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Obtaining a thin-film coating of a composite material based on titanium dioxide and silver nanoparticles by the sol-gel method

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Abstract: **The article presents a method for obtaining thin-film mesoporous coatings for optical and other applications, including: obtaining titanium oxide sols with the addition of silver nitrate, coating by "dipcoating" with further heat treatment. Kinetic constants were also calculated: the constants of fast and slow Smolukhovsky coagulation, the activation energy of the process at different concentrations of silver nitrate, XRD and AFM studies were carried out. The optimal concentration of silver in the ash was calculated by the MLC method.**

Keywords: **titanium oxide; mesoporous coatings; activation energy; silver; coagulation constant**

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Contents

1. INTRODUCTION

One of the main needs of modern industry is the creation of new materials with the required properties, such as energy efficiency, safety for the environment and humans. This is primarily due to the optimization of the costs of industrial enterprises for the purchase of energy and payment of quotas for greenhouse gas emissions. The creation of new hybrid antireflection materials based on sol-gel glass by the method allows to reduce reflection losses in solar panels by 12% compared to a battery without a special coating [1], thereby increasing electricity generation. The coating enriched with silver nanoparticles gives the effect of additional light transmission due to surface plasmon resonance, which increases the efficiency of the solar battery by 8-10% and 30-35% depending on the size of silver nanoparticles [2,3].

In the future, titanium oxide coating with the addition of silver nanoparticles will be considered, the use of titanium oxide is due to the pronounced effect of photocatalysis, which presumably prevents contamination of the surface of the solar battery [4]. The kinetics of particle growth can be considered [5] as the polymerization process of titanium hydroxocomplexes, that is, the addition of charged hydroxocomplexes to electroneutral particles of the composition $[(TiO)_x(OH)_{2x}]$. In this case, the limiting factor is the low concentration of neutral complexes in acidic solutions. The degree of supersaturation by OH-ions of the solution is decisive in the sol-gel synthesis of titanium oxide [6]. At pH less than 2, there is a relatively small supersaturation, the particle growth rate decreases, conditions are created for the deposition of a thermodynamically stable crystalline phase – rutile. With an increase in the concentration of hydroxyl ions in the solution, the deposition rate increases, and the reaction leads to the formation of anatase.

The aim of the work is to study the process of hydrolytic polycondensation of the sol-gel TiO_2 process in the presence of a silver nitrate solution, the solution of which will allow choosing the optimal reaction parameters.

2. MATERIALS AND METHODS

In this paper, the synthesis of spherical TiO_2 particles is realized by the modified Stober method [7,8]. The essence of the method is the hydrolysis of titanium alkoxides in an aqueous alcohol medium in the presence of an inhibitor – acetic acid, which lowers the acidity level by binding excess OH groups formed during the hydrolysis reaction. For the experimental study, titanium oxide sols were prepared: TiO_2 base sol, as well as TiO_2 sol with the addition of 3%, 6%, 10% (wt.) silver nitrate (ch.d.a., GOST 1277-55) in terms of metallic silver: 1.905%, 3.81%, 6.35% (mass.) accordingly. The synthesis technique is considered in detail in [9].

Titanium oxide sol is obtained by hydrolysis of tetrabutoxytitane $(C_3H_8O)_4Ti$ (the mass fraction of the main substance is 98.9%, os.h.; TU 2637-059-44493179-04). A 96% solution of ethyl alcohol was used as a solvent (GOST 18300-87). Acetic acid CH_3COOH was used as an inhibitor of the reaction (the mass fraction of the main substance was 99.8%, h.h.; GOST 61-75).

The ratio of the components of the mixture by weight TBT:H_2O:C_2H_5OH:CH_3COOH = 0.46:1.76:14.78:0.09. Ethanol and acetic acid are mixed in the reaction vessel for 2-3 minutes, and then tetrabutoxitane – TBT, 97% (Sigma-Aldrich 244112) is added. When conducting an experiment with the addition of silver nitrate, an $AgNO_3$ solution is additionally added to the solution (h.d.a., GOST 1277-75), the final mixture is mixed at a temperature of 23±10°C using a magnetic stirrer for 5±0.5 min. The optimal mixing time was determined by preliminary experiments.

3. RESULTS AND DISCUSSION

The kinematic viscosity of the synthesized salts was measured for 5 days on an Ostwald-Pinkevich capillary viscometer ($d_{capillary}$ = 0.86 mm) (GOST 33-2000) at a temperature of T = 22±1°C.

The photometric study was the calculation of Smoluchowski's slow coagulation constants based on the measured optical density of the sol samples for each time point. The optical absorption spectra of TiO_2 sols were measured using an *Evolution300 UV-VIS* spectrophotometer. The experimental samples were standard optical PET cells 1 cm thick filled with TiO_2 sols. The time for studying the change in optical characteristics is no more than 5 days, the measurements were carried out at

Table 1
Reference data for calculations [10].

Index	Meaning
Density of the dispersed phase - titanium oxide (anatase)	4.05 g/cm^3
Refractive index of the dispersed phase	1.46
Refractive index of the dispersed medium – 96% ethanol	1.363
Cuvette length	0.5 cm

regular intervals at a temperature 23±1°C. The necessary data for calculating Smoluchowski's slow coagulation constants were taken from [10] and are given in **Table 1.**

The resulting sols were applied to soda-lime silicate glasses by *dip-coating* at room temperature 23±1°C. Coatings were applied immediately after the maturation of the sols, preventing gelation in solutions. Glass substrates were cleaned by boiling in a hydrogen peroxide solution. The developed device (**Fig. 1**) makes it possible to extract a sample from a solution at a predetermined rate. The extraction rate from the solution is 105, 125 and 160 mm/min.

The study of the roughness of the obtained film was carried out on the microscope of the probe nanolaboratory *NT-MDTNtegraSpectra*, in the semi-contact mode, probes of the NSG_{10} series were used with dimensions – the radius of the probe curvature was 10 nm, the length of the cantilever was 95 μm. Images with a scale of 40×40 μm were obtained at a scanning frequency of 0.7 Hz (one line pass time), image resolution 256×256 pixels. To process the obtained data, namely, to determine the film thickness and roughness of the coatings, the *Gwyddion* scanning probe microscopy data analysis software was used.

Fig. 1. *Dip-coating device.*

4. CALCULATION OF FAST COAGULATION RATE CONSTANT - k_b

The process of transition of the sol to the gel –the process of gelification of the sol is a special case of coagulation of the disperse system. For a comprehensive description of the kinetics of this process, it is necessary to refer to the theory of fast coagulation by Smoluchowski [11]. The resulting sol can be conditionally considered monodisperse, which is one of the conditions for the applicability of the Smoluchowski theory; we also make the assumption that the sol particle size is equal to the average particle size [12]. The dynamic viscosity coefficient of the titanium oxide sol is calculated from the data of the viscometer:

$$k_q = \frac{2(2r)^2 kT}{3\mu r^2} = \frac{8kT}{3\mu}. \qquad (1)$$

5. CALCULATION OF THE SLOW COAGULATION RATE CONSTANT - k

During the coagulation of spherical particles of titanium oxide, aggregates consisting of several particles are formed. During the coagulation process, the mass of the aggregate increases.

$$\frac{4}{3}\pi r_0^3 N\gamma = \frac{4}{3}\pi r^3\gamma', \qquad (2)$$

where r_0 – the radius of an individual particle, cm; r – particle aggregate radius, cm; N – the number of particles contained in the aggregate, units; γ – density of an individual particle, g/cm^3; γ' – particle aggregate density, g/cm^3.

The ratio of the current optical density to the initial:

$$\frac{D}{D_0} = \frac{V^2 v}{V_0^2 v_0^2}. \qquad (3)$$

Assuming that: N = C_0/C and β = γ'/γ is the packing density. We get:

$$\left(\frac{r}{r_0}\right)^6 = \left(\frac{v_0}{v}\right)^2 \cdot \frac{1}{\beta^2}, \quad (4)$$

$$D = D_0 \frac{v_0}{v\beta^2}. \quad (5)$$

Let's use the Smoluchowski equation and substitute the previous expression into it.

$$\frac{1}{\frac{D_0}{D} - \frac{D}{D_\infty}} = \frac{v_0}{\beta^2} K\tau + \frac{1}{\beta^2 - \frac{D_0}{D_\infty}}. \quad (6)$$

6. PARTICLE SIZING

The determination of the particle size in the alcohol sol of titanium oxide was carried out by turbidimetry using the Rayleigh method. To determine the radius, the expression obtained by transforming the Rayleigh equation is applied by introducing the value of the weight concentration:

$$C = \left[\frac{\Gamma_{\text{dispersed phase substance}}}{1\ \text{cm}^3_{\text{disp. phases}}}\right] = V \cdot v \cdot \rho_{ph}, \quad (7)$$

$$r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{0.07197 D\rho_{ph}\lambda^4}{\pi^4 CL}\left(\frac{n^2 - n_0^2}{n^2 + 2n_0^2}\right)^2}, \quad (8)$$

where D – optical density of the dispersed system; ρ_{ph} – density of the dispersed phase; v – the number of colloidal particles in 1 cm^3 of the dispersed system; V – volume of one particle, cm^3; L – cuvette length, cm; n – optical refractive index of the dispersed phase; λ – optical wavelength; n_0 – dispersed phase refractive index.

Having data on the radius of particles at the zero moment of time and knowing the weight concentration, it is possible to calculate the number of particles at the zero moment of time.

7. ACTIVATION ENERGY CALCULATION

Smoluchowski's fast coagulation rate constant (k_B) is a theoretical constant that is achievable provided that each collision of particles leads to their aggregation. In a real system, there are repulsive forces between particles, so not every collision leads to aggregation (sticking together). For aggregation, particles need to overcome a potential barrier – activation energy (E_A).

Table 2

Results of a photometric study of the coagulation of titanium oxide sols and composite sols containing silver nitrate

C ($AgNO_3$), mass%	C(Ag^+), %	K, m^3/(mole·day)	$k_{\text{б}}$, m^3/(mole·day)	β	E_A, J/mole·
0	0	$2.82\cdot10^{-18}\pm6.01\cdot10^{-21}$	$7.26\cdot10^{-7}$	0.8924	64442
3	1.905	$8.99\cdot10^{-18}\pm6.12\cdot10^{-20}$	$7.02\cdot10^{-7}$	0.9672	61516
6	3.81	$1.81\cdot10^{-17}\pm3.40\cdot10^{-19}$	$6.62\cdot10^{-7}$	0.9828	59656
10	6.35	$1.60\cdot10^{-17}\pm1.93\cdot10^{-19}$	$6.34\cdot10^{-7}$	0.9782	59852

$$K = k_q \cdot e^{\frac{E_A}{RT}}.$$

or

$$E_{\grave{A}} = -RTln\frac{K}{k_q}.$$

The results of calculating the rate constants of fast and slow Smoluchowski coagulation, activation energies and coefficients for sols with different concentrations of silver nitrate are given in **Table 2.**

After analyzing the dependence obtained, we can conclude that the addition of silver nitrate to the titanium oxide sol reduces the activation energy of the condensation process, catalyzing the nucleation (aggregation) process. On **Fig. 2** shows the analytical correlation dependence of the activation energy on the mass concentration of silver nitrate, obtained by the least squares method based on the results of experimental data:

$y = 3.6393x^3 + 26.455x^2 – 1087.5x + 64442.$

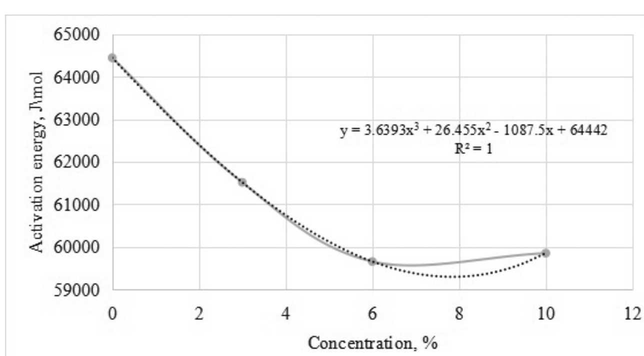

Fig. 2. *Correlation dependence of the activation energy on the mass concentration of silver nitrate.*

By searching for a local extremum, one can find the optimal concentration of silver nitrate, at which the activation energy of the process will be minimal, when the experiment is set up under absolutely identical conditions, i.e. at the same temperature, pressure, pH, etc.

$(3.6393x^3 + 26.455x^2 - 1087.5x + 64442)dx = 388.56x - 2679.5 = 0.$

Get $x = 7.89\%$

After drying the TiO_2 and Ag composite sol (7.89% $AgNO_3$ or 5.01% Ag), *X*-ray phase analysis of two samples was carried out, one of which was dried at 230±10°C, and the second at 500±50°C for 4 hours. The resulting diffraction patterns are shown in **Fig. 3**.

An analysis of *X*-ray diffraction patterns showed that during firing, a transition from the amorphous state of TiO_2 to the crystalline state

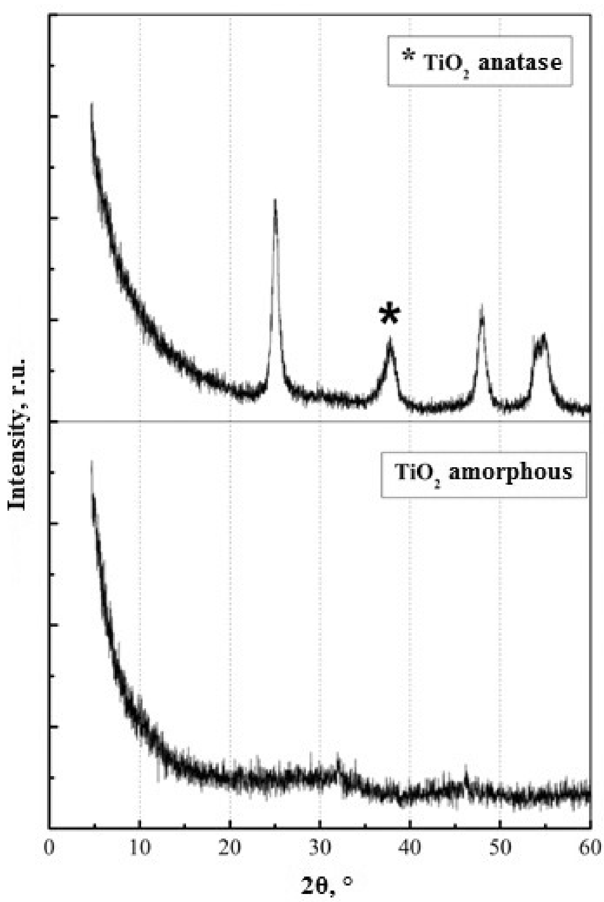

Fig. 3. *X-ray diffraction patterns of TiO_2@Ag (5.01%) powders: a) the sample was processed at 500±50°C, the asterisk shows the XRF reflections referred to anatase; b) sample, air dried.*

Table 3

Determination of roughness and film thickness by atomic force microscopy

Sample	Roughness, nm	Film thickness, mkm
Uncoated glass	2.21	-
TiO_2,105 mm/min	41.05	0.16
TiO_2+Ag(5.01%), 105 mm/min	26.47	0.15
TiO_2+Ag(5.01%), 125 mm/min	27.22	0.22
TiO_2+Ag(5.01%), 160 mm/min	29.32	0.26

of anatase occurs, as evidenced by an intense peak at $2\theta = 38°$. The detection of anatase is a consequence of the fact, that the synthesis was carried out at pH 5.2–5.5. It is assumed that the diffraction line of metallic silver was not detected for two reasons: an insufficient concentration of silver in the ash that served as the material for the film, as well as a possible overlap of the silver diffraction peak $2\theta = 38°$ by a more powerful anatase line.

Subsequently, a TiO_2 sol was deposited on a solid substrate by the dipcoating method, with heat treatment at a temperature of 500±50°C, which led to crystallization with the formation of an anatase structure.

The results of measurements of the roughness and thickness of the coatings by atomic force microscopy are presented in **Table 3**. Micrographs of the surface of coatings of different compositions are shown in **Fig. 4**.

The solution for obtaining a coating with the addition of silver makes it possible to obtain a smoother surface relief, as well as to reduce the roughness by one and a half times compared to coating with pure titanium oxide. In this case, the higher the rate of extraction of the substrate from the solution, the greater the roughness.

Titanium oxide deposited on a glass substrate presumably eliminates microcracks, which leads to the glass strengthening observed in the experiment, and the manifestation of this effect is possibly associated with the formation of bonds between the surface oxygen atoms in the

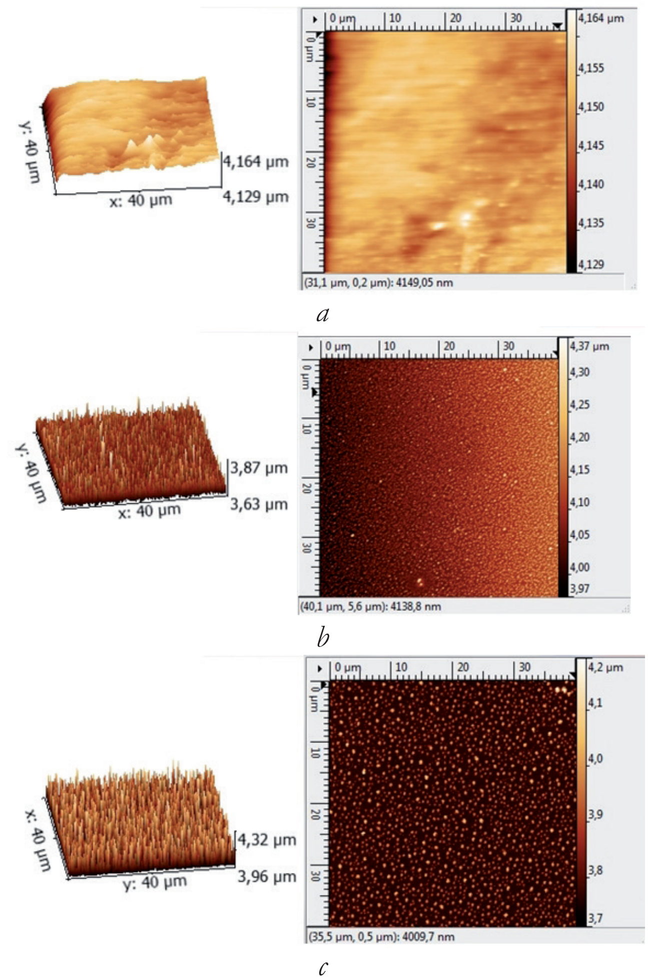

Fig. 4. *Micrographs of the surface of uncoated glass (a), TiO_2 coated glass (b), and TiO_2@Ag coated glass (c).*

SiO_4 tetrahedron and titanium atoms. To reveal the glass strengthening effect, the microhardness of uncoated glass samples coated with a TiO_2 layer and a TiO_2 + Ag composite coating layer was measured. The most accurate and suitable for determining the microhardness of the surface layer of brittle materials is the Vickers method [15]. In table the results of measuring the microhardness of glass substrates coated with TiO_2 + Ag (5.01%) at different rates of extraction from solution are presented in **Table 4**.

Table 4

Determination of the microhardness of glass substrates for different rates of extraction from solution

Coating	Extraction rate from solution, mm/min	Average value of microhardness, GPa
Uncoating	-	4.620
TiO_2 + Ag (5.01%)	105	4.720
	125	4.923
	160	5.475

8. CONCLUSION

Based on the results of the study, it can be concluded that:

The rate constants of fast and slow coagulation calculated according to Smoluchowski indicate the catalytic effect of the addition of silver nitrate on the rate of the sol-gel process. According to equation (11), the calculated activation energy of the titanium oxide precipitation reaction when using the addition of silver nitrate in the amount of 7.89% $AgNO_3$ or 5.01% Ag will be equal to 59296 J/mol, i.e. less than 8.67% of the base result.

The viscosity of the sols increases with an increase in the concentration of silver nitrate from 0 to 6%, this is due to an increase in the rate of the reaction of homogeneous nucleation with an increase in the ionic strength of the solution; in addition, the high viscosity of sols with the addition of silver nitrate can be explained by the formation of positively charged silver ions during the dissociation of silver nitrate, which act as a coagulant for negatively charged micelles of titanium oxide.

The least squares method (LSM) was used to find the optimal concentration of silver nitrate in the ash, at which the activation energy of the process is minimal under given initial conditions of the experiment.

X-ray phase analysis showed that during firing, a transition occurs from the amorphous state of TiO_2 to the crystalline state - anatase. The thickness of the Ag+TiO_2 (6.3%) coatings at a pulling speed of 105 mm/min is about 150 nm, and at 125 mm/min it is 220 nm. The introduction of silver nanoparticles into the coating structure reduces the coating roughness by approximately one and a half times. Controlling the rate of extraction of the sample from the solution allows you to control the thickness and properties of the sample coating.

Coating increases the microhardness of glass at a extraction rate of 105 mm/min by 2.16%, at 125 mm/min by 6.56%, and at 160 mm/min by

18.5%. It is known that with an increase in the extraction rate, the coating thickness increases, respectively, and the value of the microhardness of a glass sample with a film of titanium oxide and a composite of titanium oxide with silver nanoparticles increases accordingly.

Authors Isaev A.E., Kosobudsky I.D. developed a methodology for conducting the experiment, Isaev A.E. conducted a study of optical density and the calculation of the rate constants of fast and slow coagulation Smoluchowski. Authors Ushakov N.M., Vasilkov M.Yu. and Mikhailov I.N. participated in data processing. Author Isaev A.E. carried out theoretical calculations. All authors participated in writing the text of the article and participated in the discussion of the results.

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REFERENCES

1. Dorofeyev SG, Kononov NN, Zverolovlev VM, Zinov'yev KV, Sukhanov VN, Sukhanov NM, Gribov BG. On The Application Of Thin Films Of Silicon Nanoparticles For Increasing Solar Cell Efficiency. *Semiconductors,* 2014, 48(3):360-368.
2. Ushakov N.M, Podvigalkin V.YA, Kosobudskiy I.D. Kremniyevyye fotoelektricheskiye preobrazovateli s nanokompozitnymi tolstoplenochnymi pokrytiyami [Silicon photovoltaic converters with nanocomposite thick-film coatings]. *Pribory,* 2014, 5(167):27-33, (in Russ.).
3. Gadomskiy ON, Altunin KK, Ushakov NM. Ideal optical clearing of composite films activated by spherical nanoparticles. *Journal of Experimental and Theoretical Physics Letters,* 2009, 90(4):251-256. DOI: 10.1134/S0021364009160061.
4. Postnikova OA, Pykin AA, Lukuttsova NP, Tuzhikova MYu. Samoochishchayushchiyesya pokrytiya na osnove nanodispersnogo dioksida titana [Self-cleaning coatings based on nanosized titanium dioxide]. *Effektivnyye stroitel'nyye kompozity,* 2015:523-530 (in Russ.).
5. Graetzel M, Rotzinger FP. Raman spectroscopic evidence for the existence of titanyl (TiO_2^+) in acidic aqueous solutions. *Inorganic Chemistry,* 1985, 24(14):2320-2321; doi: 10.1021/ic00208a041.
6. Nikolenko AN, Chaban EV, Mel'nikov BI. Sintez i issledovaniye svoystv rutil-anataznogo kompozitnogo fotokatalizatora [Synthesis and study of the properties of rutile-anatase composite photocatalyst]. *Voprosy Khimii i khim. Tekhnologii,* 2010:105-114 (in Russ.).
7. Avci N, Smet P, Lauwaert J, Vrielinck H, Poelman D. Optical and structural properties of aluminium oxide thin films prepared by a non-aqueous sol–gel technique. *Journal of sol-gel science and technology*, 2011, 59(2):327-333.
8. Nikitina LV, Kosobudskiy ID, Gvozdev GA. Polucheniye zol'-gel' metodom opticheskikh nanokompozitnykh pokrytiy [Obtaining a sol-gel by the method of optical nanocomposite coatings]. *Nauchnyy al'manakh,* 2016, 2-3:179-183, (in Russ.).
9. Yes'kin SV, Kosobudskiy ID, Zhimalov AB, Ushakov NM, Kochubey VI, Zakharevich AM, Gorbachev IA, Gorin DA, Kul'batskiy DM. Prosvetlyayushchiye pokrytiya na osnove amorfnykh submikronnykh chastits dioksida kremniya dlya silikatnogo stekla: polucheniye, morfologiya poverkhnosti, opticheskiye svoystva [Antireflection coatings based on amorphous submicron particles of silicon dioxide for silicate glass: preparation, surface morphology, optical properties]. *Rossiyskiye nanotekhnologii*, 2013, 8(11-12):69-75, (in Russ.).
10. Sigov AS, Surzhikov AP, Ivanov VI, Luchnikov PA, Gulyaev YuV. Osnovy konstruirovaniya i tekhnologii proizvodstva radioelektronnykh sredstv. Integral'nyye skhemy [Fundamentals of design and production technology of

radio electronic equipment. Integrated circuits]. Moscow, Yurayt Publ., 2018, 460 p., (in Russ.).

11. Korepanov MA, Gruzd' SA. Modelirovaniye gomogennoy kondensatsii s uchetom kvaziravnovesnoy kontsentratsii malykh aglomeratov [Simulation of homogeneous condensation taking into account the quasi-equilibrium concentration of small agglomerates]. *Khimicheskaya fizika i mezoskopiya*, 2014, 16(1):22, (in Russ.).
12. Masalov VM Sukhinina NS, Emel'chenko GA. Colloidal particles of silicon dioxide or the formation of opal-like structures. *Physics of the Solid State,* 2011, 53(6):1135-1139. DOI: 10.1134/S1063783411060229.
13. Startsev YuK. *Stekla v displeyakh. Trebovaniya, osobennosti tekhnologii, modelirovaniye svoystv* [Glasses in displays. Requirements, technology features, property modeling]. Saint-Petersburg, SPbGTI(TU) Publ., 2008, 134 p.