Optical properties of sol-gel coatings containing silver nanoparticles

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Abstract. The technology of receiving the antireflective coating increasing efficiency of use of sunlight in various service conditions is described. Suspensions of nanodimensional silicon dioxide with tetraethoxysilane as a precursor were synthesized to solve the assigned task. The received suspensions were applied by a dipping method on glass samples followed by the coating formation on a surface of the substrates at various temperatures. As a result of a cure of the received samples under natural conditions transparent film of about 500 nanometers thick having very low strength properties on the surface of glass were formed. Heat treatment led to the improvement of strength of coatings in process with increase of temperature up to 600 °C. Exceeding of this temperature resulted in cracking of coatings. In the course of heat treatment higher than 300 °C formation of a coating was accompanied by the thermolysis of silver nitrate that was introduced into silicon dioxide suspension with a formation of silver particles which size was in the nanoscale distance limits according to the results of Auger electron spectroscopy. Presence of evenly distributed silver nanoparticles provided an antireflective effect to coatings which at visual observation found expression in the form of the interference phenomenon. The obtained data confirmed prospects of use of nanosilver as a component of coatings on the basis of silicon dioxide in order to confer the antireflective properties.

1. Introduction

All currently widely used optical systems that allow the transmission of light energy and images are based on the effects of reflection and refraction. Reflection increase means the reduction of light transmittance through a transparent medium. For example, about 8.6% of the incident light at an angle of 0° is reflected from the two interfaces of glass and air, when the refractive index of silicate glass n = 1.51.

Improving the efficiency of optical devices is an urgent issue [1-3]. The antireflection coating application (or anti-glare coating) is used in areas where light passes through an optical element and it is necessary to reduce the loss of intensity or eliminate reflection (lenses, solar cells, etc.). The most well-known solution to the problem of reducing reflection and increasing light transmittance is the use of low-reflection thin-film interference coatings, the main limitation of which is the impossibility of their application on the large-size optical components. In addition, it is necessary to create multilayer coatings of this type in order to achieve the antireflective effect in a wide range of wavelengths.

Therefore, other ways to reduce reflection and thereby increase the light transmittance of optical objects are searched for. The common cases are eyeglass lenses and camera lenses.

In this study, the low-reflection properties of sol-gel coatings formed on the basis of silicon dioxide and the influence of dispersed nanoscale silver on their optical properties were investigated. The
possibility of using nanosilver in low-reflective coatings was shown in the studies, where coatings based on polymethyl methacrylate were used as an example [4, 5].

2. Experimental
At the first stage of the study, aqueous nanosuspensions of silicon dioxide were synthesized, which were the precursor for obtaining the investigated coatings. Synthesis of SiO₂ sols was carried out according to the known method, including the hydrolysis of tetraethoxysilane (TEOS) and polycondensation according to the reaction equations:

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\begin{align*}
\equiv\text{Si}−\text{O} \text{C}_2\text{H}_5 + \text{H}_2\text{O} &= \equiv\text{Si}−\text{OH} + \text{C}_2\text{H}_5\text{OH} ; \\
\equiv\text{Si}−\text{O} \text{C}_2\text{H}_5 + \text{HO}−\text{Si}≡ &= \equiv\text{Si}−\text{O}−\text{Si}≡ + \text{C}_2\text{H}_5\text{OH} ; \\
\equiv\text{Si}−\text{OH} + \text{HO}−\text{Si}≡ &= \equiv\text{Si}−\text{O}−\text{Si}≡ + \text{H}_2\text{O}.
\end{align*}
\]

The process of hydrolysis of TEOS occurs most quickly and completely when an appropriate catalyst is used. To obtain silicon dioxide of various structures, two types of synthesis catalyst were used, viz. hydrochloric acid as an acid catalyst and ammonia as alkaline one.

The sols were synthesized by successively mixing a solvent (ethanol), distilled water, a catalyst, and introducing TEOS with continuous stirring. The resulting mixture was stirred for 24 hours until a homogeneous sol was obtained.

During the preliminary experimental studies, the following molar ratios of the components of the reaction mass were selected as optimal ones, TEOS / water / ethanol / hydrochloric acid = 0.25 / 0.95 / 8.00 / 0.10 and TEOS / water / ethanol / ammonia = 0.25 / 1.15 / 8.00 / 0.10.

The study of the dispersion composition of the obtained sols was carried out by the method of dynamic light scattering (DLS) using a Brookhaven 90Plus nanoparticle size analyzer.

3. Results and discussion
Figure 1 shows the lognormal distribution of particles by volume in the SiO₂ sol (a) and the bimodal distribution of particles per volume unit according to the data of the DLS (b), which is characterized by the presence of two main fractions.

Figure 1b shows that the suspension contains mainly (70 vol.%) nanoparticles, the size of which is between 22.5–26.0 nm. However, particles of a larger size are also present in the suspension (30 vol.%), they correspond to the second maximum on a bimodal distribution curve with particle sizes of 95.0 - 136.5 nm.

Figure 2 shows the unimodal distribution of particles by volume in the SiO₂ sol obtained in the presence of an acid catalyst (a) and the bimodal distribution according to the data of the DLS (b), which is characterized by the presence of two fractions.
According to Figure 2b, it can be said that the sol contains mostly (95 vol.%) isolated nanoparticles, the size of which is between of 69.00 - 109.00 nm. However, an insignificant proportion (5 vol.%) of aggregates is present in the suspension, it corresponds to the second maximum on the bimodal distribution curve with particle sizes of 205.00 - 300.00 nm.

Coatings based on the obtained suspensions were applied onto the stage glass by a dipping method, thus varying the rate of substrate extraction from the bath with the precursor, using RM-50 tension testing machine. The coating thickness was determined by using probe microscopy.

The study of the optical properties of the coatings was carried out by recording curves of the light reflection and light transmittance of the obtained coatings and painted glasses in the 400-700 nm wavelength range using X-Rite Color and Proscan MC 122 spectrophotometers, respectively. Pure glass similar to the one on which the coatings were applied was used as a reference standard when measuring optical characteristics.

Figure 3 shows the light transmittance spectra of coatings based on the sol prepared with an alkaline catalyst.

The obtained data allow us to conclude that coatings based on the SiO₂ sol synthesized in the presence of an alkaline catalyst increase the light transmittance of glass (an antireflective effect is observed) in the wavelength range of 350-1100 nm. The largest increase in optical transmittance is
recorded for samples with a 2% concentration of SiO$_2$ in the resulting sol (curve 3), with a maximum of about 97.94% at a wavelength of 450–500 nm (Figure 3).

Figure 4 shows the light transmittance spectra of coatings based on a sol obtained from TEOS in the presence of an acid catalyst.

![Transmittance spectrum of glasses with SiO$_2$ coatings](image)

**Figure 4.** Transmittance spectra of glasses with SiO$_2$ coatings, obtained by dipping in sols with different concentrations (acid catalyst).

Coatings based on the SiO$_2$ sol obtained in the presence of an acid catalyst also increase the light transmittance of glass (the antireflective effect) in the wavelength range of 350–1100 nm. The greatest increase in optical transmittance is observed in the 3% sol of SiO$_2$ (curve 3), with a maximum of about 94.7% at a wavelength of 450–500 nm.

Further studies used a silica sol obtained in the presence of an alkaline catalyst, which had a large low-reflection effect, according to the research.

An Olympus LEXT OLS4000 3D Laser Measuring Microscope was used to evaluate the external appearance of the obtained coatings. Micrographs of coatings of sols with different contents of silicon dioxide obtained in the presence of an alkaline catalyst are shown in Figure 5 and 6.

![Micrographs of glasses with SiO$_2$ coatings](image)

**Figure 5.** Micrographs of glasses with SiO$_2$ coatings obtained by dipping in sols of various concentrations (alkaline catalyst) (% by mass): (a) – 1%, (b) – 2%, (c) – 3%, (d) – 5%.

According to the data presented in Figure 5, we can conclude that the obtained coatings have a certain texture, which varies depending on the content of silicon dioxide in the precursor.

A glass with a coating of 2% silica sol prepared in the presence of an alkaline catalyst was taken as a reference sample (Figure 3, curve 3).

Figure 6 show the transmittance and reflection spectra of glasses coated by silica with different silver contents regarding the reference sample. Visual observations from different view angles permitted to establish that the coatings had an interference effect.
As it can be seen from Figure 6a, the introduction of silver increases the transmittance and reduces reflection, but the ratio silica/silver being 10:1 has a more favorable effect on this indicator. This ratio was used later on.

The insignificant antireflection effect after the introduction of nanosilver, suggests that calcination results in leveling of the surface of the coatings, in other words, in a decrease of the antireflection effect from its texture, as compared with the previously obtained data for polymethylmethacrylate coatings. Therefore, the result of the experiments is the net effect of the summation of effects from the introducing nanosilver into the composition of coatings and changing the texture of their surface.

The comparison results of reflectivity and light transmittance of coatings obtained at different temperatures are an indirect proof, they are presented in Figure 7. This comparison allows us to conclude that when the calcination temperature increases, the reflectivity of the coatings increases, and the light transmittance decreases, which is most likely due to the formation of their texture.

4. Conclusion
Determination of a particulate composition of the synthesized silicon dioxide sols by dynamic light scattering showed that in the presence of the acid catalyst larger particles are formed. Their existence has negative effect on aggregative and sedimentation stability of the studied colloidal systems. In turn, the analysis of transmittance spectra of glass plates coated with received sols at different concentration of silicon dioxide allowed to make a conclusion about higher antireflective effect at coatings on the basis of the sol received with use of an alkaline catalysis. As a result of visual inspection of coatings by means of an optical microscope the specific texture of their surface which depends on the content of silicon dioxide nanoparticles was found. It is established that excess of a certain concentration of
nanoparticles leads to a cracking of coatings as a result of reaching of the critical value of internal tensions. Introduction to the structure of silver nanoparticles to the coatings formed at the room temperature allows to improve optical properties, however upon calcinating of the samples at temperatures higher than 500 °C a tendency to deterioration in optical properties is observed. Generalization of experimental data allows to draw a conclusion on prospects of the research aimed to study the regularities of the formation of sol-gel coatings with silver nanoparticles for use in the field of optical instrumentation and solar power.

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