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Sol-gel Derived Optical Coating with Controlled Parameters

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The optical properties and structure of antireflective coatings (AR) deposited from hydrolysed TEOS sol were characterized in detail in this study. The influence of different parameters on the formation of colloidal silica antireflective coatings by 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 increases with increasing the temperature of sol-gel processing. The Nd:YAG laser damage threshold of AR coating exceeded 15.22 J/cm^2 at 1064 nm and 26.82 J/cm^2 at 355 nm.

Keywords: antireflection coatings, colloidal silica nanoparticles, sol-gel synthesis, laser threshold.

INTRODUCTION

The reflection loss of an optical surface is related to the difference between the refractive indices of environment and the optical material. Antireflection (AR) coatings reduce the reflection considerably improving the quality of optical lens systems [1 – 5]. The theory explaining the optical behavior of single and multiple homogeneous coatings is well understood. For good antireflection properties, a coating must satisfy the phase and amplitude conditions that lead to complete destructive interference. The refractive indices of glass and transparent plastic substrates are typically $n_s \approx 1.5$. The optimal refractive index for a single-layer broad-band antireflection coating is $n_f = \sqrt{n_s} \approx 1.22$. The lowest refractive indices for the dielectrics are about 1.35 (CaF_2, MgF_2). A value of $n_f = 1.22$ is therefore unreachable for conventional single layer AR coatings. There are two approaches to produce graded refractive index coatings. One is to pattern the substrate surface with a subwavelength periodic structure. and the second is to use a nanoporous coating. The "moth-eye" type of AR coating introduces a smooth transition between the optical properties of environment and substrate. Second approach is the nanoporous type of AR coating. The refractive index of the coating depends by its porosity and is the average between the refractive index of the pores and the matrix [6 – 11]. The coatings of layers of colloidal silica nanoparticles, which packed in a manner that result in an overall porosity of ~50 %, have refractive index about 1.22. Besides, such silica AR coatings are distinguished for large threshold of the laser damage that it is very important for the optics used in high-peak-power laser systems.

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

Wet chemistry has already been used for a long time for the preparation of oxide powders ant 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 [2, 8, 19]. The commercial production of sol-gel coatings onto flat glass was developed in the seventies; however, academics still are very interested in this process. High quality coatings for various applications 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.

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

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 on 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 normally incident light was measured using a UV-vis spectrophotometers (Perkin-Elmer Spectrum Lamda 19 and LOMO) over the spectral range of 350 nm – 900 nm. For the glass substrates, variable angle spectroscopic ellipsometry (SOPRA) was used to characterize the film thickness and transmittance.

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The angle of incidence was fixed at 70° (from the normal), and the spectral range probed was 350 nm – 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 the 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 is 4.6 ns, frequency 10 Hz) using a spot size of approximately 586 µm diameter. The laser damage threshold, i.e. the lowest intensity to cause on irreversible change, of the coatings was evaluated using a high power laser system.

Dip-coating method on both sides glass was employed to produce AR films. In our investigations, for the preparation of thin colloidal silica films the dip-coating apparatus KSV Instruments Ltd. KSV D™ was used. The different rate of dip-coating was used (5, 10, 20, 40, 60, and 80 mm/min). The coating procedure was also performed at various temperatures (20, 26, 30, and 34 °C). Sol-gel synthesis of colloidal SiO_2 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 (Fluka, 99 %) by the following method of preparation of Stöber et al.'s silica [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 with continuous stirring at room temperature (20 °C ±2 °C). The solutions with final silica concentration of 2 %, 3 %, and 5 % SiO_2 were prepared. The molar ratio of ammonium hydroxide to alkoxide was 0.2 mol, to water – 0.4 mol, to ethanol – from 25 mol 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 SiO_2 nanoparticles in an anhydrous solvent.

RESULTS

The sol-gel derived thin films find 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 role in the final physical properties of a sol-gel derived coatings: (i) sol-gel solution (starting chemicals, sequence of mixing, concentration and ratio of components, temperature, pH); (ii) method of application (dip, spin, spray, laminar flow); (iii) substrate (glasses, plastics, metals, ceramics) and it's surface conditions; (iv) coating (porosity, residual OH, structure, roughness, thickness). Dip-coating is the most popular method in which the colloids are evaporation induced and self-assembled on the substrate as it slowly withdrawn from the colloidal suspension.

Several different silica sols were used and studied in an effort to find the optimal 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 the small particle size. The transmission spectra of silica coatings obtained on the glass substrate using different concentration of SiO_2 and deposition rate 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 Figures 1 and 2, respectively.

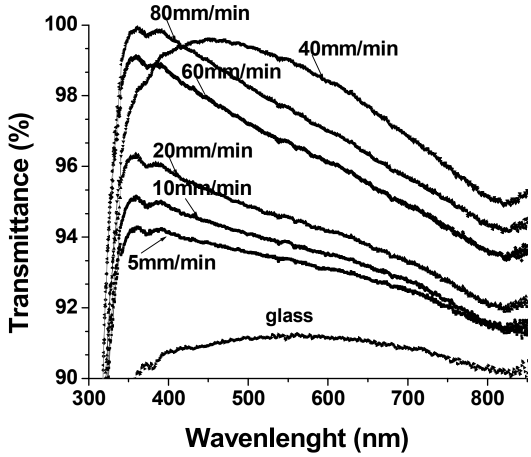

Fig. 1. Transmission spectra for silica coating on glass substrates obtained from 2 % SiO_2 using different deposition rate

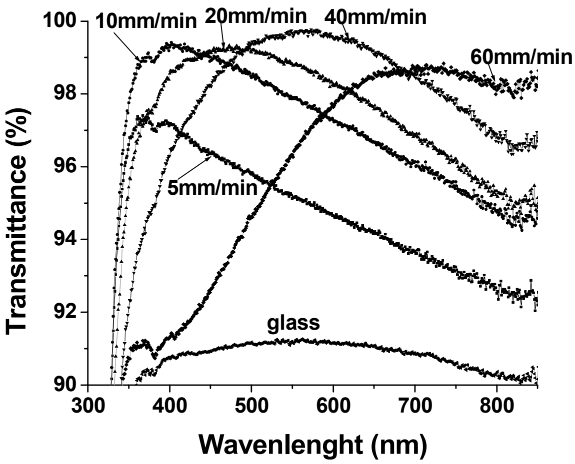

Fig. 2. Transmission spectra for silica coating on glass substrates obtained from 3 % SiO_2 using different deposition rate

It is evident that in all cases the coatings visibly reduced the reflectance of the glass substrate. As seen, the transmission spectra show a sinusoidal shape with a single maximum if the quarter-wave thickness occurred over the range of 400 nm – 850 nm. Such behaviour is typical and expected for the single layer coatings. However, no optimal coatings exhibited minima over this "visible" wavelength range (Fig. 1), because they were either too thick or too thin in comparison to the desired quarter-wave thickness. The determined maximum of transmission for both side coated film and obtained from 2 % SiO_2 sol on glass was about 94.5 % – 99.7 % (see Fig. 1). The data collected for the deposition rates of 5, 10, 20, 40, 60, and 80 mm/min showed the 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 is caused mostly by variation of film thickness. The observed shift in the transmission maxima correlates very well with 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 % (see Fig. 2).

As 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 the longer wavelength. So, 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.

Three colloidal SiO_2 sols of the different concentration (2 %, 3 %, and 5 % SiO_2) were selected to study the influence of particles size and concentration on the transmittance (Fig. 3).

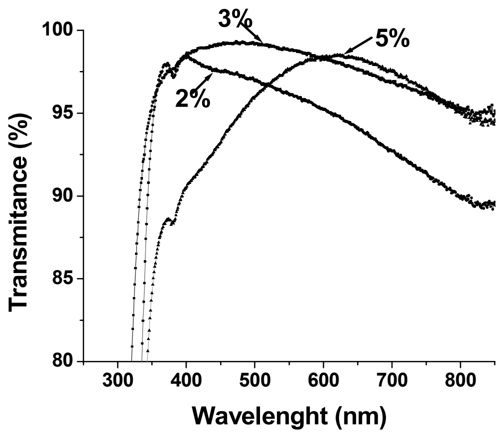

Fig. 3. Transmission spectra for silica coating on glass substrates obtained from 2 %, 3 %, and 5 % SiO_2 solution. The dipping rate was 40 mm/min

The coatings were obtained using the optimal dipping speed (40 mm/min) and temperature (20 °C). The best AR behaviour showed 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 silica concentration of the sol solution.

The temperature can influence the final physical properties of sol-gel derived coatings as well. The sol viscosity decreases with increasing the dipping temperature and the velocity of solvent evaporation increases dramatically with temperature. The coating samples were prepared from 3 % SiO_2 sol at 26 °C, 30 °C and 34 °C using the dipping rate 40 mm/min. The reflectance spectra of silica coatings obtained at different temperatures are shown in Fig. 4.

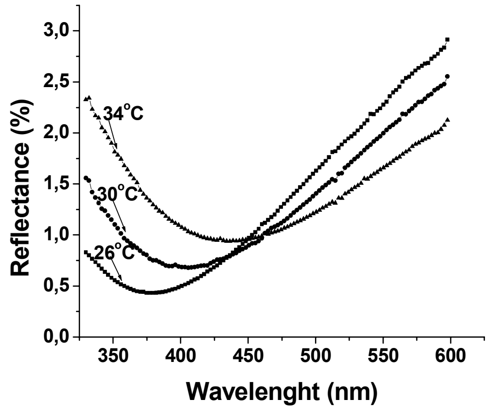

Fig. 4. Reflectance spectra for glass surface coated 2 % SiO_2 solution at different coating temperatures

As seen, the reflectance spectra for the samples obtained at different temperatures are qualitatively the same. However, the minimum value of reflectance is shifted to the longer wavelengths for higher deposition temperatures. The coatings deposited at 26 °C showed the best antireflective properties in the range of 375 nm – 400 nm, while coatings at 34 °C were most antireflective in the range of 400 nm – 450 nm. The highest reduction (0.31 %) in the reflectance occurred at 26 °C.

The colloidal silica coatings were obtained at the optimal 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. The particle size was determined by transmission electron microscopy. The results for particle size, thickness (*d*) and refractive index (*n*) determination of investigated samples are summarized in Table 1.

Table 1. Colloidal particle size and AR coating data

	Particle size (nm)	Refractive index, n_c	Thickness, *d* (nm)
Glass		1.465	
SiO_2 (2%)	20 – 35	1.230	92.28
SiO_2 (3%)	30 – 45	1.234	108.49
SiO_2 (5%)	40 – 55	1.235	132.48

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

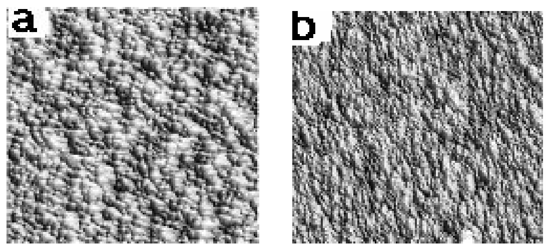

Fig. 5. AFM images of surface morphology of silica coatings: a – non-heated; b – heated for 2 h at 80 °C; 1.96 μm × × 1.96 μm

From the AFM image (Fig. 5, a) we can conclude that just obtained colloidal silica coating is composed of ≈40 nm silica particles. However, the particles show tendency to form agglomerates of ≈100 nm ÷ 200 nm in size. The 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 2 h at 80 °C has been observed using AFM, too. The roughness and the globule dimension are decreased (A – 24.96 nm; R_a – 2.10 nm; R_m – 2.76 nm), compared with the non heated sample. As can be also seen, the morphology of AR coating is sensitive for drying temperature. However, the transmittance maxima of heated and non-heated coatings were almost identical.

Very important property of silica antireflective films is the high laser damage threshold. While conventional multiple layer dielectric stacks are typically designed to withstand 4 J/cm^2 to 6 J/cm^2 in pulses a few to ten nanoseconds wide, AR obtained via sol-gel method coatings can handle 40 J/cm^2 in this pulse regime at 1064 nm. The laser damage tests were carried out on a Nd:YAG lasers at 1064 nm (1H) and 355 nm (3H) (single-shot 4.61-ns, pulse repetition rate 10 Hz). The laser damage threshold AR coating exceeded 15.22 J/cm^2 at 1064 nm and 26.82 J/cm^2 at 355 nm.

CONCLUSIONS

The 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 by 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 non-coated glass substrate. It was determined that the reflectance of AR coating increases with increasing temperature of formation process. The laser damage threshold of as deposited films was measured at 1064 nm (1H) and 335 nm (3H) wavelength using an Nd:YAG laser. The laser damage threshold AR coating exceeded 15.22 J/cm^2 at 1064 nm and 26.82 J/cm^2 at 355 nm. In conclusion, the obtained antireflective coatings via sol-gel method accept higher intensities than conventional dielectric AR coatings promoting more effective utilization of nonlinear optical media.

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