic® F127 ($m = 106$, $n = 70$, $M_w = 12\,600$).

EXPERIMENTAL

Tetraethoxysilane (TEOS) was purified by distillation in a vacuum, the content of the main substance was 99.9% (determined by liquid chromatography). As solvents served ethanol [96.0 vol %, GOST (State Standard) 51652−2000] and deionized water ($\rho \geq 10$ MΩ cm). The Pluronic® F127 block-copolymer (henceforth F127, Sigma-Aldrich), hydrochloric acid (37 wt %, chemically pure), and toluene (chemically pure) were used without preliminary preparation.

Synthesis of silicon dioxide sol in the presence of F127 block-copolymer. To 29.35 mL of ethanol was added dropwise under agitation the necessary amount of hydrochloric acid (0.03, 0.07, 0.09, 0.12, 0.14 mL), and the volume of the mixture was brought to 30.00 mL with deionized water. Then, the target amount of F127 was added to the resulting solution (0, 0.208, 0.416, 0.624, 0.832, 1.040, 1.247, 1.455 g) and the mixture was agitated for 1 h at room temperature. TEOS was added dropwise (3.12 g, 15 mmol) to the resulting transparent solution and the mixture was agitated during 12 h. The sol was aged in the course of 18 h at room temperature. The concentration of the resulting sol in terms of SiO_2 was 0.45 M. The concentration of F127 varied from 0 to 3.5 mM, and that of HCl, from 0.01 to 0.05 M.

Synthesis of a silicon dioxide sol in the presence of F127 block-copolymer and a hydrophobic additive (toluene). To 25.00 mL of ethanol were added dropwise 0.03 mL of hydrochloric acid, 0.66 mL of water, and 0.832 g of F127 and the mixture was agitated for 1 h at room temperature. The necessary amount of toluene (0.17, 0.33, 0.67, 1.33 mL) was added to the resulting solution, the volume of the mixture was brought to 30.00 mL with ethanol, and it was agitated for 3 h more. Then TEOS was added dropwise (3.12 g, 15 mmol) to the reaction mixture and the mixture was agitated for 12 h. The sol aged during 18 h at room temperature. The concentration of the resulting sol in terms of SiO_2 was 0.45 M. The concentration of toluene varied from 0.05 to 0.4 M, that of F127 was 2.0 mM, and that of HCl, 0.01 M.

Deposition of a SiO_2 xerogel film onto silicate glass. As substrates served 25 × 75 × 1 mm object silicate glasses for microscopy. The refractive index of silicate glass was 1.506. The glass surface was cleaned to remove contaminants by dipping into an alkali solution with hydrogen peroxide, washed with deionized water, and dried in a thermostat at 150°C for 6–8 h. The coatings were deposited onto glass by the dip-coating method at a temperature of 20–25°C and humidity of 40–60%. This was done on an installation for deposition of coatings, designed and fabricated at the laboratory [7]. Glasses with coatings were kept at room temperature for 18 h, and then annealed for 2 h at various temperatures (200, 300, 400, 500°C). A thermogravimetric analysis (TGA) of F127 block-copolymer was made on a Perkin Elmer Pyris 6 TGA thermogravimetric analyzer in the atmosphere of air and nitrogen (heating rate 5 deg min^{-1}, flow rate 80 mL min^{-1}). The optical transmission of the coated glasses was determined on a Perkin Elmer Lambda 25 spectrometer. The thickness and the refractive index of the film coatings were determined with an LEF-3M1 ellipsometer. The surface structure of the films was analyzed with a Solver-P47 atomic-force microscope. The hardness of the coatings was determined with a pencil-type hardness meter in conformity with GOST ISO (International Standardization Organization) 15184.

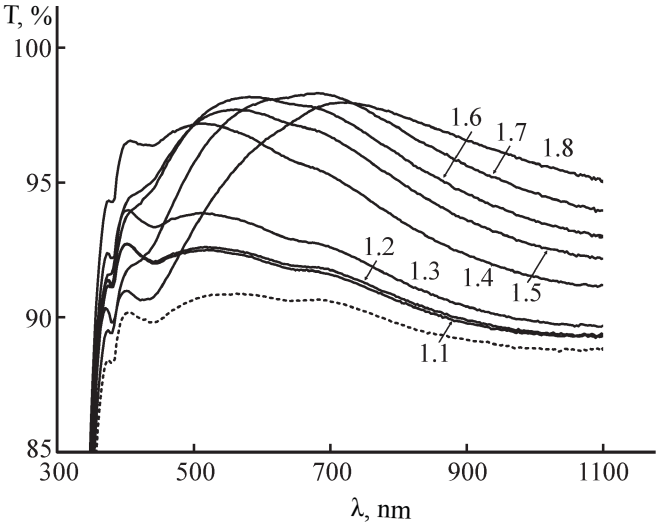


Fig. 1. Electronic spectra of transmission T of glasses with coatings produced on the basis of formulations 1.1–1.8. Curing temperature 500°C; the same for Figs. 4–6. (λ) Wavelength; the same for Figs. 2, 4, 5. The dashed line shows the spectrum of glass without a coating; the same for Figs. 2, 4, 5.

RESULTS AND DISCUSSION

According to electronic-spectroscopic data, the film coatings obtained exhibit an increase in the antireflection capacity with increasing Pluronic® F127 concentration in the starting sol (Table 1).

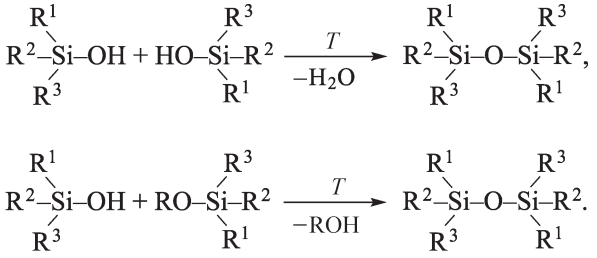
For example, glasses with coatings obtained from 1.1–1.8 formulations at 500°C show a rise in the optical transmission from 92.5 to 98.3% upon an increase in the concentration of the block-copolymer in solution to 3 mM (the optical transmission of a glass having no coating is 90.9%) (Fig. 1).

The coatings of this kind exhibit an antireflection capacity because a mesoporous structure of silicon oxide is formed on the basis of F127 block-copolymer [8] in hydrolysis of TEOS, with nanoparticles growing in size as the concentration of the block-copolymer increases. In calcination of the samples obtained, the template F127 is removed thereby forming a mesoporous SiO_2 skeleton whose structure is provided by the mutual cross-linking of nanoparticles.

Table 1. Optical properties of glasses with coatings based on formulations 1.1−1.8, calcined at various temperatures

Formulation parameters			Maximum optical transmission T, %, at indicated wavelength λ, nm							
formulation	[F127], M	viscosity, cP	500°C		400°C		300°C		200°C	
			T	λ	T	λ	T	λ	T	λ
1.1	0	2.25	92.5	510	92.8	517	92.7	533	92.9	519
1.2	0.5	2.59	92.7	517	93.1	516	93.4	523	92.9	519
1.3	1.0	3.00	93.9	513	94.5	516	93.8	538	92.9	552
1.4	1.5	3.39	97.2	510	97.3	524	97.0	576	94.2	684
1.5	2.0	3.40	97.7	558	97.8	583	97.9	676	94.2	723
1.6	2.5	4.26	98.2	580	97.7	684	98.1	692	94.5	781
1.7	3.0	4.74	98.3	672	98.0	692	97.6	724	95.0	932
									95.7	395
1.8	3.5	4.95	98.0	725	97.2	757	97.0	873	95.9	1095
									97.7	399

When an antireflection coating is calcined, the following chemical reactions occur:



Thus, an increase in the content of F127 results in that the coating becomes more porous and, as a consequence, its refractive index decreases (Table 2). Raising the content of F127 further (3.5 mM) leads to a decrease in the optical transmission due to the significant loosening and disruption of the mesoporous structure, with the refractive index somewhat increasing.

It is known that the wavelength at which the maximum optical transmission is observed is directly proportional to the refractive index and thickness of a single-layer antireflection coating ($\lambda = 4nd$). With increasing concentration of the block-copolymer in solution, the viscosity of the latter grows (Table 1) and the content of F127 in a film becomes higher, which leads, in the end, to an increase in the thickness of a coating produced

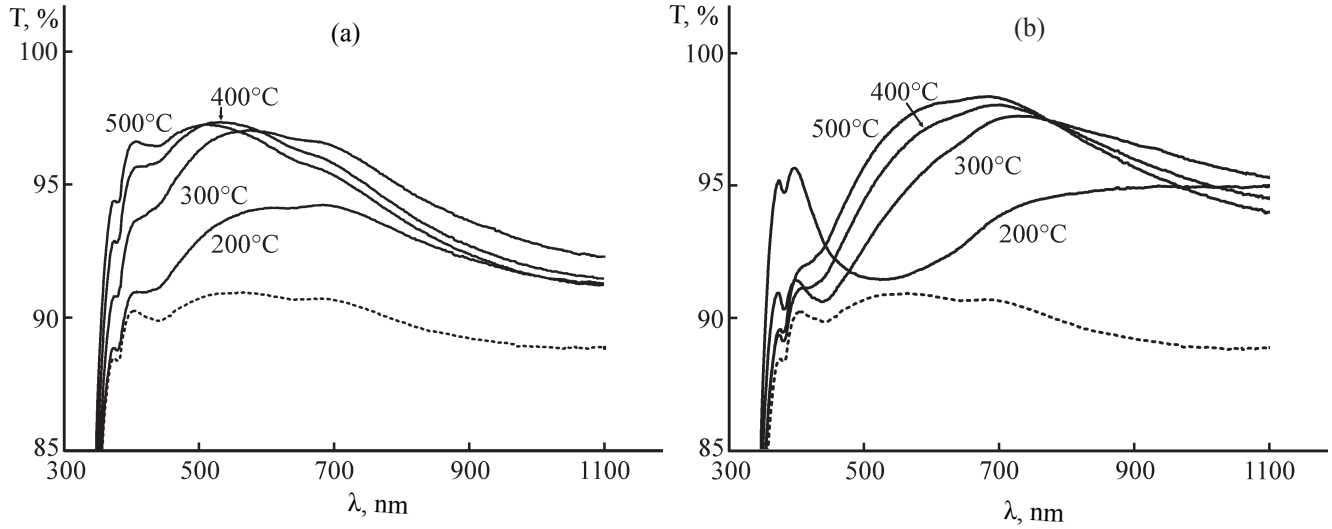


Fig. 2. Electronic spectra of transmission T of glasses with coatings based on formulations (a) 1.4 and (b) 1.7, calcined at various temperatures.

Table 2. Parameters of coatings based on formulations 1.1−1.8, calcined at various temperatures

Formulation	Coating hardness			Refractive index			Coating thickness, nm		
	500°C	400°C	300°C	500°C	400°C	300°C	500°C	400°C	300°C
1.1	9H	9H	9H	1.447	–	–	50.4	–	–
1.2	9H	9H	9H	1.456	–	–	55.0	–	–
1.3	9H	9H	8H	1.436	–	–	89.0	–	–
1.4	8H	4H	2H	1.416	1.412	1.400	97.7	97.7	109.8
1.5	4H	2B	2B	1.375	1.390	1.396	112.8	112.9	148.3
1.6	1H	5B	5B	1.362	1.356	1.335	134.1	149.3	164.0
1.7	5B	5B	5B	1.333	1.330	1.326	152.0	162.3	176.6
1.8	5B	5B	5B	1.362	–	–	173.5	–	–

by the dip-coating method. Thus, the maximum optical transmission shifts to longer wavelengths with increasing F127 concentration in solution.

As the temperature at which glass samples with deposited film coatings are calcined is lowered, the refractive index decreases (samples based on formulations 1.1−1.5, 400°C; Table 1). Supposedly this occurs because of the formation of a less dense coating structure at lower temperatures. By contrast, samples with higher concentration of the block-copolymer (samples based on formulations 1.6−1.8, 400°C) demonstrate a lower optical transmission under these conditions, which points to an even more pronounced loosening and disruption of the mesoporous structure of a film, with the coating hardness sharply decreasing. Figure 2 shows transmission spectra of samples based on formulations 1.4 (a) and 1.7 (b).

F127 is not fully removed under the experimental conditions at a curing temperature of 200°C, which is reflected in the decrease in the optical transmission of glass with the coatings under study and in the low hardness of these latter (Table 1). According to TGA data, the thermal decomposition of the block-copolymer in air begins at about 200°C and has the maximum rate at around 250°C (Fig. 3).

It is known that, in aqueous solutions of F127, introduction of a hydrophobic additive and, in particular, toluene into the sol leads to coarsening of micelles formed by surfactant molecules due to the solubilization of toluene [9]. In this case, the structure of a coating being obtained becomes more porous and, as a consequence, the antireflection capacity grows.

In the case of aqueous-alcoholic solutions, introduction of toluene (0.5−2 vol %) leads to an insignificant increase in the optical transmission (by 0.5%), with the hardness of the samples being obtained becoming lower (Table 3, Fig. 4).

Doubling the content of the acid in the starting sol also leads to a 0.5% increase in the optical transmission, with further increase in the concentration leading to a gradual decrease in this parameter (Table 3, Fig. 5).

On the whole, the hardness of the coatings obtained shows a dependence on the F127 concentration and calcination temperature (Table 2). Simultaneously, a "borderline" concentration of the block-copolymer was

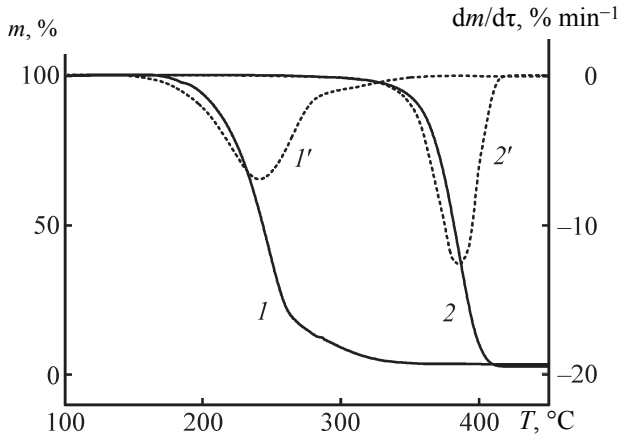


Fig. 3. TGA curves describing the thermal decomposition of Pluronic® F127 in (*1*) air and (*2*) atmosphere of nitrogen. (*m*) Sample mass, (τ) time, and (*T*) temperature. (*1*', *2*') The corresponding differential curves.

Table 3. Optical properties of glasses with coatings based on formulations 2.1−2.4, 3.1−3.4, calcined at various temperatures, and the hardness of the coatings

Formulation parameters			Maximum optical transmission T, %, at indicated wavelength λ, nm				Coating hardness	
formulation	[HCl], M	[toluene], M	500°C		400°C		500°C	400°C
			T	λ	T	λ		
2.1	0.01	0.05	98.3	543	98.2	559	4B	4B
2.2	0.01	0.1	98.3	526	98.2	571	4B	4B
2.3	0.01	0.2	98.3	524	98.3	571	4B	4B
2.4	0.01	0.4	98.4	520	98.2	556	4B	4B
3.1	0.02	–	98.3	524	97.8	592	4B	4B
3.2	0.03	–	98.1	525	98.2	543	4B	4B
3.3	0.04	–	98.2	528	98.3	529	4B	4B
3.4	0.05	–	98.0	536	98.2	545	4B	4B

observed (2.0 mM, sample based on formulation 1.5), below which the hardness of the samples is high (8H−9H, samples based on formulations 1.2−1.4). Further increase in the polymer concentration to 3.5 mM leading to a sharp decrease in hardness down to 5B, with this occurring at both high (500°C) and lower (400, 300°C) temperatures (samples based on formulations 1.6−1.8).

The surface structure of the antireflection coatings was examined by the AFM method. According to the experimental data, the surface is smooth, with the height of irregularities not exceeding 3 nm (Fig. 6). This can be observed for the example of the surface of the coating based on formulation 1.8.

CONCLUSIONS

(1) Introduction of block-copolymer F127 into silicon dioxide sol improves the antireflection capacity

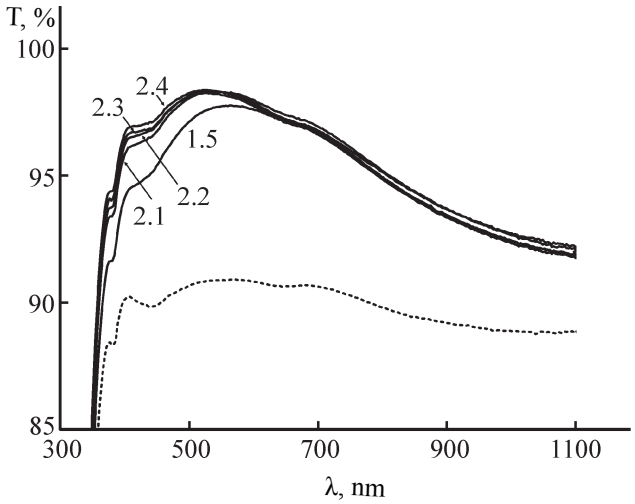


Fig. 4. Electronic spectra of transmission T of glasses with coatings produced on the basis of formulations 2.1−2.4 in the presence of toluene. For comparison, the figure shows the spectrum of a glass with coating based on formulation 1.5; the same for Fig. 5.

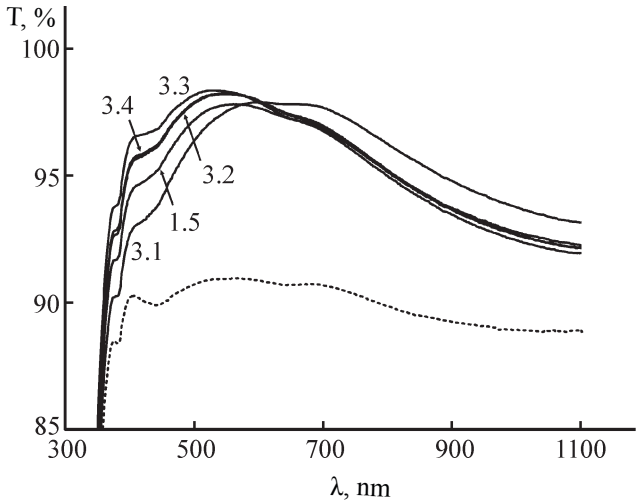


Fig. 5. Electronic spectra of transmission T of glasses with coatings produced on the basis of formulations 3.1−3.4 in the presence of various amounts of hydrochloric acid.

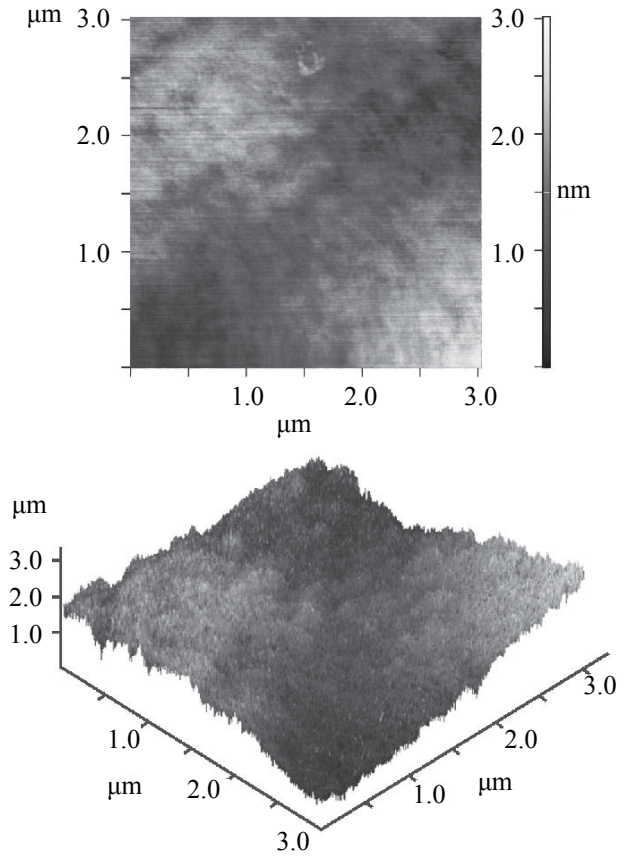


Fig. 6. Micrograph of the surface of a coating based on formulation 1.8, furnished by atomic-force microscopy.

of coatings deposited on silicate glass, with the optical transmission of glass samples being proportional to the F127 concentration in solution.

(2) With increasing F127 concentration in solution, the maximum optical transmission of the glasses is shifted to longer wavelengths.

(3) The hardness of the coatings under study is correlated with the content of F127 in the starting solution. The formulations containing less than 2.0 M of the block-copolymer have a 8H-9H hardness, with further increase in the F127 concentration leading to a sharp decrease in hardness.

(4) An increase in the acid concentration in the sol leads, as also does introduction of toluene, to a slight increase in the optical transmission of a glass with an antireflection coating.

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REFERENCES

1. Kresge, C.T., Leonowicz, M.E., Roth, W.J., et al., *Nature,* 1992, vol. 359, pp. 710–712.
2. Inagaki, S., Fukushima, Y., and Kurod, K.*, J. Chem. Soc., Chem. Commun*., 1993, vol. 8, pp. 680–682.
3. Kresge, Ch.T. and Roth, W.J., *Chem. Soc. Rev*., 2013, vol. 42, pp. 3663–3670.
4. Zhao, D., Huo, Q., Feng, J., et al., *J. Am. Chem. Soc.,* 1998, vol. 120, no. 24, pp. 6024–6036.
5. Yang, P., Zhao, D., Margolese, D., et al., *Nature*, 1998, vol. 396, no. 6707, pp. 152–155.
6. Yunfeng, L., Hongyou, F., Nilesh, D., et al., *J. Am. Chem. Soc*., 2000, vol. 122, pp. 5258–5261.
7. Troitskii, B.B., Denisova, V.N., Novikova, M.A., et al., *J. Appl. Chem*., 2015, vol. 38, no. 5, pp. 746–750.
8. Wu, S.-H., Mou, C.-Y., and Lin, H.-P., *Chem. Soc. Rev*., 2013, vol. 42, pp. 3862–3875.
9. Huang, L. and Kruk, M., *Chem. Mater*., 2015, vol. 27, pp. 679–689.