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Hydrophobic Antireflective Silica Coatings via Sol-gel Process

Jurgis PHILIPAVIČIUS[1], Ivan KAZADOJEV[1], Aldona BEGANSKIENĖ[1*], Andrius MELNINKAITIS[2], Valdas SIRUTKAITIS[2], Aivaras KAREIVA[1]

[1]*Department of General and Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania*
[2]*Laser Research Center, Vilnius University, Saulėtekio al. 10, LT-10222 Vilnius, Lithuania*

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The optical properties and structure of hydrophobic antireflective coatings (AR) deposited from silica sol and HMDS and MTMS were characterized in detail in this study. The influence of sol modification parameters on the antireflective behaviour of coatings has been investigated. For the characterization of hydrophobic coatings the water contact angle measurements, UV-visible spectroscopy and atomic force microscopy were used. HMDS modified silica coating show the highest contact angle (165°) due to its better hydrophobic covering. It was determined that the hydrophobic HMDS modified coatings reduced reflectance as well as unmodified silica AR coatings. The Nd:YAG laser damage threshold of AR modified silica coating exceeded 35 J/cm^2 at 1064 nm.
Keywords: hydrophobic, antireflection coatings, colloidal silica nanoparticles, sol-gel synthesis, laser damage threshold.

1. INTRODUCTION

The reflection loss of an optical surface is related to the difference between the refractive indices of environment and the optical material. Due to their ability to decrease the reflectance and increase the transmittance of light and remove ghost images, antireflective (AR) coatings have recently attracted much interest for their applications in displaying devices and optical lenses systems [1–3]. The refractive index (n_c) for an ideal homogeneous AR coating meets the condition of $n_c = (n_a n_s)^{1/2}$, reflection will be decreased at the wavelengths near the quarter-wavelength optical thickness, where n_a and n_s are the refractive indices of the air and the substrate, respectively. For a glass substrate (n_s ~1.5), the refractive index of AR material should be ~1.22. However, nature materials with such low refractive index are either rare. An effective method to obtain coatings with reduced refractive index is to introduce nanopores during the coating fabrication. The refractive index of porous coatings can be well tailored by controlling the percentage of pores introduced, in which larger percentage of pores leads to lower refractive index [4–7]. The most popular methods of preparation porous films are chemical vapour deposition, chemical etching and sol-gel processes [2, 8, 9].

The silica nanoparticles (20 nm–40 nm) made by the Stober sol-gel process is convenient for use as antireflective (AR) coatings for optics in high power laser system [10–14]. The AR coatings of porous silica are very attractive, due to low refractive indexes, low scatter and high laser damage thresholds. However, such AR coatings have one weakness – the water condensation on the surface of hydrophilic silica coating, what very important for the moisture sensitive optic elements or crystals as potassium dihydrogen phosphate. Because of absorption of water apour into the hydrophilic pores of normal porous silica

AR film can increase n_c and then lowers the anti-reflection, and it is necessary to make the AR films that possess hydrophobicity. Therefore, the fabrication of AR coatings with water-repellent properties is quite important.

The wettability of liquid to solid surface is governed by the chemical properties of solid surface and its surface morphology. So, commonly the acquirement of hydrophobic surface is out of two approaches chemical modification to surface or roughening the surface. Chemical modification is the way to achieve substitution of the hydrogen of hydroxyl group by attaching some alkyl or fluoralkyl groups. The modification of silica sol has been performed using hexamethyldisilazane (HMDS), trimethylalkokxysilane and dimethylalkokxysilane [15–17]. The methyl or trimethylsilyl (TMS) functionalization of silica colloids greatly modified the water adsorption isotherms, making them significantly more resistant to water absorption.

In this study, we demonstrate the preparation of hydrophobic sol-gel AR coatings on glass substrates by spin-coating technique showing the dependence of variation of the AR behaviour on chemical modification parameters. The surface of silica nanoparticles was modified by adding different ration of reagents hexamethyldisilazane (HMDS) or methyltrimethoxysilane (MTMS) to colloidal silica sol.

2. EXPERIMENTAL

The particle size was determined from the micrographs obtained from TEM measurements. 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. The results summarized from over hundred particles were used for the calculation of the average particle size and standard deviations of each sample. The 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. The angle of incidence was fixed at 70° (from the normal), and the spectral range probed was 350 nm–850 nm. The AFM images of the

*Corresponding author. Tel.: + 370-5-219-3109, fax.: +370-5-233-0987.
E-mail address: *aldona.beganskiene@chf.vu.lt* (A. Beganskienė)

silica coatings on glass were performed on Multimode Scanning Probe Microscope (Digital Instruments). For the characterization of surface properties, the measurements of water contact angle on KVS Instrument CAM 100 were recorded. The viscosity measurement was made using a viscometer (Anton Paar) at a shear rate of 200 s^{-1} and constant 25 °C temperature. The laser damage tests were carried out according (ISO 11254-2 standard) by Nd:YAG lasers (the output laser pulse duration is 3.41 ns at 1064 nm, 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. Light scattering losses were measured on apparatus for total scattering measurements at Laser Research Center of Vilnius University.

Spin-coating methods on glass (lime, Bk-7) for producing AR coatings were used. In our investigations, for the preparation of thin colloidal silica films SCS P 6708 (Specialty Coating Systems) was used. The coatings were used to deposit spinning-coating on well cleaned optical glass substrates at 2500 rpm – 3000 rpm. The coatings were dried at room temperature. 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 silica. 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 25 °C temperature. 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 3 % SiO_2 nanoparticles in an anhydrous solvent. Methyl-modified SiO_2 sols were prepared by adding different amount: 0.05, 0.1, 0.25, 0.5, 1.0 p.p.vol. of hexamethyldisilazane (HMDS) or methytrimethoxysilane (MTMS) to the 3 % colloidal silica suspension. The modified sols were aged 7 days at 25 °C temperature and for variation contact angle with aging time sample of HMDS (0.25 p.p.vol.) sol was aged from 1 to 50 days.

3. RESULTS

The monodispersed silica colloidal suspension that was mostly synthesized from modified Stöber method [10] was used to prepare single-layer porous AR films. The colloidal silica particles formed via the base-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) in a non-aqueous mixture containing ethanol and ammonia were found to be colloidaly stable, having a narrow size (25 nm – 35 nm) distribution. After, the surface of silica nanoparticles was modified by adding different ratio of modification reagents hexamethyldisilazane (HMDS) or methytrimethoxysilane (MTMS) to colloidal silica sol. The colloidal silica particles were covered by hydroxyl groups, after HMDS or MTMS addition, some of the hydroxyl groups were replaced by methyl groups.

The TEM images of particles obtained from reaction mixtures 3 % SiO_2 sol and modified with HMDS and MTMS are shown in Fig. 1.

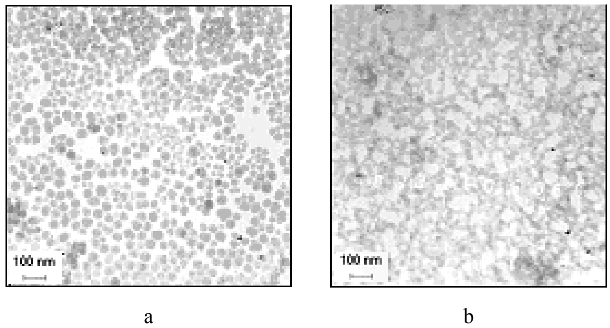


Fig. 1. TEM images of particles obtained from reaction mixtures 3 % SiO_2 sol and: a – HMDS (0.25), b – MTMS (0.25)

TEM images showed that particles modified with MTMS were connected into large and irregular clusters. After mixing the unmodified silica sol and MTMS, the mono-dispersed particles linked and hydrophobic methyl group were introduced into clusters. The HMDS modified particles were spherical, besides in better dispersion than modified with MTMS. The methyl group could easily replace the Si-OH group on SiO_2 particles surface. So, the surface morphology of HMDS modified was composed of spherical small particles (25 nm – 35 nm).

Viscosity measurements are also of fundamental interest because they can furnish quantitative information concerning the structure of the colloid suspension and hence the specific interactions among particles. Fig. 2 shows the change in viscosity with time for two modifiers HMDS and MTMS addition. As seen, the viscosity increased with increasing aging time, while the changes of viscosity of HMDS modified sol was small.

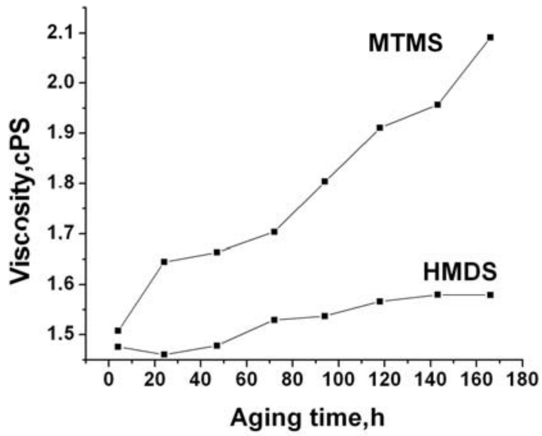
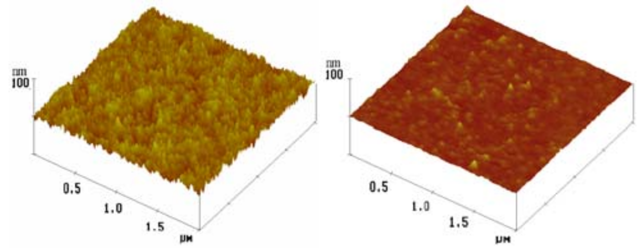


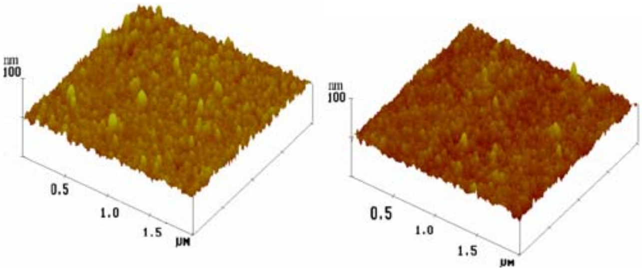
Fig. 2. Variation of viscosity with time of modified sol with MTMS (0.25) and HMDS (0.25) sol

Atomic force microscope (AFM) was used for the characterization of surface morphology of silica coatings. AFM images exhibited a direct relation between the surface and morphology with nature and concentration of modified reagents. The AFM images of unmodified and modified with MTMS and HMDS coatings with 1.5 and 0.1 ratio are shown in Figs. 3 and 4.



a b

Fig. 3. AFM images of surface morphology of coatings obtained from sol: a – unmodified silica sol, b – MTMS (0.25) modified

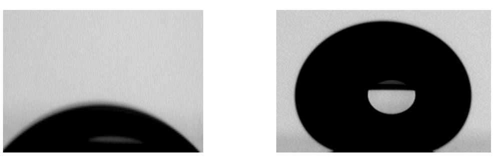


a b

Fig. 4. AFM images of surface morphology of coatings obtained from sol: a – modified HMDS (0.25), b – HMDS (0.1)

The surface morphology of the coatings has a large effect on water on water repellence as well on light scattering on surface. The MTMS modified coating have a smooth and continuous surface (roughness R_q 1.8 nm), rather than typical particle-bump morphology of unmodified silica coating (R_q 3.2 nm). The average surface roughness R_q of HMDS modified film increases with the modifier content. The coating obtained from sol with highest HMDS (1.5 p.p.v.) content have the biggest R_q – 3.5 nm, while with 0.1 p.v. of HMDS R_q – 2.8 nm. From the AFM image we can conclude that just obtained HMDS modified coating is composed of ≈40 nm silica particles. This kind of morphology on coatings modified with HMDS generally meant lots of mesopores in film, which ensured the low refractive index n_c needed for antireflective behaviour of coatings. But, that roughness is small enough not to impact intence surface light scattering, which reduces antireflection.

The hydrophobicity of coating was shown by the water/coating contact angle as a function of the ration modification reagents and aging time of modified MTMS and HMDS sols (Fig. 5 and Fig. 6). The hydrophobicity was not the same for the coating from different methyl-modified silica sols.



a b

Fig. 5. Images of water drops on coatings surfaces: a – colloidal SiO_2 (21°), b – HMDS modified (165°)

For the MTMS modified coating, the water contact angle increased from 32° to 71° after 14 days aging of sol. And, for the HMDS modified coating/water contact angle has reached 140° after 14 days. The maximal value 165° of the coating prepared from modified with HMDS after 40 d. aging, while after 50 aging day small decreasing of hydrophobicity was observed (Fig. 7).

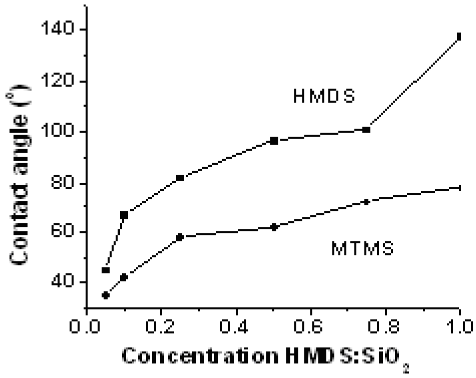


Fig. 6. Contact angles with modifier concentration for coatings after 14 day aging

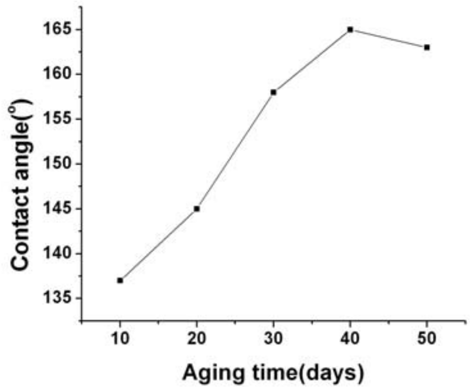


Fig. 7. Variation water contact angles with aging time for HMDS (0.25) modified silica coatings

The antireflection of modified one-side coatings is represented by the transmittance shown in Figs. 8 and 9. It is evident that in both cases of modification with HMDS and MTMS the obtained modified coatings visibly reduced the reflectance of the glass substrate as compared to the unmodified colloidal SiO_2 coating.

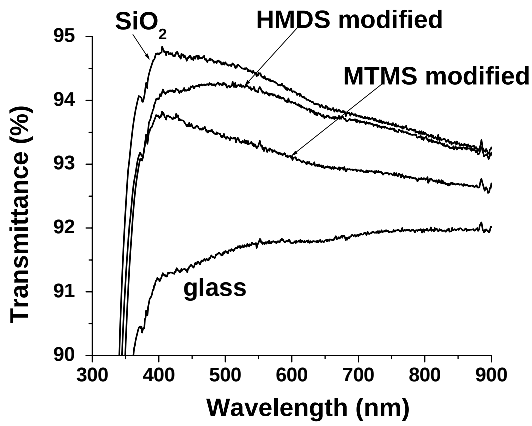


Fig. 8. Transmission spectra for BK-7 glass and coating obtained from sol: a – 3 % SiO_2, b – modified 0.25 HMDS, c – 0.25 MTMS

As seen (Fig. 8), the transmission spectra show a sinusoidal shape with a single maximum if the quarter-wave thickness occurred over the range of 400 nm – 800 nm. Such behaviour is typical and expected for the single layer coatings. The determined maximum of transmission for one side coated film obtained from HMDS modified sol on glass was 94.2 % (400 nm – 550 nm), while for uncoated glass was 91.3 %. The highest transmittance (93.7 %) for MTMS modified coating was achieved at 410 nm.

The best AR behaviour showed the coatings obtained from HMDS: silica sol (0.25 : 1) (Fig. 9). The highest absolute transmittance (95.0 %) was achieved at 527 nm. The transmittance of modified coating decreases to with decreasing HMDS amount.

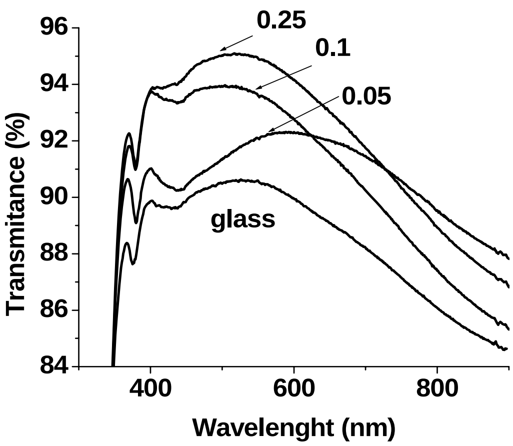


Fig. 9. Transmission spectra for coating on lime glass obtained from modified silica sol with different concentration HMDS

The surface topology of the substrate and the coating determine the quality of the coating in terms of their optical transmission. The surface morphology of the coatings can lead to surface scattering and can reduce the transmitted. The map of light scattering loses for modified coating is presented in Fig. 10.

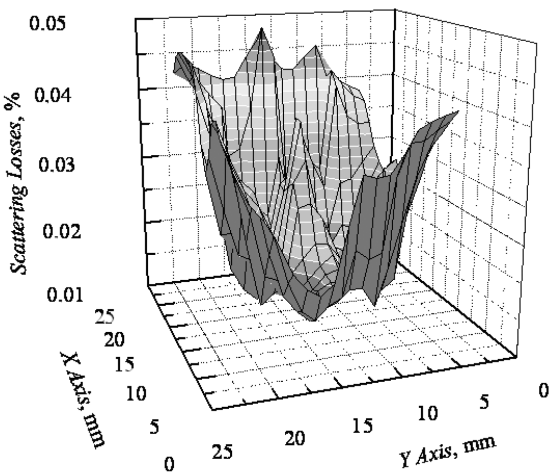


Fig. 10. Light scattering losses map of HMDS modified silica coating on BK-7 glass

The bigger light scattering losses around the sample sides were obtained. The HMDS modified coating has total 0.02 % scattering losses.

The laser-induced damage threshold (LIDT) is very important parameter of antireflective coatings. To compare with the coating obtained from unmodified sol and HMDS modified sol were tested under the same conditions. The laser damage tests were carried out on a Nd: YAG lasers at 1064 nm (1 H) (single-shot 3.4 ns, pulse repetition rate 10 Hz). The laser damage threshold AR unmodified silica coating exceeded 15.22 J/cm^2 at 1064 nm and 21.82 J/cm^2 at 355 nm [18], while modified HMDS – 35 J/cm^2 at 1064 nm.

4. CONCLUSIONS

The optical properties and structure of hydrophobic antireflective coatings (AR) deposited from silica sol and HMDS or MTMS as modifiers were characterized in detail. The contact angle of water increased with increasing amount of HMDS or MTMS, but HMDS modified coating had much higher contact angle. It was determined that the hydrophobic HMDS modified coatings reduced reflectance as well as unmodified silica AR coatings. The HMDS modified sample has total 0.02 % scattering losses. The laser damage threshold modified silica coating exceeded 35 J/cm^2 at 1064 nm The obtained hydrophobic antireflective coatings via sol-gel method could be used for the coating optical elements sensitive to humidity.

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