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SOL-GEL SYNTHESIS OF ANTI-REFLECTIVE MESOPOROUS COATINGS BASED ON SILICON DIOXIDE

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The results of synthesis of anti-reflective, mesoporous, silicon dioxide based coatings obtained by acidic hydrolysis of tetra-ethoxy-silane (TEOS) in the presence of organic additives are presented. The effects of the acidity of the medium and the nature and mass content of the modifier on the optical properties of coated glass were investigated. The optimal parameters of synthesis were determined.

Key words: sol-gel synthesis, mesoporous coating, anti-reflective coating, float-glass, dopant, surfactant [SAA], tetraethoxysilane (TEOS), silicon dioxide, light transmission, size of nanoparticles, polydispersity, abrasive resistance, precursor, silica-sol.

Glass with an anti-reflective coating is widely used in the production of solar batteries, display screens, optical instrument engineering, and other special areas of science and technology.

Today, the high transparency of sheet glass is an indicator of a new quality and one of the advantages in the market for glass articles. Work on effective anti-reflection of large-size glass is actively being pursued worldwide and is of high-priority and promising.

In the past primarily multilayer systems of vacuum and pyrolytic coatings were used to make optics anti-reflective. In last few decades sol-gel technology has been used effectively in the deposition of single-layer mesoporous films of silicon dioxide to create anti-reflective coatings.

One technological technique for obtaining nanoporous SiO_2 coatings is to introduce into the composition of a film-forming solution (FFS) organic pore-forming additives playing the role of a matrix determining the spontaneous microseparation of organic and inorganic phases in the sol.

Alkoxy compounds of group III, IV, V, and VIII elements of the periodic system are most often used as film-forming substances (precursors) for depositing coatings, while alkoxysilanes, preferably tetraethoxyxsilane (TEOS), are used for anti-reflective coatings.

Oligomers of ethylene and propylene oxide with different molecular mass, carbochain polymers containing ester side groups, organic acids and their derivatives, and other substances, mainly with mass content 0.1 – 5.0%, are used as additives. In the deposition of such films, mesoporous anti-reflective coatings with refractive index 1.18 – 1.44 are formed upon subsequent heat-treatment [1 – 3].

For practical application of large-size glass with anti-reflective coatings, aside from the optical properties their operational characteristics are extremely important — chemical stability and abrasive resistance. In connection with the fact that the sol-gel technology is a multifactorial process, while directly opposite solutions are often needed in order to realize polyfunctional properties, a large amount of experimental development work is required in searching for the optimal parameters of synthesis that ensure a balance between physical-mechanical and optical properties [4, 5].

There are two variants of the sol-gel process: under conditions of acid catalysis or base catalysis [6].

Acid catalysis is preferable for anti-reflective coatings, since the obtained fractal structure of the particles ensures higher-order structural parameters of porosity in contrast to base catalysis where spherical nanoparticles are formed [7].

The aim of the present work was to create by the sol-gel method anti-reflective abrasion-resistant mesoporous films based on silicon dioxide and to study the influence of technological factors of synthesis on the properties of the formed coatings.

The silica-sols were synthesized by hydrolysis of alcohol solutions of tetraethoxysilane in the presence of hydrochloric

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acid as a catalyst with introduction of organic modifiers (dopants).

The following were varied in order to optimize the composition of the sol: the ratio of the inorganic components (H_2O/TEOS, C_2H_5OH/TEOS, solution pH) and the type and mass content of the organic dopants. At the same time the effect of the method of formation and the heat treatment regime on the quality and properties of the obtained coatings were investigated.

Different classes of organic compounds, including cationic surfactants (cSAA) and non-ionogenic surfactants (nSAA), were used as dopants: β-benzoylpropionic acid (BPA), dinonyl ester of phthalic acid (DEPA), Bridge-35, cetyltrimethylammonium chloride (CTMA), cetylpyridinium chloride (CPC), Triton X-100, and polyethylene glycol.

The films were obtained by centrifuging with rotational speed of the substrate 2000 rpm and by drawing from a solution at a controlled rate onto 100 × 100 × 4 mm samples of colorless sheet float-glass with light transmission Tv = 89.5%.

The glass substrates were prepared by manually polishing using an ammonia-chalk suspension, washing with running and distilled water, and degreasing with ethyl alcohol.

Heat treatment of the samples was conducted in a SNOL 10/11 muffle furnace at temperatures 350 – 500°C for 30 – 60 min.

The following methods were used to study the physical and mechanical properties of the synthesized sols and films:

– a Zetasizer Nano (ZS) particle size analyzer (Malvern Instruments) was used to measure the average size and polydispersity of silica-sol particles at the moment of coating deposition;

– the acidity and viscosity of the medium were determined using, respectively, an IT-1101 pH-meter with automatic thermal compensation and a VNZh-type glass capillary viscometer;

– a Shimadzu UV-3600 spectrophotometer was used to measure in the visible range of the spectrum (380 – 780 nm) the optical transmission and reflection of the glass samples with a coating were in accord with GOST EN 410–2014 ‘Glass and glass articles. Methods of determining the optical characteristics. Determination of light and solar characteristics’;

– an LÉF-3M-1 ellipsometer was used to measure the index of refraction;

– the abrasive resistance of the coatings was determined according to their resistance to wear in accord with the EN 1096-2 procedure ‘Glass in building — Coated glass. Part 2. Requirements and test methods for class A, B, and S coatings’;

– atomic force microscopy (AFM) was used to investigate the surface relief of anti-reflective coatings and the optical thickness of films using an ACM AURIGA CrossBeam Workstation (Carl Zeiss).

The following were accomplished in the preliminary experiments:

TABLE 1. Characteristics of Sol Solutions with Different pH and the Effect of pH on the Maximum Light Transmission Tv_{max}

Sol characteristics				Coated glass Tv_{max}, %	
Catalyst, pH	Viscosity, mPa · sec	Temperature, °C	Particle size, nm	before heat treatment	after heat treatment
HCl, 2.4	1.40	22.4	3.6	90.5	90.0
HCl, 4.7	1.41	22.4	220.2	90.6	89.9
HCl, 6.0	1.40	22.4	255.0	90.5	89.9
NaOH, 11.6	1.43	22.7	825.0	89.8	89.6

TABLE 2. Effect of the Type of Dopant on the Light Transmission of Coated Glasses

Dopant type	Tv_{max},, %
–	90.2
BPA	87.5
DEPA	88.1
Bridzh-35	91.8
CTMA	92.7
CPC	92.5
Triton X-100	91.0
Polyethylene glycol	90.6

– a method was developed for synthesizing silica-sol [8];

– a method was determined for coating deposition — the method of drawing from a solution at velocity 0.23 to 1.85 mm/sec; visual quality evaluation of the coatings established that this method gives transparent, uniform, and defect-free films;

– a two-stage regime was chosen for heat treatment: air soaking for 15 min and firing at temperature 450°C for 30 min.

Subsequent investigations were aimed at optimizing the parameters of sol synthesis in order to maximize the anti-reflective effect.

The results obtained for the effect of the solution pH on the sol characteristics and the light transmission of glass coated with the experimental films obtained by the sol-gel method are presented in Table 1.

It follows from Table 1 that as the solution pH increases, particle size increases in the sol solution and has practically no effect on light transmission.

The dependence of the light transmission of coated glasses on the type of modifying additive (dopant) is presented in Table 2.

It follows from the obtained data that the increase in light transmission is greatest for samples of obtained by using CPC and CTMA as the modifying additive (dopant) cSAA.

Subsequent studies were performed using CPC as the dopant in sol.

TABLE 3. Characteristics of Silica-Sol Solutions and Their Impact on Light Transmission

Silica-sol characteristics				Coated glass Tv_{max}, %	
CPC additive, %	Viscosity, mPa · sec	Temperature, °C	Particle size in sol, nm	before heat treatment	after heat treatment
0.5	1.39	21.4	3.6	93.4	92.8
1.0	1.60	21.4	4.2	90.6	89.9
1.5	1.70	21.4	4.2	90.9	90.0

TABLE 4. Light Transmission versus FFS Deposition Rate on Glass

Additive	Draw rate, mm/sec	Film thickness, nm	Tv_{max}, %
CPC 0.5%	1.85	85 ± 10	93.6
	0.93	80 ± 10	91.9
	0.46	60 ± 10	90.6
	0.23	40 ± 8	90.1
CPC 1.5%	1.85	80 ± 10	92.2
	0.93	75 ± 10	91.1
	0.46	65 ± 10	90.8
	0.23	60 ± 10	90.5

The impact of the mass content of organic additive on the parameters of the silica-sol and the light transmission of samples coated with silica-sol films is presented in Table 3.

According to the obtained data the optimal film is one with *Tv* = 93.4%, containing 0.5% CPC. Analysis of the sol characteristics showed that as the CPC mass content increases, the viscosity of the solution and the size of the primary SiO_2 nanoparticles increase.

Next, the mass content of the additives and the draw rate of the samples were measured simultaneously. The result was that for the best sample the film was deposited in the presence of 0.5% CPC with maximum draw rate 1.85 mm/sec. The data are presented in Table 4.

It is evident from Fig. 4 that as the draw rate of the substrate increases, the thickness of the deposited sol-gel coating grows and the light transmission increases; the concentration dependence is less significant. The growth of the film thickness with increasing draw rate is due to the increase of the friction force impeding the gravity flow of the sol off the substrate.

The spectral transmission and reflection curves for the optimal sample, including before and after heat treatment and the initial sample, are displayed in Fig. 1. The computed values of the integral light transmission coefficients of the given samples are, respectively, equal to 93.6, 93.2, and 89.5%. The integral reflection coefficient equals 4.4% for the coated glass and 8.0% for the uncoated glass.

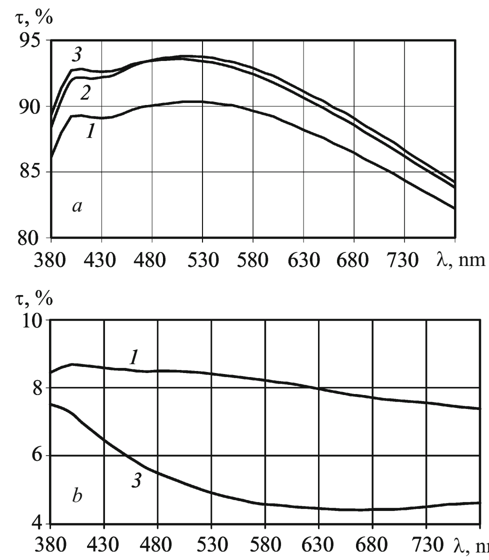

Fig. 1. Transmission (*a*) and reflection (*b*) spectrograms of SiO_2-coated samples: *1*) initial glass; *2*) coated glass before heat treatment; *3*) coated glass after heat treatment.

It follows from the obtained data that the increase of light transmission of coated glass relative to the initial glass was equal to 4.1% and the reduction of light reflection 3.6%. Heat treatment of the film resulted in a very small reduction of light transmission of the glass (by 0.4%), a small shift of the spectrum into the blue region, and an increase of light transmission in the UV region.

For samples with the maximum light transmission, measurements of the refractive index and abrasive resistance of the coating and microscopic studies of the surface of the film were performed.

The refractive index of a film, measured by the method of ellipsometry, was equal to 1.42.

Abrasive resistance tests of coatings performed in accord with EN 1096-2 showed that heat treated samples with a film correspond to class A in terms of operating conditions and can be used for external applications.

The investigated samples were also exposed to household washing; there was no visible damage or changes in optical properties. The difficulty of the deposition of mechanical scratches during AFM measurements of film thickness attests indirectly the high mechanical strength of the samples.

The surface relief (determined by the AFM method) of the optimal sample before and after heat treatment is shown in Fig. 2.

Analysis of the results showed that the surface roughness of a glass substrate equals 65 nm without a film and 7 and 10 nm before and after, respectively, heat treatment. After heat treatment a film becomes denser, and the average roughness increases very little. Thus, a silicon dioxide film ‘heals’ the unevenness of the glass surface, i.e. confers protection.

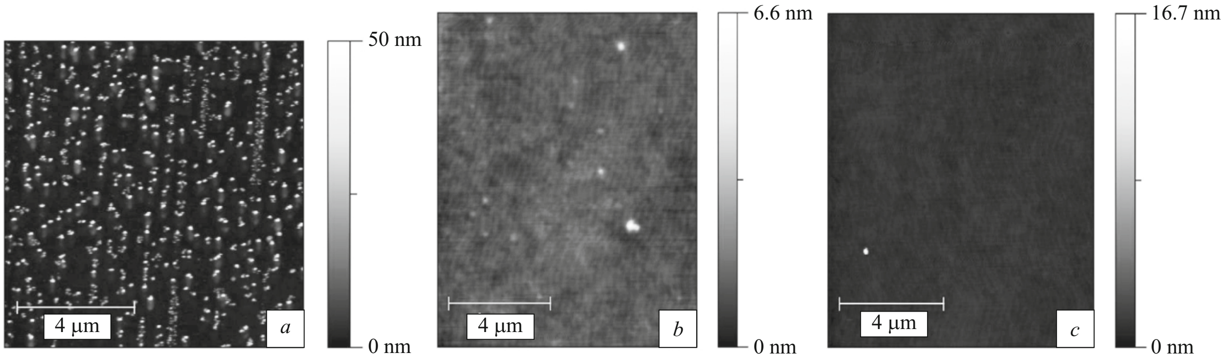

Fig. 2. AFM photograph of the surface: *a*) glass without a film; *b*) glass with deposited film before heat treatment; *c*) film-coated glass after heat treatment.

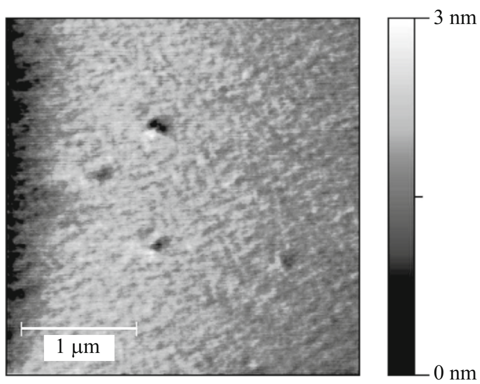

Fig. 3. AFM photograph of the surface of a film.

It is evident in the AFM photograph (Fig. 3) with higher magnification that a film has a grainy texture consisting of compactly arranged elongated SiO_2 particles.

The AFM method was used to determine the thickness of the obtained coatings: 40 to 85 nm.

Basic Conclusions Drawn from the Experimental Results

A method of synthesizing silica-sol and depositing anti-reflective single-layer mesoporous coatings of silicon dioxide on float-glass was developed.

Silica-sol with 3 – 5 nm nanoparticles was synthesized.

Optically transparent and mechanically stable 40 – 90 nm thick SiO_2-based films with the lowest refractive index 1.42 and highest light transmission 93.6% were obtained.

The effect of solution pH, type and mass content of organic dopants, and deposition and heat treatment conditions on the optical and strength properties of films was investigated.

The optimal parameters of synthesis were determined: dopant — CPC, dopant mass content — 0.5%, and substrate draw rate from sol — 1.85 mm/sec. Heat treatment regime: temperature — 450°C, time 30 min.

The effect of the conditions of sol-gel synthesis on the characteristics of the obtained sol and the optical properties of the glass was studied.

The obtained films have a grainy texture with 7 – 10 nm roughness and level microdefects in the glass surface.

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