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Nanostructures of surfaces of silica films obtained by sol—gel method in the presence of organic additives

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The dependence of the antireflection properties of film coatings deposited on the silicate glass obtained by sol—gel method in the presence of organic additives on the dimensions of nanostructures of the silica films was studied.

Key words: mesoporous materials, sol—gel method, silica, antireflections coatings, organic additives, nanostructures.

Starting from the discovery of template synthesis of mesoporous silicates and aluminosilicates,[1,2] sol—gel synthesis of different mesoporous materials in the presence of surfactants or amphiphilic block-copolymers (ABC) rapidly developed.[3,4] Thus, for the first time thin transparent mesoporous silica films with a small refractive index (1.23) were obtained.[5—7] Another method of synthesis of mesoporous powdery materials by sol—gel method with additives of organic hydroxy acids, which do not belong to surfactants or ABC, was also proposed.[8—12]

Recently we have shown,[13—17] that the transparent mesoporous silica films with a small index of refraction (1.20—1.30) were obtained by sol—gel method during hydrolysis of tetraethoxysilane in the presence of organic acids, derivatives of organic acids,[13,14] carbon chain polymers, statistical copolymers,[15] or oligoesters.[16,17] The high antireflection effect of the films on the silicate glass was found.[13—17]

The purpose of the present work is the study of the nanostructures of the film surfaces by atomic force microscopy (AFM) and the influece of film topography on their optical properties.

Experimental

Tetraethoxysilane (TEOS) was purified by triple distillation *in vacuo*; the purity of the substance was 99.9% (according to HPLC). Laprol 1000 is commercially available and was not subjected to additional purification. Poly(methyl methacrylate) (PMMA) was obtained by bulk polymerization of methyl methacrylate in the presence of azoisobutyric acid dinitrile as an initiator and in the presence of butyl ester of thioglycolic acid as a chain transfer agent. The weight-average molecular weight of the polymer was 61800, the number-average molecular weight was 40700, the polydispersity index was 1.52 (determined by gel permeation chromatography). Isopropanol (chemically pure), THF, purified by known procedures, water (bidistilled), and hydrochloric acid (chemically pure) were used.

The procedures for obtaining sol by TEOS hydrolysis in the presence of organic additives and xerogel film deposition on the silicate glass have been described in detail previously.[13—17]

The light transmission in the wavelength range of 200—1100 nm was studied on a Perkin—Elmer Lambda 25 spectrophotometer.

The optical thickness of the films and their refractive indices were determined on an LEF-3M1 ellipsometer.

The images of the film surfaces were obtained on a SOLVER P-47 atomic force microscope (NT—MDT company, Zelenograd); the cantilever made from silicon with a radius of curvature of 10 nm was used.

Results and Discussion

The light transmission curves of both the uncoated glasses and those with double-sided monolayer coatings based on mesoporous silica obtained by sol—gel method in the presence of Laprol 1000 and PMMA are shown in Figs 1, *a* and 1, *b*, correspondingly.

The uncoated glass has a light transmission maximum of 91.1% at 515—520 nm (see Fig. 1, *a*, *b*, curve *1*), the light transmission monotonically decreases to 83.3% at shifting to the near-infrared range. At shifting to the UV region two absorption bands are observed: a narrow band at ~380 nm, and a band at 420—430 nm. The glass does not transmit UV radiation at wavelengths less than 325 nm.

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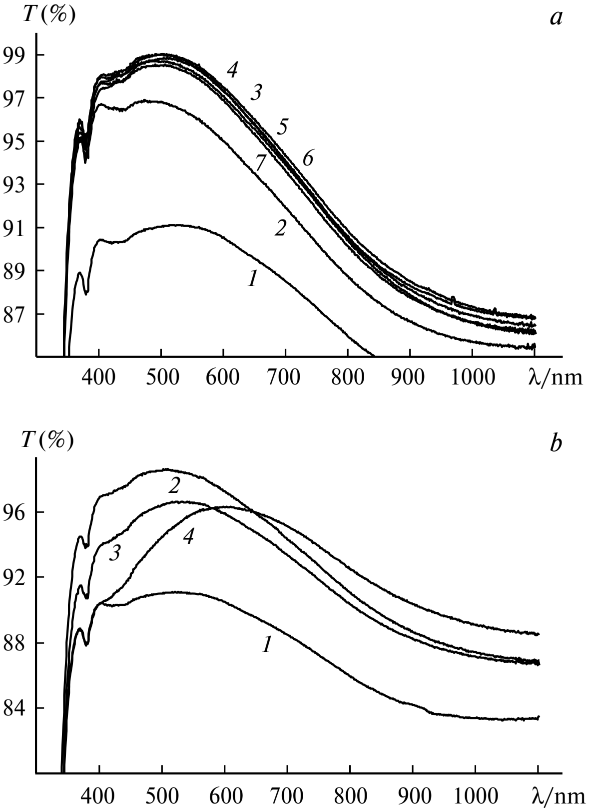

Fig. 1. The influence of additives to the sol on the clarifying effect of double-sided monolayer coatings: *a,* uncoated glass (*1*) and in the presence of 1.0 (*2*), 1.8 (*3*), 2.0 (*4*), 2.5 (*5*), 3.0 (*6*), and 3.5% w/w of Laprol 1000 (*7*); *b,* uncoated glass (*1*) and in the presence of 1.5 (*2*), 2.8 (*3*), and 3.0% w/w of PMMA(*4*).

The transparent coatings of mesoporous silica with the additives of organic compounds of different classes, such as acids,[13,14] oligoesters,[16,17] (see Fig. 1, *a*), and carbon chain polymers[15] (see Fig. 1, *b*), increase the light transmission of glass (antireflection effect) in the wavelength range of 350—1100 nm. The antireflection effect is dependent on the concentration of an organic substance in the sol: at the beginning it increases, passes through a maximum, and then decreases with the increase in the additive amount (see Fig. 1).

If Laprol 1000 is added to the initial gel, then the transmission maximum (99.0%) is observed at 500—510 nm (see Fig. 1, *a*, curves *4* and *5*) at the optimal concentration of the additive equal to 2.0—2.5% w/w (the optical thickness of the film is 120 nm, the refractive index is 1.23, the geometric thickness of the film is 98 nm (the geometric film thickness is the optical thickness divided by the refractive index)). As it is seen from Fig. 2, the given mesoporous silica film consists of spheres joined together 20—30 nm in diameter. It should be noted that the amorphous silica film with an optical thickness of 99 nm obtained in the absence of organic additives, has the refractive index of 1.45 at 633 nm, AFM revealed no inhomogenities on the surface of this film.

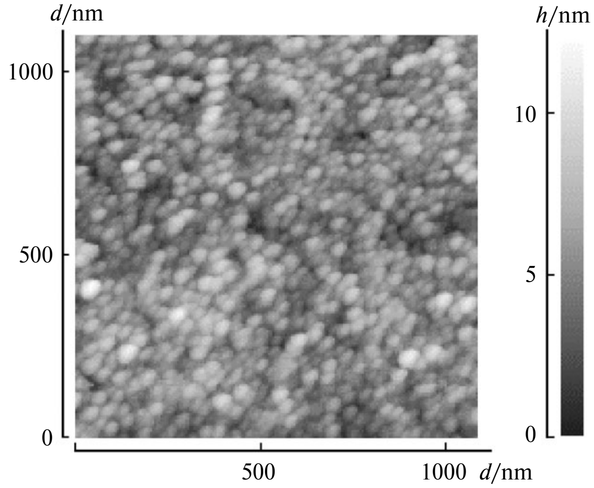

Fig. 2. AFM image of the surface of the silica film obtained by sol—gel method in the presence of Laprol 1000 (2.0% w/w).

The transmission maximum of 98.6% at 500 nm is observed when PMMA is added to the sol (see Fig. 1, *b*, curve *2*) at the polymer concentration of 1.5% w/w (the optical thickness of the film is 126 nm, the refractive index is 1.25, the geometric thickness is 101 nm). The surface of the film consists of spheres with the diameter of 50—60 nm joined together (see Fig. 3, *a*).

When the concentration of PMMA in the sol increases to 3.0% w/w the light transmission of the glass decreases (see Fig. 1, *b*, curve *4*). If 4.0% w/w of PMMA is introduced into the sol, the completely opaque film with submicron-sized inhomogenities is obtained (see Fig. 3, *b*).

The above-described experimental data (see Figs 1—3) allow the analysis of some features of the mechanism of formation of transparent films with a small refractive index (1.20—1.30) obtained by sol—gel method from silica.

In the step of the sol production in the course of hydrolysis of TEOS under the given experimental conditions, spherical silica nanoparticles with sizes of 20—30 nm are formed in isopropanol, and with a bit larger size (50—60 nm) in THF. After the introduction of an organic additive (Laprol 1000, PMMA) into the sol, a part of molecules is adsorbed on the surface of nanoparticles, the other part is left in the solution.

When several drops of the sol with the organic additive are applied onto the silicate glass followed by the rapid glass rotation to obtain the thin film, the volatile organic solvent (isopropanol, THF) and water are evaporated from the support and the spontaneous phase microseparation occurs with the formation of a transparent film of an organic-inorganic material. The molecules adsorbed on the nanoparticles prevent their fusion to larger aggregates. Therefore, the silica nanoparticles are uniformly distributed in the bulk of the film and are separated by nanosized layers of the organic additive.

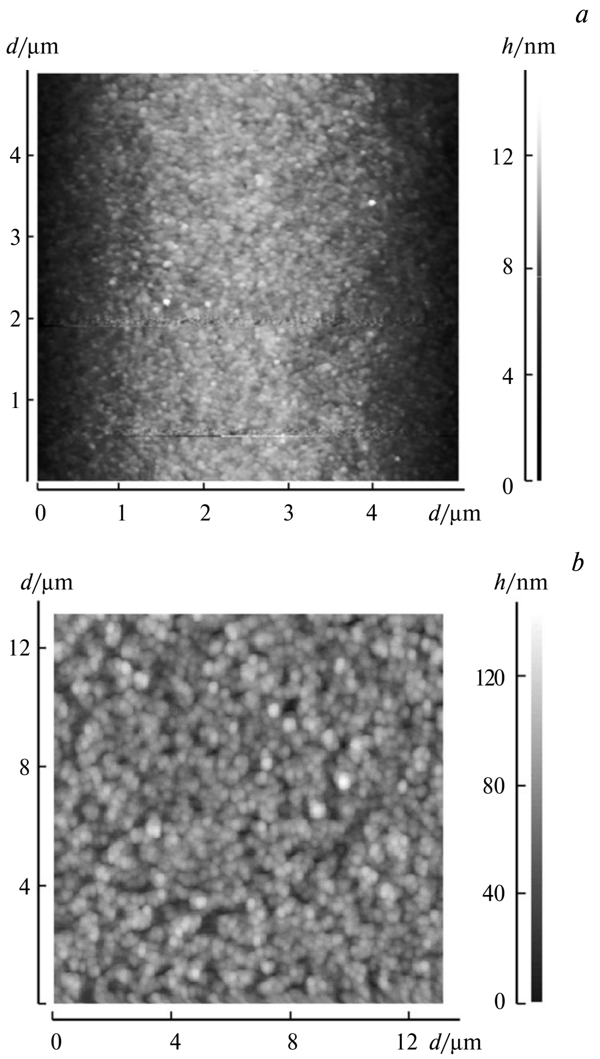

Fig. 3. AFM image of the surface of the silica film obtained by sol—gel method in the presence of 1.5 (*a*), and 4.0% w/w of PMMA(*b*).

In the last step of the heating of the glass with organic-inorganic coatings to high temperatures (500 °C) in the air atmosphere, the organic phase of the film burns out resulting in the formation of connected nanopores in the carcass of the joined with each other silica nanoparticles, which is seen from the AFM images of the surface of the films (see Figs 2 and 3).

Based on the geometric thickness of the film (~100 nm) and the size of constituent nanoparticles (20—60 nm), no more than two—five nanoparticles can be deposited vertically onto the glass surface.

It is obvious that the sizes of nanopores and their total volume, which determine the decrease in the refractive index of the film, are dependent on the ratio of the concentrations of TEOS to the organic compound. With the decrease in this value, *i.e.* with the increase in the concentration of the organic compound in the sol, the size of nanopores and their total volume would be expected to increase, and, consequently, the refractive index of the film would be expected to decrease and the light transmission of the glass with the coating would be expected to increase, which is experimentally observed (see Fig. 1). However, the increase in the size of nanopores of the films with the simultaneous increase in the light transmission of the glass proceeds only to the defined limit, equal to the wavelenthes of the studied spectral interval (maxima in the light transmission curves are observed at 500—510 nm (see Fig. 1). When the pore sizes approach to this limit, the sharp increase in the light scattering and the decrease in the light transmission of the coated glass would be expected to occur. If concentrations of the additive to the sol is high, the forming film is completely opaque, and pores are of submicron sizes (see Fig. 3, *b*). The influence on the light transmission of the sample of the two optical phenomena, *viz.*, the clarification of the glass with coatings with a small refractive index and the light scattering by the coatings, are opposite. Hence, in all of the studied cases (see Fig. 1) the optimal concentrations of the additive are observed (1.5—2.5% w/w), whereby the maximal clarifying effect is observed (98.0—99.0%).

It should be noted that using sol—gel method, the mesoporous, as well as the macroporous materials, can be obtained depending on the concentration of the organic additive (see Figs 2 and 3).

Hence, the results obtained by us previously[13—17] and the experimental data of the present work allow the following conclusions.

1. Thin transparent films with a small refractive index of 1.20—1.30 can be obtained from mesoporous silica by sol—gel method with inorganic acid as the catalysts for the tetraalkoxysilane hydrolysis and in the presence of organic compounds (organic acids, functional derivatives of organic acids, carbon chain polymers, statistical copolymers, oligoesters, in particular, based on ethylene oxide and propylene oxide).

2. The films have a high antireflection effect. Thus, the maximum light transmission of the glass with double-sided monolayer coating is 98.0—99.0%, the maximum light transmission of the uncoated glass is 91.1%.

3. There is the optimal concentration of organic additive in the sol (1.0—3.0% w/w at the silica concentration of 1.0% w/w), at which the maximal antireflection effect of the silicate glass is observed.

4. Mesoporous films obtained at the optimal concentration of an organic additive in the gel have a framework structure formed by spherical silica nanoparticles with a size of 20—60 nm (studied by AFM).

5. The films, which are obtained at the concentration of an organic additive in the sol higher than the optimal value (4.0—5.0% w/w), are opaque, since they contain optical inhomogenities comparable or exceeding the wavelengths of visible light (demonstrated by AFM).

6. Two optical phenomena, *viz.*, the antireflection properties of the glass with coatings with a small refractive index and the light scattering by coatings, have the opposite influence on the light transmission of the sample; therefore, in all the studied cases the optimal concentration of an organic additive is observed, whereby the maximal optical transmission is recorded.

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