ISSN 1087-6596, Glass Physics and Chemistry, 2013, Vol. 39, No. 4, pp. 409–413. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © S.V. Es'kin, I.D. Kosobudskii, A.B. Zhimalov, N.M. Ushakov, D.M. Kul'batskii, S.V. German, P.A. Muzalev, 2013, published in Fizika i Khimiya Stekla.

Antireflecting Coatings for Glass Based on Monolayers of Amorphous Silica Nanoparticles

S. V. Es'kin[a, c], **I. D. Kosobudskii**[a, c], **A. B. Zhimalov**[b], **N. M. Ushakov**[c], **D. M. Kul'batskii**[c], **S. V. German**[d], **and P. A. Muzalev**[d]

[a] *Gagarin Saratov State Technical University, ul. Politekhnicheskaya 77, Saratov, 410054 Russia*
e-mail: vn.stanislav@gmail.com
[b] *Saratov Institute of Glass, Moskovskoye shosse 2, Saratov, 410041 Russia*
[c] *Saratov Branch, Kotel'nikov Institute of Radioengineering and Electronics, Russian Academy of Sciences, ul. Zelenaya 38, Saratov, 410019 Russia*
[d] *Chernyshevskii Saratov State University, ul. Astrakhanskaya 83, Saratov, 410012 Russia*

Received February 19, 2012

Abstract—The results of investigations into monolayered antireflective coatings based on silicon dioxide (silica) nanoparticles obtained according to the zol-gel technology using a simple and efficient technique of dipping into a zol of soda-lime glass are presented. The influence of silica-zol synthesis parameters and the size of the deposited nanoparticles on the structure and properties of the obtained coatings are revealed.

Keywords: silicon dioxide, nanoparticles, antireflection, coatings, glass

DOI: 10.1134/S1087659613040093

INTRODUCTION

Nowadays, the largest global producers on the market present soda-lime glass with antireflecting coatings, which possess an optical transmission in the visible wavelength range of more than 93%. The optical transmission of such glass in the visible wavelength range increases on average by more than 4–5% at the expense of the deposition of antireflecting coatings. However, the cost of these products substantially exceeds that of conventional silicate soda-lime glass due to the expensive and relatively complicated technology of vacuum magnetron deposition of the antireflecting coatings.

For the most widely spread soda-lime glass with a refractive index of 1.52 ($\lambda = 550$ nm), the theoretical value of the refractive index for an efficient monolayered antireflecting coating should be approximately 1.23 [1]. Such a low value can be achieved by depositing amorphous silica nanoparticles onto a glass substrate using a dip coating technique [2, 3]. Such coatings have a lower cost compared to the existing antireflecting coatings, and therefore, their development and investigation are topical.

The coatings based on amorphous silica are distinctive from other materials by their relatively low refractive index (1.46, $\lambda = 550$ nm), robustness, and durability. Moreover, when the size of material pores is much smaller than the visible light wavelengths, the refractive index of a coating based on amorphous SiO_2 depends on its porosity [4]. For example, a coating composed of spherical SiO_2 nanoparticles and having a porosity of ~50% has an efficient refractive index of 1.22 [5].

Hence, by depositing amorphous silica spherical nanoparticles onto glass, we can obtain an efficient monolayered antireflecting coating with a low refractive index because the loose arrangement of the particles creates the necessary material porosity. In addition, the porosity of the coating increases at the expense of the porosity ofSiO_2 particles themselves.

Thus, our work was aimed at obtaining and investigating antireflecting coatings of amorphous silica nanoparticles deposited onto soda-lime glass using a technologically simple and economical method of dipping.

EXPERIMENTAL

Silica sols were synthesized by hydrolysing tetraethoxisilane (TEOS) (the mass fraction of the basic substance was 98.9%, SPG 14–5, TC 2637-059-44493179-04) in the presence of ammonia (aqueouus solution of 30–33%, puriss., N 1272/2008 [EU-GHS/CLP]) as a catalyst. Since TEOS and water are not miscible liquids, they were dissolved in ethanol ($\omega = 96\%$, first grade, State Standard 18300-87).

The synthesis was carried out in the following sequence. First, an aqueous solution of ammonia was dissolved in half of the ethanol needed for the synthesis

Characteristics of synthesized silica sols

Number of samples	Molar ratio of silica sol components TEOS/ethanol/ammonia/water	Exposure duration, h	Average diameter of particles, nm	Index of polydispersity
1	0.25/8.00/0.05/1.20	24	14	0.197
		72	31	0.207
2	0.25/8.00/0.10/1.30	24	105	0.089
		72	107	0.091
3	0.25/8.00/0.30/1.70	24	177	0.133
		72	219	0.217
4	0.25/8.00/0.50/2.20	24	273	0.090
		72	379	0.160

(for 1 ± 0.5 min), then TEOS was dissolved in the second half of the ethanol needed for the synthesis (for 1 ± 0.5 min).

The solutions of TEOS and ammonia in ethanol were mixed together and then stirred for 4 ± 0.1 h, and then, the colloid formed was stored in a closed container at a temperature of 20 ± 1°C from 1 to 3 days for the growth of disperse phase particles (the solutions were stirred with the help of a magnetic stirrer).

The average diameter and index of the polydispersity of silica particles were controlled by changing the concentration of the alkali catalyst and water at constant temperature, duration, and the intensity with which the solutions were stirred (see table).

In order to measure the optical transmission, we used slides of 76 × 26 × 1 mm (CP-7101, State Standard 9284-75), and to measure the thickness and effective refractive index, we used soda-lime float glass of 25 × 15 × 4 mm (State Standard 111-2001). The coatings were deposited on glass substrates by dipping them into the synthesized silica soles and subsequently pulling them out at a controlled velocity (50 ± 5, 100 ± 5, 150 ± 5 mm/min). The substrates were preliminarily degreased by ethanol.

When the glass with the deposited coatings was dried in air for 10 min at a temperature of 20 ± 1°C, the samples were thermally treated at a temperature of 500 ± 10°C for 1 h to remove ammonia, ethanol, and water.

The average diameter, polydispersity index, and ζ-potential of silica sol particles were measured on an analyzer of series Zetasizer Nano (ZS).

In order to determine the structure of silica particles obtained from silica soles, we used the X-ray phase analysis (XPA), diffractometer DRON-4 (CuK_α-radiation). Prior to this procedure, the sediments separated by spin were dried and baked at a temperature of 500 ± 10°C for several hours. The diffractograms were analyzed using data base of PCPDFWIN, v. 2.02, 1999 (JCPDS).

The structure of the obtained antireflecting coating surface on a glass substrate was studied using atomic force microscopy (AFM) with the help of Solver P47 microscope produced by NT-MDT. As the samples to be analyzed, we used slides of 8 × 8 × 1 mm (CP-7101, State Standard 9284-75) without a coating and with a deposited coating of silica sol 2 (see the table, exposition duration is 72 h).

The optical transmission of the glass samples with the deposited antireflecting coatings was measured on a Lambda-950 (Perkin Elmer) spectrophotometer at an angle close to normal in the wavelength range from 300 to 1000 nm with a step of 10 nm. A change in the optical transmission was fixed as the difference between the transmission of the glass half with the coating and that without a coating. An error in the measurement of the optical transmission was ±0.01%.

The optical constants of these coatings were measured on an Ellyps-1000 ASG spectral fast ellypsometric complex. In order to calculate the refractive indices and thicknesses of the coatings, the ellypsometric results were processed by the Spectran software with the use of the Bruggeman model for a two-component medium, SiO_2—air.

The area of the specific surface and the sizes of the pores of SiO_2 particles obtained by spinning from silica sol 2 were determined on a Quantachrome NOVA 1200 analyzer and by the methods of Brunauer—Emmett—Teller (BET) and Barrett—Joiner—Halenda (BJH), respectively.

RESULTS AND DISCUSSION

The average particle diameter of the obtained silica soles depends on the parameters of their nucleation and growth. During the hydrolysis reaction, an ethoxi-group of a TEOS molecule reacts with a water molecule forming an intermediate compound $Si(OC_2H_5)_{4-x}(OH)_x$ with a hydroxyl group instead of ethoxi-group of TEOS:

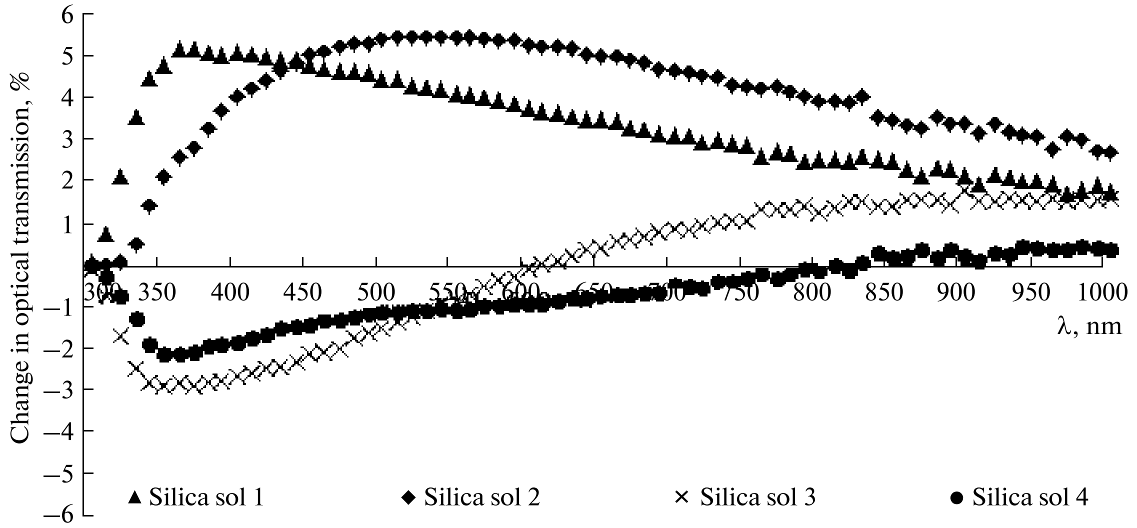

Fig. 1. Change in the optical transmission of glass with deposited coatings (velocity of removal of substrates from silica sols is 100 ± 5 mm/min) in comparison to glass without coatings.

Figures by the curves are numbers of samples from the table, and exposure is 72 h.

$$\mathrm{Si(OC_2H_5)_4} + x\mathrm{H_2O} = \mathrm{Si(OC_2H_5)_{4-x}(OH)_x} + x\mathrm{C_2H_5OH}. \quad (1)$$

Ammonia is a catalyst in this reaction.

After hydrolysis, a reaction of condensation occurs immediately. A hydroxyl group of the intermediate compound $\mathrm{Si(OC_2H_5)_{4-x}(OH)_x}$ reacts either with an ethoxi group of another molecule of TEOS, or with a hydroxyl group of another hydrolysis product forming bridges Si—O—Si [6].

Finally, the hydrolysis can be written as the following scheme:

$$\mathrm{Si(OC_2H_5)_4} + 2\mathrm{H_2O}\ \mathrm{SiO_2} + 4\mathrm{C_2H_5OH}. \quad (2)$$

It is considered that in the course of the reactions of hydrolysis and condensation, a specific basic catalysis takes place ($\mathrm{OH^-}$); however, understanding of its mechanism is impeded due to the change in the sol pH in the course of the reactions.

The table shows the characteristics of the synthesized silica sols.

An acceleration in the reaction of hydrolysis and, probably, an increase in the size of the obtained silica particles takes place in the reaction mixture at the expense of an increase in the concentration of the catalyst.

The aggregative stability of colloid particles is determined by the value of ζ-potential. For an electrostatic stabilization of particles, the value of ζ-potential should be between |40| and |60| mV [7]. In this work, the ζ-potential of silica sols ranged from −35 to −45 mV, which proves the rather high stability of the obtained colloid solutions. However, with a growth in the duration of the colloid exposure, the growth of the dispersed phase particles takes place (see table).

A diffusion halo was observed in the diffractogram of these particles, which is typical for an amorphous silicon dioxide, and this is required for the coatings because the amorphous $\mathrm{SiO_2}$ possesses a lower refractive index compared to a crystalline one.

The obtained antireflecting coatings possess different optical transmission (see table). Figure 1 shows the spectra of changes in the optical transmission for glass with deposited coatings in comparison to the spectra of glass without coatings. It can be seen from the figure that the antireflection maximum shifts to the spectrum long-wavelength with an increase in the size of the deposited $\mathrm{SiO_2}$ particles. This dependence is observed for all the samples. In particular, a maximum of the optical transmission of sample 1 is located in the range of 350–400 nm, while the antireflecting properties of the coating obtained by the use of silica sol 4 start appearing only on a wavelength of ~800 nm (see table). The shift in the transmission maximum towards the long-wavelength region of the spectrum is accounted for by an increase in the coating thickness.

A rather important circumstance is the change in the increase of the amplitude of the optical transmission, depending on the silica sol used for the coating deposition. For example, the greatest increase in the optical transmission in the measured wavelength region occurred in samples of glass 2 (exposure 72 h) with the deposited antireflecting coatings (a maximum of ~5.5% for λ = 500–550 nm) and the samples 1 (an exposure of 72 h) (a maximum of ~5% for λ = 350–400 nm) (see Fig. 1). In the case under consideration, a change in the amplitude of the antireflection depends on the coating's refractive index, which in

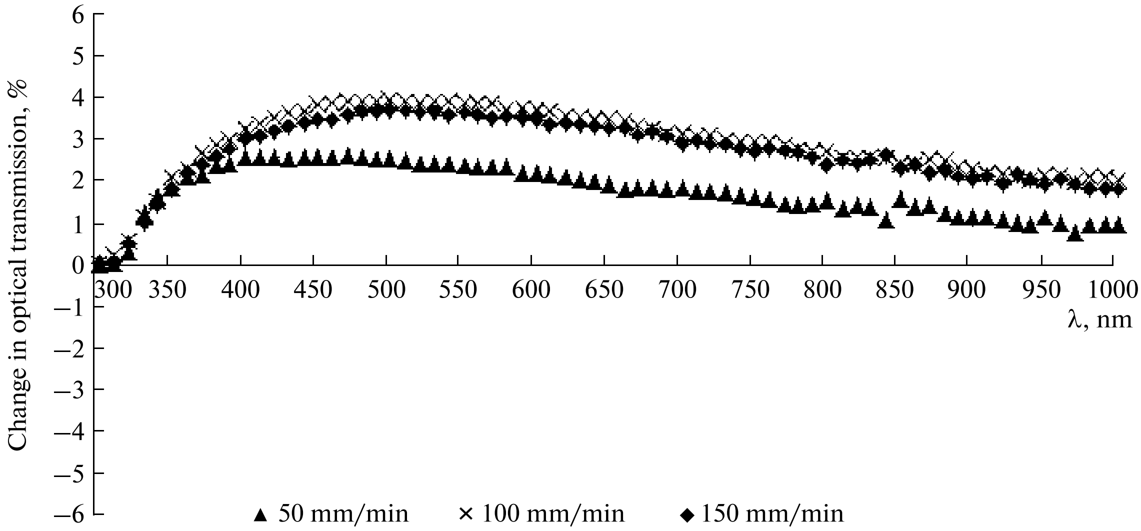

Fig. 2. Dependence of the optical transmission of samples 2 (exposure of 24 h) on the velocity of removal from sols in comparison with the substrates without coatings.
The velocities of pulling out (mm/min): *1* is 50, *2* is 100, *3* is 150.

turn depends on the coating porosity. And the porosity of the coatings is to a substantial degree determined by the packing factor of silica particles. In the case of a material composed of spherical or similar particles, an important parameter is their polydispersity index (PDI) being a dimensionless value characterizing the width of the particle size distribution curve. Particles whose PDI is smaller than 0.1 are often called monodisperse particles. The smaller the PDI of the SiO_2 spherical particles deposited onto the substrate the more nondense the package they have and, hence, a low refractive index. For example, coating 2 (an exposure of 24 h) had an efficient refractive index of 1.28 on $\lambda = 550$ nm at the smallest PDI of the deposited particles (0.091).

It was also found that the velocity at which the substrate pulls out of the silica sols affects the optical transmission of the composition of the glass (Fig. 2).

So, by an increase in the removal velocity (v) the coating thickness d increased: $d = 112$ nm at $v = 50 \pm 5$ mm/min, $d = 170$ nm at $v = 100 \pm 5$ mm/min, and $d = 180$ nm at $v = 150 \pm 5$ mm/min. It is noticeable that an increase in the coating thickness is not material when the removal velocity increases from 100 ± 5 to 150 ± 5 mm/min.

According to the AFM results (Figs. 3 and 4), the average arithmetic roughness of the coating obtained on sample 2 (table, an exposure of 72 h) at the velocity of the substrate's removal from the solution of 100 ± 5 mm/min was 20 nm, while the profile greatest height was 55 nm. The value of the profile's greatest height of the glass substrate did not exceed 9 nm, and its average arithmetic roughness was equal to 3 nm (Fig. 3). The increase in the unevenness of the substrate's profile due to the deposition of silica particles barely affects

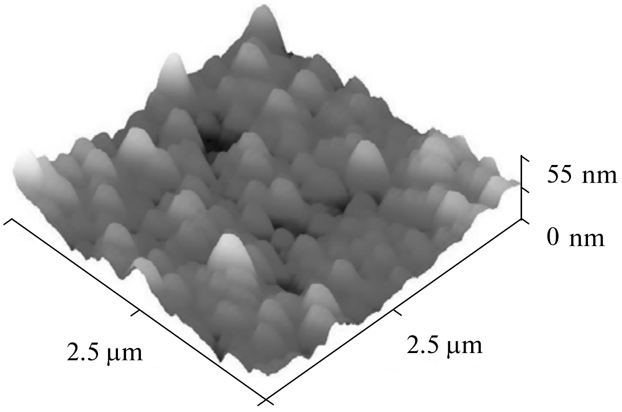

Fig. 3. Image of surface relief of the glass substrate (area of scanning is 2.5 × 2.5 μm).

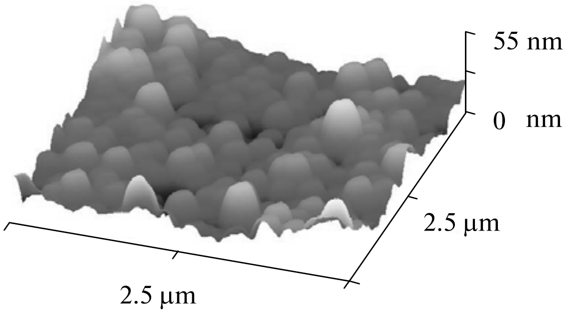

Fig. 4. Image of the surface relief of an antireflecting coating (area of scanning is 2.5 × 2.5 μm).

the material's optical properties, because it is known that the surface of an optical piece starts noticeably dissipating the light flux at the value of the profile's greatest height ($R_{\max}$) of more than 10% of the wavelength of the impinging light. Therefore, for a visible radiation, the surface's cleanliness should be limited by an index $R_{\max}$ of $\leq$ 100 nm [8].

It follows from the AFM data (Fig. 4) that an antireflecting coating is composed of SiO_2 nanoparticles whose shape is close to spherical. The coating has a porous structure possibly because of the loose arrangement of such particles.

The results of the measurements of the specific surface area and the sizes of the pores of the SiO_2 particles obtained by spinning silica sol 2 (see table, exposure of 72 h) showed that the particles had a specific surface of 376.4 m^2/g and an average radius of pores of 1.6 nm. Thus, it is possible to conclude that the porosity of the coating depends not only on the arrangement of silica spherical nanoparticles but also on their own porous structure.

CONCLUSIONS

Antireflecting coatings based on SiO_2 amorphous nanoparticles on silicate soda-lime glass were obtained and studied.

The obtained colloid solutions had different average particle diameters of the dispersed phase in the range of 14–379 nm. The polydispersity index of silica sols varied within a wide interval from 0.089 to 0.217. The ζ-potentials of silica sols ranged from –35 to –45 mV, which proves the rather high stability of the obtained colloid solutions.

The greatest increase in the optical transmission in the visible wavelength range (a maximum of 5–5.5%, $\lambda = 500–550$ nm) was fixed for a glass sample with a coating obtained from silica sol with the average particle diameter of 107 nm. The velocity of the substrate removal from the sol was equal to 100 ± 5 mm/min. The greatest surface profile height for the coating under consideration did not exceed 55 nm. The area of the particle's specific coating surface amounted to 376.4 m^2/g, and the pore's average radius was 1.6 nm. Hence, the coating of the porous structure was caused not only by the tight packing of particles (because they were approximately of the same size, PDI = 0.091) but also by their own porosity. Due to this, the efficient refractive index of the coating at $\lambda = 550$ nm was equal to 1.28. Thus, by obtaining a coating of suitable thickness, we managed to "antireflect" soda-lime glass.

We have shown that by using a simple and economical sol-gel technology it is possible to obtain efficient monolayered antireflecting coatings for silicate soda-lime glass. Moreover , by varying the average diameter of the SiO_2 particles deposited onto the substrate and the conditions of their deposition, we can control the thickness of the obtained coating and, hence, the range of the antireflection.

ACKNOWLEDGMENTS

The work was carried out with the financial support of the Russian Foundation of Fundamental Research (grant no. 11-08-00351).

REFERENCES

1. Putilin, E.S., *Opticheskie pokrytiya* (Optical Coatings), St. Petersburg: St. Petersburg State University of Information Technologies, Mechanics, and Optics, 2010.
2. Thomas, I., High laser damage threshold porous silica antireflective coating, *Appl. Opt.*, 1986, vol. 25, no. 9, pp. 1481–1483.
3. Beganskienė, A., Sirutkaitis, V., Kurtinaitienė, M., Ju@k@nas, R., and Kareiva, A., FTIR, TEM, and NMR investigations of Stöber silica nanoparticles, *Mater. Sci. (Medžiagotyra)*, 2004, vol. 10, no. 4, pp. 287–290.
4. Braun, M.M., Braun, M.M., and Pilon, L., Effective optical properties of non-absorbing nanoporous thin films, *Thin Solid Films*, 2006, vol. 496, no. 2, pp. 505–514.
5. Thomas, I., Method for the preparation of porous silica antireflection coatings varying in refractive index from 1.22 to 1.44, *Appl. Opt.*, 1992, vol. 31, no. 28, pp. 6145–6149.
6. Lee, K., Look, J.-L., Harris, M.T., and McCormick, A.V., Assessing extreme models of the Stöber synthesis using transients under a range of initial composition, *J. Colloid Interface Sci.*, 1997, vol. 194, no. 1, pp. 78–88.
7. Greenwood, R. and Kendall, K., Selection of suitable dispersants for aqueous suspensions of zirconia and titania powders using acoustophoresis, *J. Eur. Ceram. Soc.*, 1999, vol. 19, no. 4, pp. 479–488.
8. Shachneva, I.B., in *Sbornik zadach dlya samostoyatel'noi raboty po distsipline "Uchebno-tekhnologicheskii praktikum"* (A Collection of Problems for Individual Work on the Subject "Educational Technological Laboratory Manual"), Shachneva, I.B., Yaroslavtseva, N.A., and Chirkin, D.P., Eds., Moscow: Bauman Moscow State Technical University, 2010.

Translated by R. Litvinov

SPELL: 1. Mikheeva