

Sol-gel derived antireflective coating with controlled thickness and reflective index

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Optical properties and structure of antireflective coatings (AR) deposited from hydrolysed TEOS sol have been characterized in detail. The influence of various parameters on the formation of colloidal silica antireflective coatings by the dip-coating technique has been investigated. For the characterization of colloidal silica films, the UV-visible spectroscopy, laser ellipsometry, and atomic force microscopy were used. Using optimal sol-gel processing conditions (dipping rate – 40 mm/min, coating time – 20 s, and temperature – 20 °C), the colloidal silica coatings were obtained and characterized in comparison with non-coated glass substrate. The reflectance of AR coatings increased with increasing the temperature of sol-gel processing. The laser damage threshold of as deposited films was measured at 1064 nm (1H) and 335 nm (3H) wavelength using a Nd:YAG lasers. The laser damage threshold of AR coating exceeded 15.22 J/cm² at 1064 nm and 26.82 J/cm² at 355nm.

Key words: *antireflective coating; colloidal silica; sol-gel method; laser threshold*

1. Introduction

Light reflections from computer monitors, car dashboards, and TV screens impair the legibility of the displays by degrading the transmission of optical components. The decrease in transmission of a transparent optical medium is caused by an abrupt change in the refractive index at the interface between the medium and its environment. Antireflection (AR) coatings reduce the reflection considerably improving the quality of optical lens systems [1–5]. The refractive indices of glass and transparent plastic substrates are typically $n_s \approx 1.5$. The optimum refractive index for a single-layer broad-band antireflection coating is $n_f = (n_s)^{1/2} \approx 1.22$. The lowest refractive indices for the dielectrics are about 1.35 (CaF₂, MgF₂). The value of $n_f = 1.22$ is therefore

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unreachable for conventional single layer AR coatings. Despite intensive research, the availability of broadband antireflection coatings is still limited by the lack of materials with low refractive indices.

Recently, Thomas [6–8] suggested using porous silica films for this purpose. When the pore size is much smaller than the visible wavelengths, the effective refractive index of the nanoporous medium is dependent on the film porosity. To reduce the refractive index to up to ~ 1.23 using the material with a refractive index of ~ 1.5 , the porosity of $\sim 60\%$ has to be introduced. The coatings of layers of colloidal silica nanoparticles, which are packed in a manner that results in an overall porosity of $\sim 50\%$, have the refractive index of about 1.22 [9–11]. Besides, such silica AR coatings are distinguished for a high threshold of the laser damage, which is very important for the optics used in high-peak-power laser systems.

The monodispersed silica colloidal suspension that was mostly synthesized with the modified Stoeber method [12–17] was used to prepare single-layer porous AR films. This was done by hydrolysis of tetraethylorthosilicate (TEOS) in ethanolic medium and in the presence of ammonia.

Wet chemistry has already been used for a long time for the preparation of oxide powders and the first synthesis of silica from silicon alkoxide was reported long time ago [18]. One of the main advantages of the sol-gel process is the easy deposition of thin films directly from the solution by techniques such as dip-coating, spin-coating, or spray technique [19]. The commercial production of sol-gel coatings onto flat glass was developed in the seventies; however, researchers still are very interested in this process. High quality coatings for various uses constitute one of the most important applications of the sol-gel process. This is because of the possibility of using liquid solutions to fabricate solid films with an extremely wide range of chemical compositions on a variety of substrates at relatively low temperatures.

The sol-gel derived thin films have many applications, especially in modifying the reflectivity of the substrates surface, altering its rigidity or modifying its surface chemistry. In general, many interdependent factors can play a part in the final physical properties of sol-gel derived coatings: sol-gel solution (starting chemicals, sequence of mixing, concentration and ratio of components, temperature, pH) (i); method of application (dip, spin, spray, laminar flow) (ii); substrate (glasses, plastics, metals, ceramics) and its surface conditions (iii); coating (porosity, residual OH, structure, roughness, thickness) (iv). Dip-coating is the most popular method in which the colloids are evaporation-induced and self-assembled on the substrate as it is slowly withdrawn from the colloidal suspension. The reproducible deposition by dip-coating enables systematic control over coating thickness and refractive index (coating porosity) for a given substrate.

In the present study, we demonstrate the preparation of AR coatings with tunable microstructure on lime glass substrates by dip-coating technique and show the dependence of variation of the AR behaviour on different deposition process parameters and particle volume fraction.

2. Experimental

The IR spectra of the materials were recorded in KBr powders using Perkin-Elmer Spectrum BX FT-IR spectrometer. Transmission electron microscopy was performed with the PEM-100 electron microscope. A copper grid with a holey carbon film was dipped in the sol, dried at room temperature and analyzed in TEM. Coating transmittance and reflectance of the normally incident light was measured using UV-vis spectrophotometers (Perkin-Elmer Spectrum Lambda 19 and LOMO) over the spectral range of 350–900 nm. For the glass substrates, variable angle spectroscopic ellipsometry (SOPRA) was used to characterize the film thickness and transmittance. The angle of incidence was fixed at 70° (from the normal), and the spectral range probed was 350–850 nm. The AFM analysis was used for the morphological characterization of the antireflective coatings. The particle size was determined from the micrographs obtained from TEM measurements. These results, summarized from over hundred particles, were used for the calculation of average particle size and standard deviations of each sample.

The laser damage tests were carried out by Nd:YAG lasers (the output laser pulse duration – 4.6 ns, frequency – 10 Hz) using a spot size of approximately 586 μm diameter. The laser damage threshold of the coatings, i.e. the lowest intensity to cause an irreversible change, was evaluated using a high power laser system. The energy H radiated on the sample was calculated by the following formula $H = Q_{\text{max}}/A_{\text{eff}}$, where Q_{max} is the output energy of Nd:YAG lasers and A_{eff} is the effective area of laser spot on the sample. The damage morphology of the AR coatings was obtained with Ergolux optic microscope.

The dip-coating method on both sides of the glass was employed to produce AR films. For the preparation of thin colloidal silica films, the KSV DTM dip-coating apparatus, KSV Instruments Ltd., was used. Various rates of dip-coating were applied (5, 10, 20, 40, 60, and 80 mm/min). The coating procedure was also performed at various temperatures (26, 30, and 34 °C).

The sol-gel synthesis of colloidal SiO₂ nanoparticles was performed in non-aqueous system of TEOS. The precursor of SiO₂ colloidal sol was prepared by the base catalyzed hydrolysis of tetraethylorthosilicate (Fluka, 99%) [12]. The required amount of ammonium hydroxide (33%, Riedel-de Haen) was added to half of the required volume of anhydrous ethanol. The alkaline solution was added to the solution of TEOS in ethanol continuously stirred at room temperature (20±2 °C). The solutions with final silica concentration of 2%, 3%, and 5% SiO₂ were prepared. The molar ratio of ammonium hydroxide to alkoxide was 0.2 mol, to water – 0.4 mol, to ethanol – from 25 to 39 mol. The obtained reaction mixture was stored for 14 days at room temperature to allow hydrolysis as much as possible. The final product consisted of colloidal suspension of SiO₂ nanoparticles in an anhydrous solvent.

3. Results and discussion

Several different silica sols were used to find the optimum deposition conditions on the microscope glass substrates for antireflective behaviour. The spherical silica particles formed via the base-catalyzed hydrolysis and condensation of tetraethylorthosilicate in an aqueous mixture containing ethanol and ammonia were found to be colloidally stable, having a narrow size distribution. The silica nanoparticles dip-coated onto the glass substrate were transparent, possibly due to a small particle size. The transmission spectra of silica coatings obtained on the glass substrate using various concentrations of SiO_2 and deposition rates were recorded. The variation of AR behaviour for different silica coatings on glass obtained from 2% and 3% SiO_2 sol solution are shown in Figs. 1 and 2, respectively. It is evident that in all cases the coatings visibly reduced the reflectance of the glass substrate. As seen, the transmission spectra showed a sinusoidal shape with a single maximum if the quarter-wave thickness occurred over the range of 400–850 nm. Such behaviour is typical of single layer coatings. However, non-optimal coatings exhibited minima over this “visible” wavelength range (Fig. 1) because they were either too thick or too thin compared to the desired quarter-wave thickness.

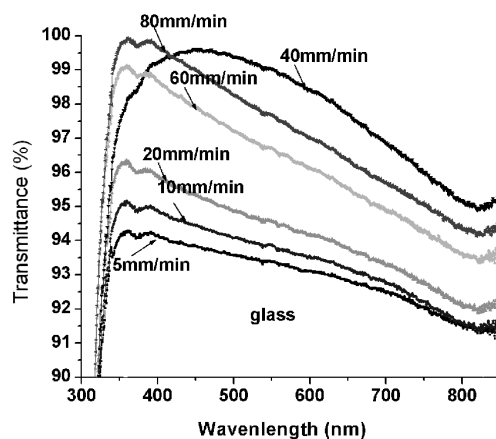


Fig. 1. Transmission spectra for silica coating on glass substrates obtained from 2% SiO_2 using various deposition rates

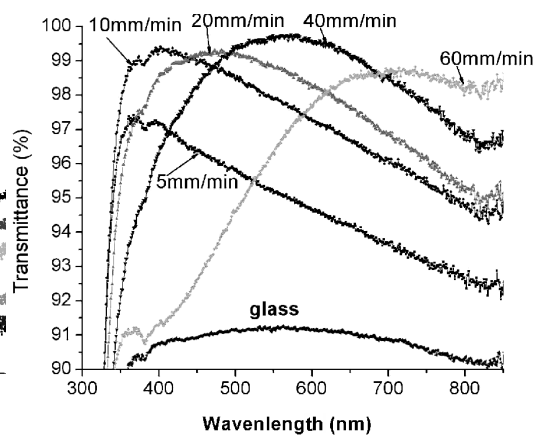


Fig. 2. Transmission spectra for silica coating on glass substrates obtained from 3% SiO_2 using various deposition rates

The determined maximum of transmission for a film coated on both sides and obtained from 2% SiO_2 sol on glass was about 94.5–99.7% (Fig. 1). The data collected for deposition rates of 5, 10, 20, 40, 60, and 80 mm/min showed a precise tuning of the spectral maxima. The optimal value of the deposition rate for these coatings was found to be about 40 mm/min. The relative difference in spectral behaviour for different rates was caused mostly by the variation of film thickness. The observed shift in

the transmission maxima correlates very well with the deposition rate, proving that the optical properties of the coatings can be controllably varied by the deposition process.

The maximum transmission for a both-sided coating obtained from 3% SiO_2 sol on glass was found to be about 97.5–99.7% (Fig. 2). As is seen, the intensity of transmission increases with increasing the immersing rate from 5 mm/min (97.5%) to 40 mm (99.7%). Besides, the transmission maximum is shifted from 380 nm to longer wavelength. Thus, the changes in the deposition rate resulted in the changes of the coloration of the reflected light from the coating, ranging from a blue tint to a yellowish tint as the deposition speed decreased.

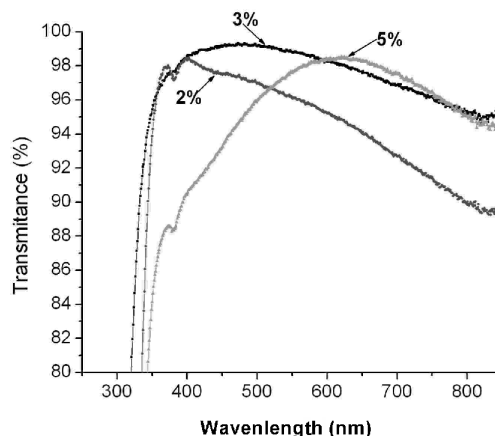


Fig. 3. Transmission spectra for silica coating on glass substrates obtained from 2%, 3%, and 5% SiO_2 ; the dipping rate – 40 mm/min

Three colloidal SiO_2 sols of different concentrations (2%, 3%, and 5% SiO_2) were selected to study the influence of particle size and concentration on the coating transmittance (Fig. 3). The coatings were obtained with the optimal dipping speed (40 mm/min) and temperature (20 °C). The best AR behaviour was exhibited by the coatings obtained from 3% SiO_2 sol. The highest absolute transmittance (99.3%) was achieved at 480 nm. The coatings obtained from 2% and 5% SiO_2 showed the highest transmittance of 98.5% at 400 nm and 610 nm, respectively. The thickness of AR coating increases with increasing the silica concentration in the sol solution.

Temperature can influence the final physical properties of sol-gel derived coatings as well. The sol viscosity decreases with increasing the dipping temperature, while the velocity of solvent evaporation increases dramatically with temperature. The coating samples were prepared from 3% SiO_2 sol at 26, 30, and 34 °C with the dipping rate of 40 mm/min. The reflectance spectra of silica coatings obtained at various temperatures are shown in Fig. 4. As is seen, the reflectance spectra for the samples obtained at different temperatures are qualitatively the same. However, for higher deposition temperatures the minimum value of reflectance is shifted to longer wavelengths. The coatings deposited at 26 °C showed the best antireflective properties in the range of 375–400 nm, while the coatings deposited at 34 °C turned out the most antireflective in the range of 400–450 nm. The highest reduction (0.31%) in the reflectance occurred at 26 °C.

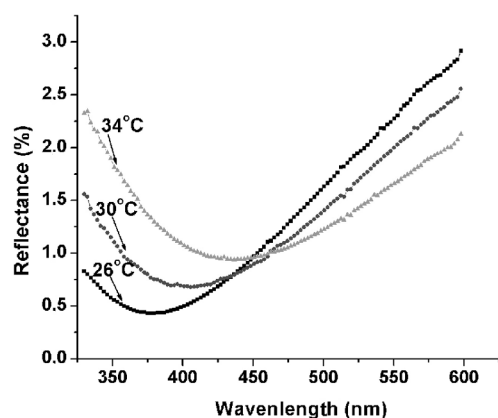


Fig. 4. Reflectance spectra for glass surface coated with silica at various temperatures

The colloidal silica coatings were obtained at the optimum sol-gel processing conditions (dipping rate – 40 mm/min, coating time – 20 s, and temperature – 20 °C) and characterized in comparison with non-coated glass substrate. Particle size was determined by the transmission electron microscopy. The results of the examination of particle size, thickness (d) and refractive index (n) of the investigated samples are summarized in Table 1.

Table 1. Colloidal particle size and AR coating data

Material	Particle size [nm]	Refractive index, n_c	Thickness d [nm]
Glass	–	1.465	–
SiO ₂ (2%)	20–35	1.230	92
SiO ₂ (3%)	30–45	1.234	108
SiO ₂ (5%)	40–55	1.235	132

Atomic force microscope (AFM) was used for the characterization of the surface morphology of silica coatings. AFM images of silica coatings (just obtained and heated) are shown in Figs. 5a, b, respectively.

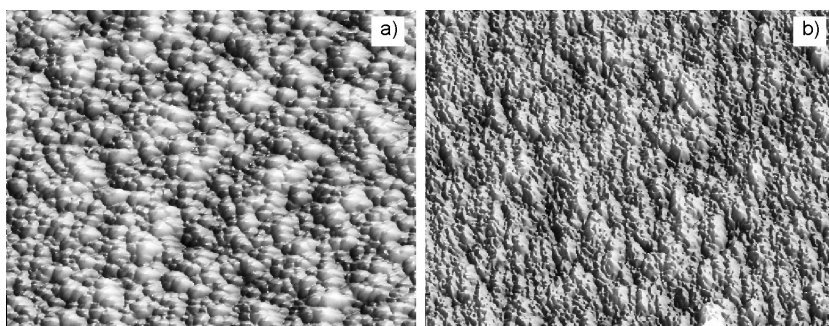


Fig. 5. AFM images of surface morphology of silica coatings:
a) non-heated; $1.96 \times 1.96 \mu\text{m}^2$, and b) heated for 2 h at 80 °C; $1.96 \times 1.96 \mu\text{m}^2$

From the AFM image (Fig. 5a) we can conclude that the just obtained colloidal silica coating is composed of silica particles ca. 40 nm in diameter. However, the particles show a tendency to form agglomerates of ca. 100–200 nm in size. The following experimental results are obtained from the AFM measurements: A – maximum roughness height 31.26 nm; R_a – average roughness 3.8 nm; R_m – root-mean-square roughness 4.34 nm. The fracture surface of the AR coatings heated for 2 h at 80 °C was also observed using AFM. The roughness and the globule dimension were smaller (A – 24.96 nm; R_a – 2.10 nm; R_m – 2.76 nm) compared with the non-heated sample. As can also be seen, the morphology of AR coating is sensitive to drying temperature. However, the transmittance maxima of the heated and non-heated coatings were almost identical.

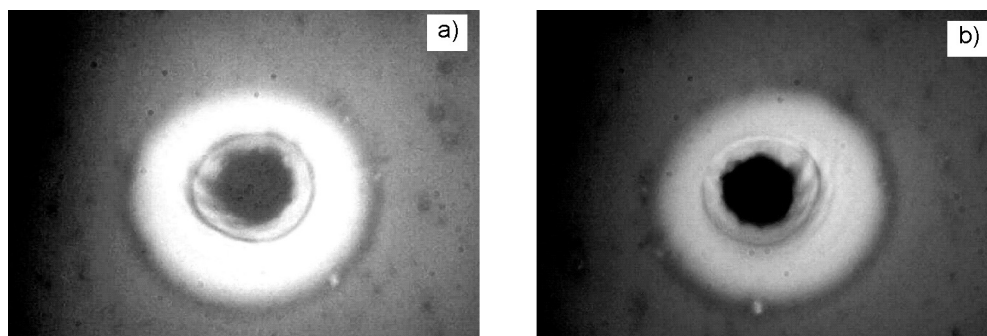


Fig. 6. The damage morphologies of silica coatings: a) non-treated side sample, and b) treated side sample

A very important property of silica antireflective films is a high laser damage threshold. While conventional multiple layer dielectric stacks are typically designed to withstand 4 to 6 J/cm² in pulses a few to ten nanoseconds wide, AR obtained via sol-gel method coatings can handle 40 J/cm² in this pulse regime at 1064 nm. The laser damage tests were carried out on Nd:YAG lasers at 1064 nm (1H) and 355 nm (3H) (single-shot 4.61-ns, pulse repetition rate 10Hz). The laser damage threshold of the AR coating exceeded 15.22 J/cm² at 1064 nm and 26.82 J/cm² at 355 nm. The damage morphology of the AR coatings was mapped with an optical microscope, and the onset damage morphology of treated and non-treated side of sample is shown in Fig. 6.

4. Conclusions

Optical properties and structure of antireflective coatings (AR) deposited from hydrolysed TEOS sol were characterized in detail in this study. The formation of colloidal silica antireflective coatings with the dip-coating technique, by changing different preparation parameters has been investigated. Using optimal sol-gel processing conditions (dipping rate – 40 mm/min, coating time – 20 s, and temperature – 20 °C), the colloidal silica coatings were obtained and characterized in comparison with the non-

coated glass substrate. It was determined that the reflectance of AR coating increases with increasing temperature of the formation process. The laser damage threshold of as deposited films was measured at 1064 nm (1H) and 335 nm (3H) wavelength using a Nd:YAG laser. The laser damage threshold of the AR coating exceeded 15.22 J/cm² at 1064 nm and 26.82 J/cm² at 355nm. In conclusion, the obtained antireflective coatings accept higher intensities than conventional dielectric AR coatings promoting more effective utilization of nonlinear optical media.

Acknowledgements

The financial support from the Lithuanian State Science and Education Foundation under project SOPTDANGOS (No. B-03025) is gratefully acknowledged.

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Received 22 June 2006

Revised 4 April 2007