SOL-GEL SYNTHESIS OF MODIFIED SILICA ANTI-REFLECTING COATINGS

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Abstract. The thickness of the modified silica coatings and their transparency at specified wavelength were easily controled by changing sol concentration and the parameters of the spin-coating formation process. It was demonstrated that the modification of sols changes the maximum of the transmittance for the certain range of wavelength. Using modification process of the sols in the technology of preparation of transparent coatings, their hydrophobic properties and resistance to humidity increased. The transmittance spectra of the 3% SiO_2 coatings, which were applied on different glass substrates, showed that the usage of suitable sol and coating program will result a formation of films which possess antireflective properties

Keywords: Sol-gel method, silica coating, anti-reflecting coating, colloidal silica.

1. Introduction

Anti-reflection (AR) coatings are often used for optical components in order to reduce optical losses.[1] The residual reflectivity for a given wavelength and angle of incidence is often of the order of 0.2%, or less (in a limited bandwidth) with careful optimization. For application on prescription glasses, the achievable suppression of reflections is significantly lower, since the coating must operate in a wide wavelength range and for a wide range of incidence angles. AR coatings are also used on laser crystals and nonlinear crystals.

AR and protective coatings are usually applied on the substrates via sol-gel technique.[2–4] This chemistry produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, optical

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transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures. The specific uses of these sol-gel produced glasses and ceramics are derived from the various material shapes generated in the gel state, i.e., monoliths, films, fibers, and monosized powders. Many specific applications include optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers, and catalysts.[5–7] Colloidal silica sols are created by the hydrolysis and condensation of silicon alkoxides in alcohol solvents in the presence of a base (e.g., NH_3) and H_2O. Controlling the amount of NH_3, it is possible to synthesize colloidal particles of different sizes.[8] In order to create an amorphous colloidal SiO_2 optical film - silica nanoparticles are used with variation in size from 20 to 35 nm. The refractive index of such films is somewhat about 1.23 and the porosity of the films is about 50–60%.[9] Though these films have a lack in being hydrophobic, they absorb molecules of water from the air on the surface of the film. This problem can be fixed by changing the properties of the nanoparticles or by modifying the surface of the film changing the from hydrophilic to hydro-phobic. Various reagents are used for the modification of silica particles and films, such as: heksamethyldisilo-zane (HMDS), methyltrietoxisilane (MTES) and methyldietoxisilane (DDS), etc.[10–16] The main aim of this study was investigation of sol-gel derived and modified silica coatings on different substrates.

2. Experimental

Colloidal silica oxide films were applied on different substrates, such as "Menzel–Glaser" (76 × 26 mm), BK-7 optical glass, quartz and KDP crystals. The coatings were formed either by dip-coating technique using "KSV Instruments Ltd. KSV D™" device, or by spin-coating technique using "Cookson electronics company SCS P-6708" device. The parameters for dip-coating were as follows: withd-rawal speed 40 mm/min, immersion time 20 s. The parameters for spin-coating were 2,000–3,000 rounds per min. Contact angle measurements were done by "KSV instruments CAM – 100" device. A drop of 0.0125 ml was introduced on the surface of the film. Coating transmittance and reflectance of normally incident light was measured using UV-VIS spectrophotometers (Perkin-Elmer Spectrum Lamda 19 and LOMO) over the spectral range of 350–1,000 nm. The particle size was determined from the micrographs obtained from TEM measurements.

Reagents used: tetraethylorthosilicate ($Si(OC_2H_5)_4$, 99–99.9%), ammonium hydroxide (33%), heksamethyldisilozane ($C_{19}H_{19}NSi_2$, 98%), anhydrous ethanol, 2-propanol, decane. Different sol-gel solutions SiO_2 (2%, 3%, 5%) and modified SiO_2 (3%, 5%) with HMDS (hexamethyldisilazane) were used for preparation silica coatings. Sol-gel synthesis of colloidal SiO_2 (2%, 3%, 5%) nanoparticles was performed in non-aqueous system of TEOS. The precursor of SiO_2 colloidal sol was prepared by the base catalyzed hydrolysis of tetraethylorthosilicate by the following method of preparation of Stöber et al.[17] colloidal silica. The alkaline solution was added to the solution of TEOS in ethanol with continuous stirring at room temperature. The solutions with final silica concentration of 2%, 3%, 5% SiO_2 were prepared. The molar ratio of ammonium hydroxide to TEOS was 0.2 mol, to water – 0.4 mol, to ethanol – 39, 38 and 25 mol respectively. The obtained reaction mixtures were stored for 14 days at room temperature to allow hydrolysis as much as possible. The final product consisted of colloidal suspension of SiO_2 nanoparticles in an anhydrous solvent was used for preparation of the sol-gel coatings. The modified solutions were prepared by adding HMDS to stirred colloidal 3%, 5% SiO_2 suspensions. The molar ratio of HMDS to colloidal silica was from 0.05 to 1.5 parts per volume. The modified sol solution was stored for 1 day, after dilution three times with anhydrous ethanol was applied for sol-gel coatings at room temperature.

3. Results and Discussion

As was already mentioned, the main goal of this work was to prepare the modified sol-gel AR coatings on different substrates. For that reason several colloidal SiO_2 sols (2%, 3%, 5%) were synthesized. The morphology of colloidal silica was analyzed using transmitting electron microscope (TEM). Pictures of particles from 2%, 3%, 5% and modified SiO_2 sols are presented in Figures 1 and 2.

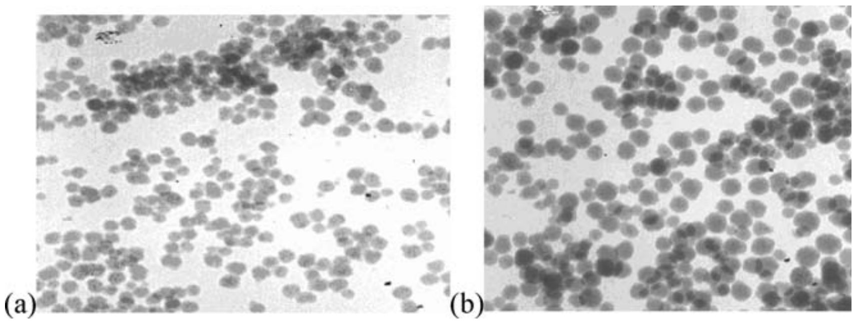

Figure 1. TEM pictures of colloidal silica particles: (a) SiO_2 (2%) (~20–35 nm) and (b) SiO_2 (3%) (~30–45 nm).

The change in the concentration affects the size of the particles, which means that the refractive index and the thickness of the coating will also change. Different amount of HMDS were mixed with SiO_2 sols and after applying them on the glass substrates via "dip-coating" technique, a number of permeability and contact angle analysis were done. The best result in this case was reached using modified sol, when the concentration of HMDS was 0.5 (p.p.v). Heating

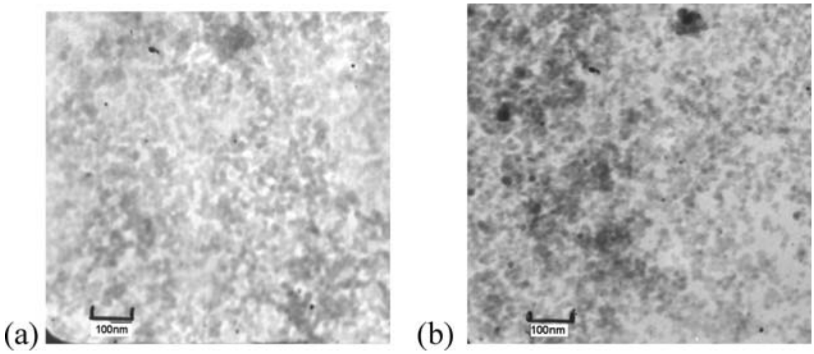

Figure 2. TEM pictures of colloidal silica particles: (a) SiO_2 (5%) sol and modified with HMDS (b) sol SiO_2 (5%) : HMDS (1:1.5).

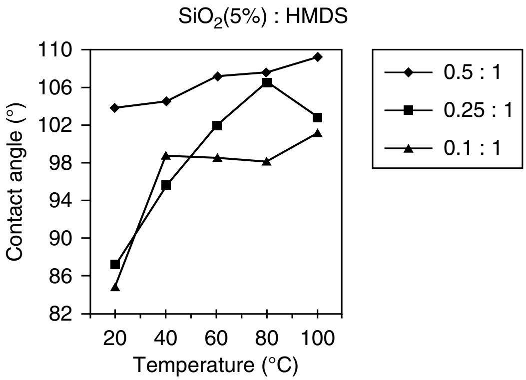

Figure 3. SiO_2(5%) : HMDS contact angle dependence on temperature of drying.

the substrates until 100°C also generates changes in contact angles of water drops on the coatings. The contact angle measurements are plot-ted in Figure 3.

The transparency of the coatings, made from SiO_2 (5%):HMDS (1:1.5 p.p.v.) reaches 97.37% in the interval of wavelength from 516.18 to 598.91 nm. The value of contact angle increases both with concentration of HMDS and in time (Figure 4).

The highest value of contact angle was obtained when the concentration of HMDS is 1.5 p.p.v, is 137.35°, after 40 days this value is changed and the contact angle of the applied coating is ~164°. There are several types of coatings, basing on the value of contact angle, hydrophilic (<60°), hydrophobic (60°–150°), superhydrophobic (>150°). Figure 5 shows us how the surface properties of our coatings are changed from hydrophilic SiO_2 (5%) – 15.73°, to superhydrophobic SiO_2 (5%):HMDS (1:1.5 p.p.v.) after 40 days – 164.98°.

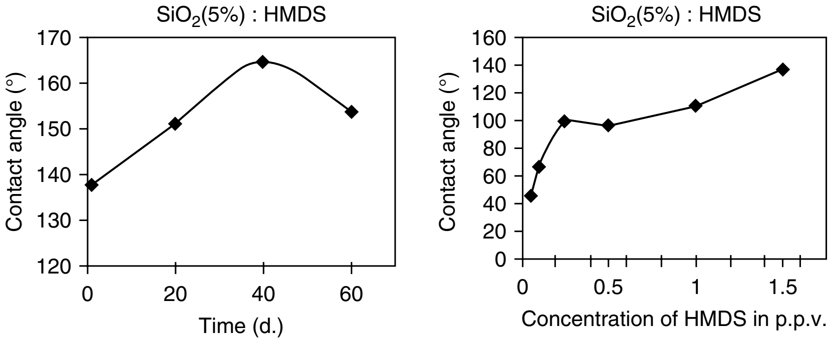

Figure 4. Contact angle of SiO_2 (5%):HMDS (1:1.5 p.p.v.) coating dependence on (a) time, (b) concentration.

The optical transparency is more likely to be dependent on the formation process of the coating, especially on the first stage of rotation. The best result is achieved using first program during the employment of SiO_2 (5%) sol, on the substrate, transparency of the coating reaches ~93%, thought it is not the best result in seeking for high optical properties. The transparency spectra of the samples are shown in Figure 6.

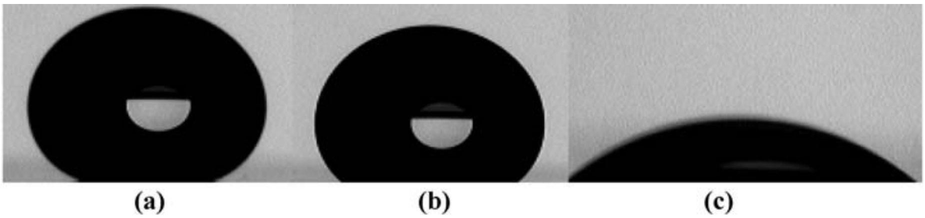

Figure 5. Pictures of water drops on the coatings made from: (a) SiO_2 (5%):HMDS (1:1.5 p.p.v.) after 40 days – 164.98°, (b) SiO_2 (5%):HMDS (1:1.5 p.p.v.) after 1 day. – 137.35°, (c) non-modified SiO_2 (5%) – 15.73°.

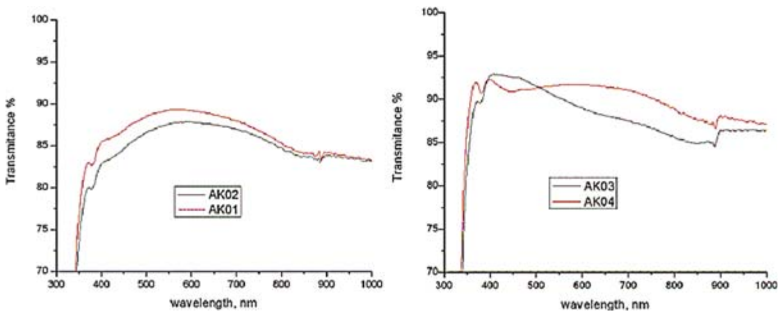

Figure 6. Transmission spectra of samples coated with: 5% SiO_2 HMDS (left) and 5% SiO_2 (right).

Nonetheless, modification of sols changes the maximum of the transmittance for the certain range of wavelength, this fact is really important in describing optical properties of the coatings. Coatings were also applied on different substrates, in order to investigate their optical properties. Lime glass, BK-7 (borosilicate glass) and quartz were coated using spin-coating technique. Glass substrates were coated with SiO_2 sols of different concentration (2%, 3%, 5%). This spectral analysis showed us, that the best transparency is ascribed to the coating which was formed using 5% SiO_2 sol. Afterwards we took 3% SiO_2 sol and applied coatings on simple glass, BK-7 glass and quartz using program No. 2. Transparency spectra are shown in Figure 7.

Analyzing the obtained data, we see that the transparency of a simple glass increased from 90.6% to 94.24% when the value of wavelength is 528 nm, BK-7 from 91.3% to 94.7% when the value of wavelength is 410 nm, quartz from 92.3% to 95.3% – 452 nm, so it is obvious that formed coatings possess antireflective properties.

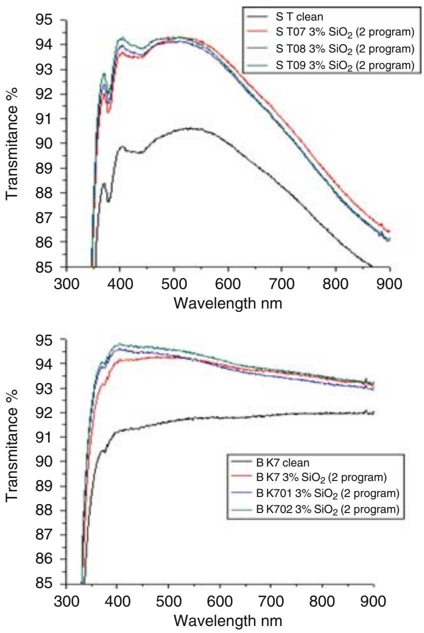

Figure 7. Transmission data for coated Lime and BK-7 glass substrates with 3% SiO_2 sol: Lime glass (top) and BK-7 glass (bottom).

4. Conclusions

Thickness and transparency of the coating depends on the first stage of the program due to the fact that viscosity of the sol solutions is small and evaporation rate of the ethanol is quite high. Modification of sols changes the maximum of the transmittance for the certain range of wavelength, the refractive index of the coating and the amount of air in it decreases, this fact is really important in describing optical properties of the coatings. Using modi-fication process of the sols in the technology of creating transparent coatings increases their hydrophobic properties and resistance to humidity. Trans-mittance spectra of the 3% SiO_2 coatings, which were applied on different glass substrates, showed that the usage of suitable sol and coating program will result a formation of films which possess antireflective properties. Simple glass 94.24% at 528 nm, BK-7 94.7% at 410 nm, quartz 95.3% at 452 nm.

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