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Investigation of the transmission and hardness of antireflective coatings of antireflective coatings on silicate glass prepared from silicon dioxide sols with addition of nonionic surfactants

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It was shown that silica-based sol-compositions with the addition of non-ionic surface-active substances ALM-2, ALM-7, ALM-10 can be used to obtain nanoporous single-layer antireflective coatings on silicate glass with a maximum light transmission of up to 99.0%. The hardness of the coating acceptable for practical use (2H – 4H) is observed when the air content in the nanopores of the coating is 23.2–25.3 vol.% (maximum of light transmission of the coated glass is 96.8–97.0%). The hardness decreases to 5B with an increase in the air content in the nanopores to 33.7 vol.%.

Keywords: *sol-gel process, non-ionic SAS, antireflective coatings, hardness of nanoporous coatings, silicate glass*

1. Introduction

The sol-gel process is becoming one of the most important methods for producing various functional inorganic and composite organic-inorganic film coatings for materials made of glass, metal, and polymer [1–4]. Modern methods of the sol-gel process, in particular, the template version of the method using surfactants (SAS), are widely used for the synthesis of mesoporous (with nanopore size 2.0-50.0 nm) metal oxides [2-7]. antireflective coatings based on silica sols with the addition of cationic SAS cetyltrimethylammonium bromide were first obtained in [6]. We have previously established [8] that the resulting thin nanoporous coatings with a high antireflective effect can be obtained from the sols of silicon dioxide, containing the surfactant compound ALM-10. The light transmission of glass with a single-layer two-sided coating at the maximum is 98.0-99.0%, while the light transmission of glass without coating at the maximum is 91.5%. It should be noted that silica sols containing non-ionic surfactants like ALM-10 type are cheap, affordable and environmentally friendly substances.

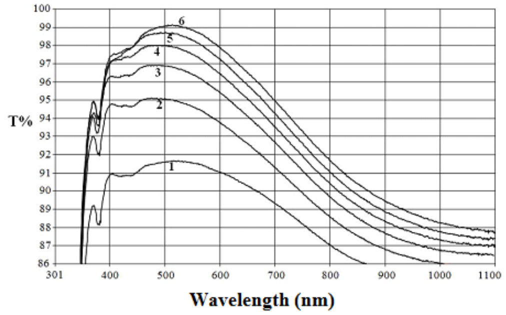

Figure 1. Light transmission of uncoated glass (curve 1) and coated glasses (curves 2–6) obtained from silica sols with ALM-10 additives (wt.%): 2 - 1.0; 3 - 1.5; 4 - 2.0; 5 - 2.5; 6 - 3.0

For wide practical use of silicate glasses with antireflection coatings in solar energy, displays, greenhouses, not only their optical characteristics are important, but also their abrasion resistance associated with the hardness of coatings and the microrelief of their surface. These properties of antireflective coatings obtained from silica sols with ALM-10, ALM-7, and ALM-2 have not been studied before. Therefore, the purpose of this work is to study the optical and physical (hardness, surface microrelief) properties of antireflective coatings obtained from silica sols with ALM-10, ALM-7, ALM-2 additives.

2. Experiment

2.1. Initial compounds

Tetraethoxysilane (TEOS, Aldrich) was purified by three-times distillation in vacuum, the content of the main substance was 99.9% (determined by liquid chromatography). Nonionic SASs ALM-10, ALM-7, ALM-2 ("Zavod Sintanolov", LLC, Dzerzhinsk, Russia) have the general chemical formula $C_nH_{2n+1}O(CH_2CH_2O)_mH$, where n = 12-14, m = 10, 7 and 2. We also used reagent-grade isopropyl alcohol, bidistillate water, reagent-grade hydrochloric acid.

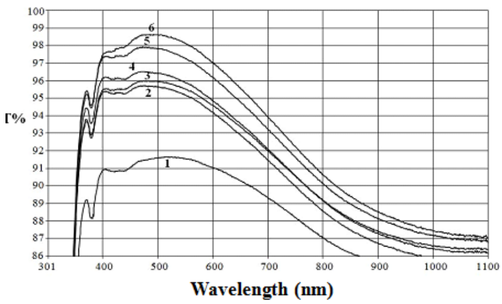

Figure 2. Light transmission of uncoated glass (curve 1) and coated glasses (curves 2–6) obtained from silica sols with ALM-7 additives (wt.%): 2 - 1.0; 3 - 1.2; 4 - 1.5; 5 - 2.0; 6 - 3.0

2.2. Preparation of silica sol by TEOS hydrolysis

5 ml of TEOS, 0.6 ml of water, 1 ml of 0.1 N hydrochloric acid and 3.3 ml of isopropyl alcohol (IPA) were placed in a glass flask with a volume of 50 ml and stirred for 4 hours at room temperature. The concentration of the resulting mixture in terms of SiO_2 is 0.4 mol/l. A certain surfactant concentration (1.0–3.0 wt.% by weight of sol) was added to the sol, which was stirred on a magnetic stirrer for 4 hours at room temperature.

2.3. Preparation of SiO_2 xerogel film on silicate glass

Silicon microscope slides for microscopy measuring 25 × 75 × 1 mm were used as the substrate. The refractive index of silicate glass is 1.506. The glass surface was cleaned of impurities by immersion in an alkali solution with hydrogen peroxide, the glasses were washed with water, distilled water, and dried in a thermostat at 150°C for 6–8 hours. The coatings were applied onto the glass by dipping at a temperature of 20–25°C and a humidity of 40–60%. For this purpose, a coating installation designed and manufactured in the laboratory was used. The installation consists of a high-precision worm gear connected with an electric stepping motor, which in turn is connected to a control unit and a computer. When the mechanism moves down, the glass is immersed in a "bath" with a sol composition. When the mechanism is moved upward at a speed of 10 cm/ min, the glass is removed and the film coating is applied. Coated glasses were left at room temperature for 1 hour. Then the glass was heated to 400°C and kept at this temperature for two hours.

The light transmission of glasses with film coatings in the wavelength range of 200–1100 nm was determined on a Perkin Elmer Lambda 25 spectrometer. The refractive index of the coatings was determined on an LEF-3M1 ellipsometer. Analysis of the microrelief of the film surface was performed using a Solver-P47 atomic force microscope.

The hardness of the coatings was determined on the instrument "Pencil type hardness tester" (RF State Standard GOST R 54586-2011). The essence of the method is as follows. There is a set of 16 standard pencils with increasing hardness, which is indicated by the following symbols: 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H, where 5B - the lowest hardness, 9H - the highest hardness. The slate-pencils are sharpened at an angle of 90°, and the pencil is inserted into an iron bar weighing 750 g at an angle of 45 °. With a sharp edge of the slate-pencil, a pencil is placed on the antireflective coating and carried out over the coating at a distance of 2–3 cm. The presence of scratches on the coating was watched through

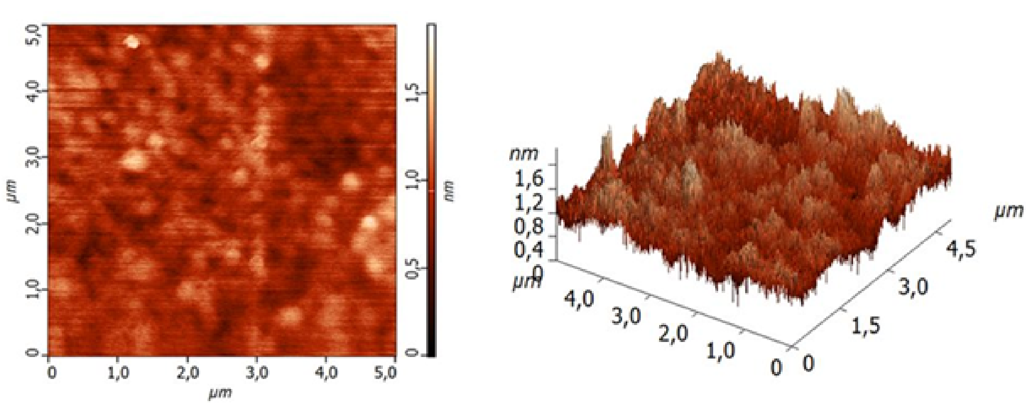

Figure 5. AFM image of the surface of the coating obtained from the silica sol with the addition of ALM-2 (1.0 wt.%)

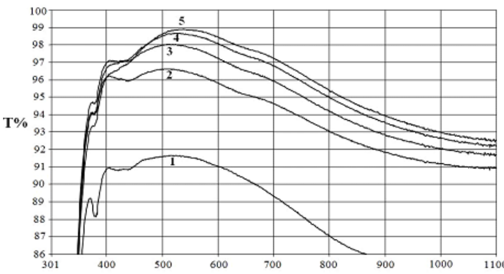

Figure 3. Light transmission of uncoated glass (curve 1) and coated glass (curves 2–6) obtained from silica sols with ALM-2 additives (wt.%): 2 - 1.0; 3 - 1.5; 4 - 2.0; 5 - 3.0

a magnifying glass. The hardness of the coating is determined by the hardness of the last pencil, which does not scratch the coating. For example, hardness 2B corresponds to the hardness of the surface of the polycarbonate; hardness 2H – 3H - hardness of the car paint coating; hardness 4H – 5H - granite surface hardness.

3. Results and Discussion

Figures 1-3 show the light transmission curves of glass without coating (curve 1) and with double-sided single-layer coatings based on silicon dioxide. These coatings were obtained from silica sols with the additions of ALM-10 (Fig. 1), ALM-7 (Fig. 2) and ALM-2 (Fig. 3). As can be seen from figures, the introduction of all three surfactants into the silica sol promotes the formation of transparent coatings on the glass with a high illuminating effect. Previously, we observed a similar effect only for ALM-10 [8]. The maximum anti-reflection effect, equal to 99.0% of the light transmission of the coated glass, is observed when 3.0 wt.% of SAS was added to the silica sol.

While the ALM-10 and ALM-7 additives in a silica sol lead to glass coatings with approximately the same illuminating effects (Fig. 1, 2), the ALM-2 additives have two significant differences (Fig. 3). First, ALM-2 is more effective than ALM-10 and ALM-7 at low concentrations (1.0 wt.%), which follows from the maxima on the light transmission curves: 98.5% (Fig. 3, curve 2) and 95.0 % (Fig. 1, curve 2), 95.5% (Fig. 2, curve 2). Secondly, for practical use of glass with antireflective coatings, not only the maximum value on the light transmission curves at a certain wavelength is important, but also the average value of the light transmission in a certain range of wavelengths, for example, in the spectral range 400–800 nm or in the interval 400 –1100 nm. The arithmetic average of the light transmission of a glass coated with a sol with ALM-2 in the visible region of the spectrum (Fig. 3, curve 5) is 97.2%; with sol with ALM-10 - 96.2% (Fig. 1, curve 6); with sol with ALM-7 - 95.6% (Fig. 2, curve 6). The light transmission in the wavelength range of 400–1100 nm is 95.7% for the ALM-2, 93.3% for the ALM-10, 92.6% for the ALM-7. Thus, the arithmetic average of the light transmission of glass coated with silica sol with ALM-2 in the wavelength intervals of 400–800 nm and 400–1100 nm is higher than for glasses with coatings of sols with additives of ALM-10 and ALM-7. Note that for glass without an antireflective coating, the average light transmission in the 400–800 nm range is 90.0% and in the 400–1100 nm range - 88.2%, which is 4.0–6.0% less than the corresponding values for glasses with single-layer antireflective coatings based on nanoporous dioxide silicon.

Figure 4 shows the dependences of the hardness of antireflective coatings on the refractive index of the coatings. As it follows from Fig. 4, the high hardness of 8H – 9H coatings is observed only in the interval of variation of the refractive index of the coating from 1.45 to 1.36, after which the hardness sharply decreases to 5B (the coating is scratched with the finger nail) at refractive indices 1.23–1.30. 2H – 4H hardness of coatings acceptable for practical use is observed at refractive indices of 1.34–1.35. Nanoporous material can be considered as an effective medium with optical constants depending on the volume fractions of the components. There are several different physical models that relate the macroscopic properties of the medium to the relative volume fraction of its components, one of which is the approximation of the Bruggeman effective medium:

$$(1-f_{pores})\frac{n_{inorg}^2-n_{eff}^2}{n_{inorg}^2+2n_{eff}^2}+f_{pores}\frac{n_{pores}^2-n_{eff}^2}{n_{pores}^2+2n_{eff}^2}=0$$

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where f_{pores} is the volume fraction of nanopores, n_{eff} is the effective refractive index obtained, and

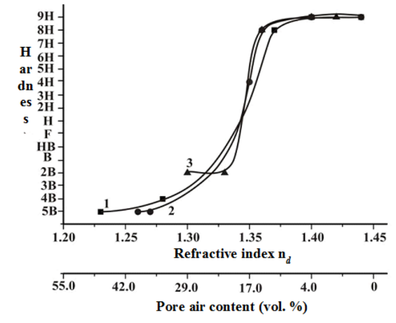

Figure 4. Dependence of hardness of antireflection coatings obtained from silica sols with additives of ALM-10 (curve 1), ALM-7 (curve 2), ALM-2 (curve 3), on the refractive indices and pore air content

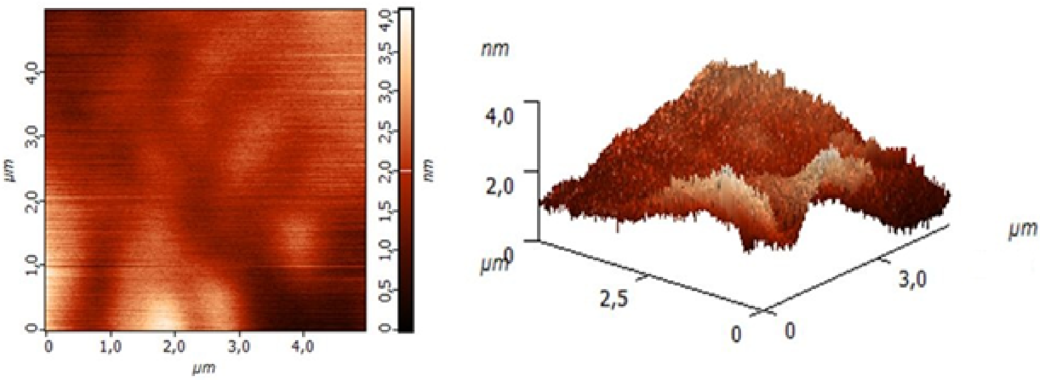

Figure 6. AFM image of the surface of the coating obtained from the silica sol with the addition of ALM-2 (3.0 wt.%)

n_{inorg} and n_{pores} are the refractive indices of the inorganic matrix and pores, respectively [9]. If n_{inorg} = 1.46 (SiO_2), n_{pores} = 1.0 (air), then with n_{eff} = 1.36, 1.35, 1.34 and 1.30, the amount of air in the coating nanopores is 21.1, 23.2, 25.3 and 33.7% by volume, respectively. With an increase in the air content in the nanopores of the antireflection coating, a decrease in its hardness from 8H – 9H to 2H – 4H is observed, and with an air content of 33.7% by volume, the hardness of the coating decreases to 5V.

As it follows from Figure 1 the maximum transmittance on curves 2–4 is observed at the same wavelength λ_{max} = 480 nm; on curves 5 and 6, λ_{max} = 500 nm and λ_{max} = 520 nm, that is, it increases slightly. For single-layer illuminating coatings, the following expressions are known: $h_{opt} = \lambda_{max}/4$, $h_{phys} = h_{opt}/n$, where h_{opt} and h_{phys} are the optical and physical thickness of the coating, n is the refractive index. The optical thickness h_{opt} is 120 nm, 120 nm, 120 nm, 125 nm, and 130 nm (Fig. 1, curves 2–6); the refractive index n is 1.44, 1.36, 1.29, 1.25 and 1.23, respectively; the physical thickness h_{phys} is 83.3 nm, 88.23 nm, 93.0 nm, 100.0 nm and 105.7 nm, respectively. Thus, the physical thickness of the coating constantly increases from 83.3 nm to 105.7 nm with a decrease in the refractive index of the coating from 1.44 to 1.23. The same dependences are also observed for antireflective coatings obtained from silica sols with the addition of ALM-7 and ALM-2 (Fig. 2, 3).

The surface microrelief is also important for optical coatings. Large surface irregularities can degrade both the optical and mechanical properties of coatings. Figures 5, 6 show the images of the surfaces of the coatings obtained by the AFM method. Figure 5 shows the surface of a coating obtained from a silica sol containing 1.0% by weight of ALM-2; the height of irregularities on the surface does not exceed 2 nm. The maximum light transmission of glass with a single-layer two-sided coating is 96.6% (Fig. 3, curve 2), the refractive index is 1.37, and the hardness of the coating is 8H (Fig. 4, curve 1). Figure 6 shows the surface of a coating obtained from a silica sol containing 3.0 wt.% ALM-2; the height of the irregularities on the surface does not exceed 4 nm. The maximum light transmission of coated glass is 98.8% (Fig. 3, curve 5), the refractive index is 1.24, and the hardness of the coating is 5B. As can be seen from Figures 5, 6, the irregularities on the surface of the coatings slightly increase from 2 nm to 4 nm, despite the strong decrease in the hardness of the coatings from 8H to 5B. Probably the main reason for the decrease in hardness of coatings is an increase in their air content.

4. Conclusion

1. It is shown that sols of silicon dioxide with the addition of non-ionic surfactants ALM-2, ALM-7, ALM-10, which are cheap, affordable and environmentally friendly sol compositions, can be used to obtain single-layer antireflective coatings on silica glass with a maximum of light transmission up to 99.0% (maximum light transmission of uncoated glass 91.6%).

2. It was established for the first time that the hardness of coatings acceptable for practical use (2H – 4H) was observed for the refractive indices of 1.34–1.35, the air content in the nanopores of the coating was 23.2–25.3 vol.% and the maximum light transmission of the coated glass was 96.8–97.0%.

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