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FULL PAPER

Template-Free Sol-Gel Preparation of Superhydrophobic ORMOSIL Films for Double-Wavelength Broadband Antireflective Coatings

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A double-layer double-wavelength antireflective (AR) coating with 100% transmittance at both 1064 nm and 532 nm, which is very important in high power laser systems, is designed using thin film design software (TFCalc). The refractive indices for the bottom and top layers of the designed AR coating are about 1.30 and 1.14. A simple, template-free sol-gel route is proposed to prepare the superhydrophobic ORMOSIL (organically modified silicate) thin film, which has an ultralow refractive index, by silica particle surface modification using hexamethylisilazane (HMDS); this treatment decreases the refractive index of the silica thin film from 1.23 to 1.13. The formation mechanism of the ultralow refractive index thin film is proposed. The particle surface modification with HMDS significantly improves the hydrophobicity of the coated film; the water contact angle of the film increases from 23.4° to 160°. The bottom layer, which has a refractive index of 1.30, is prepared from acid-catalyzed and base-catalyzed mixed silica sol. A double-layer silica AR coating is obtained with transmittances of 99.6% and 99.8% at 532 nm and 1064 nm, respectively.

1. Introduction

Antireflective (AR) coatings have been widely used in optical devices and energy-related applications to reduce light reflection.[1–4] In high-powered laser fusion systems, there are thousands of optical components. Each optical component creates optical reflection at the air-components surface. The optical reflection will not only confuse the target diagnostic but also obviously reduce the output energy. It is thus highly desirable to maximally suppress the reflection of the optical components with AR coatings. The refractive index is the most fundamental characteristic of an AR coating and should be equal to the square root of that of optical substrate to achieve zero reflectance. The transmissive optical components in high power laser systems are mostly made from fused silica and BK7 glass, which have refractive indices of 1.46 and 1.52, respectively; this implies that the refractive index of a quarterwave AR coating must be approximately 1.22. Sol-gel silica AR coating consists of a layer of silica particles randomly stack on the substrates' surface. The porosity between silica particles lowers the refractive index of silica AR coating to about 1.22.[5] In addition, the laser damage threshold of silica AR coating from sol-gel process is two to three times higher than that of AR coatings from physical vapor deposition method. Consequently, sol-gel silica quarterwave AR coatings have been widely used in high-powered laser fusion systems for several decades.[5]

A single layer quarterwave sol-gel silica AR coating can only give maximum transmittance at one wavelength. This is of little importance in most applications dealing with lasers because they are a single wavelength. In the high power laser system, the original 1064 nm light is converted to the third harmonic (355 nm) with two frequency conversion crystals before being directed to the target.[6] The outlet surface of the first crystal and the inlet surface of the second crystal are subject to the transmission of light of two wavelengths (1064 nm and 532 nm). Therefore, a double-wavelength broadband AR coating that works simultaneously at 1064 nm and 532 nm is of great interest. This double-wavelength broadband AR coating had been proposed by Thomas for the first time.[6] However, Thomas did not optimize the refractive indices of AR coating, probably due to the limited available coating materials, giving only the double-wavelength broadband AR coating theoretical transmittance of 99.5% and 99.4% at 532 nm and 1064 nm, respectively. Here, a series of double-layer double-wavelength broadband AR coatings on BK7 substrate were designed with the aid of thin film design software (TFCalc). The results show that a silica thin film with an ultralow refractive index was of great importance in preparation of high quality double-wavelength broadband

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Table 1. Refractive index of broadband AR coatings on BK7 substrates and their transmittance at 1064 nm and 532 nm modeled by TFCalc. The central wavelength for these coatings is 710 nm and the optical thickness is quarter-wave.

Sample number	Bottom layer		Top layer		$T_{1064\ nm}$ [%]	$T_{532\ nm}$ [%]
	n_1	thickness [nm]	n_2	thickness [nm]		
C1	1.41	125.89	1.22	145.49	98.96	98.95
C2	1.37	129.56	1.22	145.49	99.31	99.30
C3	1.33	133.46	1.22	145.49	99.40	99.41
C4	1.37	129.56	1.20	147.92	99.47	99.44
C5	1.33	133.46	1.20	147.92	99.64	99.65
C6	1.30	136.54	1.20	147.92	99.60	99.61
C7	1.33	133.46	1.18	150.42	99.80	99.80
C8	1.30	136.54	1.18	150.42	99.81	99.82
C9	1.33	133.46	1.16	153.02	99.87	99.87
C10	1.30	136.54	1.16	153.02	99.94	99.95
C11	1.30	136.54	1.14	155.70	99.99	99.99

AR coatings. A double-wavelength broadband AR coating with transmittance of 100% simultaneously at 1064 nm and 532 nm can be obtained while the refractive index of top layer is about 1.14. Recently, a silica nanorod-array film with a refractive index of 1.05 has been demonstrated by oblique-angle deposition,[7,8] and nanoporous silica thin films with refractive index of 1.14, and even 1.07, were prepared using a sol-gel process with polymer and surfactant CTAC (cetyltrimethylammonium chloride) as templates.[9,10] However, AR coatings from physical vapor deposition have low laser-induced damage threshold, which limits their application in high power laser system, and the high-temperature treatments for removing templates from the film in the surfactant CTAC method may result problems for optical components.

Here we also report a simple template-free sol-gel process to prepare superhydrophobic ORMOSIL (organically modified silicate) thin film with refractive index varying from 1.23 to 1.13. The formation mechanism of this ultralow refractive index thin film was proposed. Finally, a double-layer silica AR coating was obtained with transmittance of 99.6% and 99.8% at 532 nm and 1064 nm, respectively.

2. Results and Discussion

2.1. Computer-Aided Design of AR Coatings

Antireflective coatings can be designed using many methods including the vector method, admittance loci, etc. However, these methods involve much calculation by hand, making them tedious and time-consuming. Computer-aided design is the preferred method because it is fast and straightforward. Consequently, the double-layer double-wavelength AR coating described here was designed with the aid of thin film design software. As shown in **Table 1**, a silica thin film with an ultralow refractive index is of great importance in preparation of high quality double-wavelength broadband AR coatings. As the refractive indices of the bottom and top layers are 1.30 and 1.14, respectively, the transmittance of the double-wavelength AR coating at 1064 nm and 532 nm is 100%.

2.2. Top Layer of the Double-Wavelength AR Coating

Figure 1 shows the change in refractive index of silica thin film with HMDS (hexamethyldisilazane) concentration. The refractive index initially decreases very fast with increasing HMDS concentration, and reaches asymptotically a minimum of approximately 1.13. This indicates that surface hydrophobic modification of silica particles can lower the refractive index of silica AR coating. To explain this phenomenon, it is helpful to consider the film formation mechanism. Two different physical stages can be considered in the dip-coating process. During the first stage, a liquid layer of sol is deposited uniformly on the substrate, then the sol concentration increases because of solvent evaporation and rapidly reaches the sol-gel transition

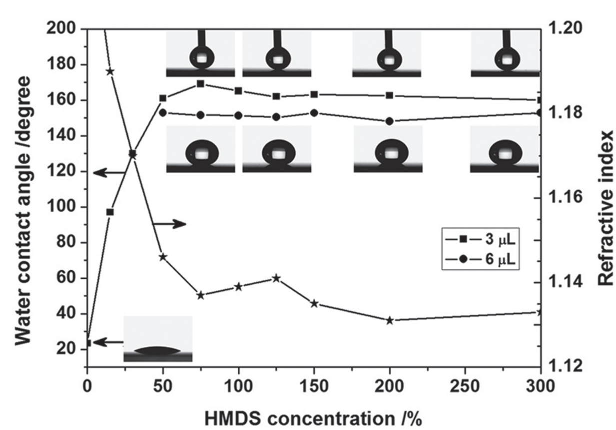

Figure 1. Change in refractive index and water contact angle of silica thin film as a function of HMDS concentration.

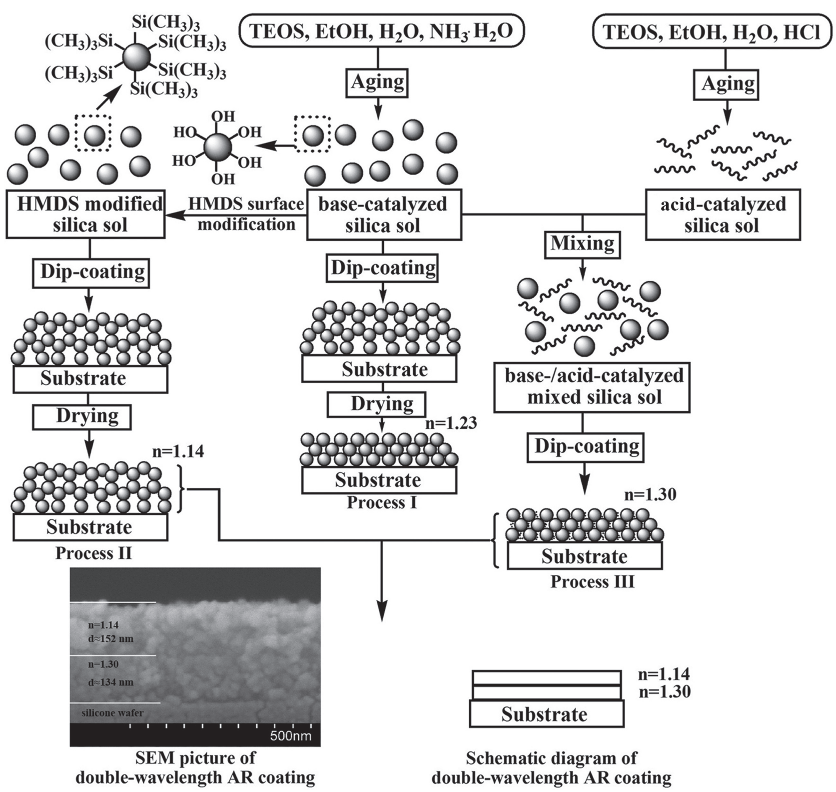

Figure 2. Schematic representation of an unmodified silica thin film (process I), HMDS-modified silica thin film (process II), base-/acid-catalyzed mixed silica thin film (process III), and a double-layer double-wavelength broadband silica AR coating.

point by forming an elastic gel-like solid and then the second stage occurs. During this stage, the solvent continues to evaporate from the gel-like solid layer and a solid silica film is finally obtained. During the second stage, the thin film is subjected to two collapsing forces: the hydroxyl groups on the surfaces of silica particles undergo condensation reaction, resulting in shrinkage of the gel network, and the surface tension creates concave menisci in the pores of the gel as the liquid evaporates from the gel, which build up compressive forces around the perimeter of the pore. These two forces impose the gel to contract to some extent and, under normal conditions, the resulting silica thin film has a refractive index of about 1.23 (process I in **Figure 2**). When a sol with surface-modified particles is concerned, the hydroxyl groups on the surfaces of the sol particles are mostly replaced by hydrophobic $-Si(CH_3)_3$ groups, which avoids the condensation reaction between hydroxyl groups on adjacent silica particles and also creates a surface constituted of the silica particles with extremely low surface energies. This can dramatically reduce surface tension (process II in Figure 2). The contracting forces are greatly reduced and the film coated with HMDS modified sol is more porous than that obtained with the normal sol. The refractive index decreases when more nanopores are created in the AR film.[11] As shown in Figure 1, the surface modification of silica particles in the sol can significantly reduce the refractive index of the coated film and a thin film for the top layer with refractive index of 1.14 can be prepared with a HMDS concentration of 125%.

2.3. Bottom Layer of a Double-Wavelength AR Coating

Thomas has described a method for preparation of silica thin film with refractive index varying from 1.22 to 1.44.[12] The bottom layer was prepared according to Thomas's work by mixing base-catalyzed silica sol and acid-catalyzed silica sol together. Figure 2 process III shows the preparation process of the bottom layer. With a basic catalyst, the growth of silica sol is biased towards spherically expanding particles, giving the film a very low refractive index of 1.22. The base-catalyzed AR coating stacked by the silica particle has a high pore volume. With an acidic catalyst, the growth of silica sol tends to form linear chains, giving the acid-catalyzed AR coating a refractive index of 1.44. By mixing the base-catalyzed and acid-catalyzed silica sols together, acid-catalyzed silica acts as a filler in the pores between silica particles. By controlling the acid-catalyzed silica ratio, the silica thin film has appropriate porosity and a refractive index of 1.30 can be obtained.

2.4. Double-Wavelength AR Coatings

The thickness of bottom and top layers was optimized by varying the dip-coating speed (withdraw rate) to give both bottom and top layers with a central wavelength of 710 nm. After this, the double-wavelength AR coating can be obtained by sequentially coating the bottom and top layers onto a BK-7 substrate. The scanning electron microscopy (SEM) image of a prepared double-layer AR coating is shown in Figure 2. The film thicknesses of the top and bottom layers from the SEM image are in good agreement with the designed values, as shown in Table 1. The transmittance spectrum of the resultant double-wavelength broadband AR coating is shown in **Figure 3** and compared with the spectra of modeled C11 coating and typical single-layer quarterwave AR coating. Figure 3 indicates that our designed double-wavelength broadband AR coating was successfully realized using the sol-gel method. The experimental transmission spectrum is in good agreement with that of modeled spectrum. The advantage of the double-layer broadband AR coating over the single-layer quarterwave AR coating is immediately apparent. The transmittances of the double-layer broadband AR coating at 532 nm and 1064 nm are more than 99.6% and 99.8%, while those of the single-layer quarterwave AR coating are only 97.8% and 97.9%.

2.5. Hydrophobicity of Double-Wavelength AR Coatings

A very interesting characteristic of surface modification of silica particles with HMDS is the hydrophobicity of the coating. Normal sol-gel silica AR coating is usually porous and polar and

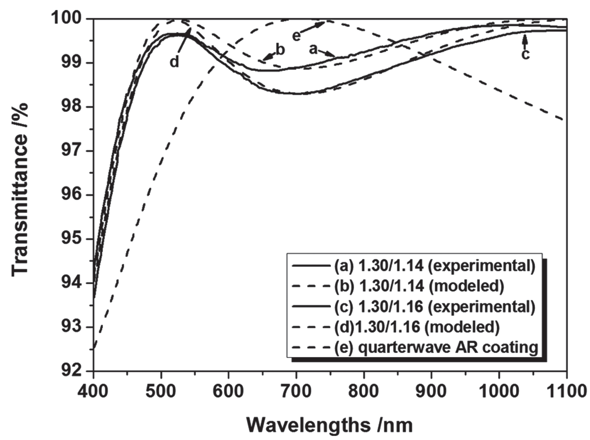

Figure 3. Transmittance spectra of a single-layer quarterwave AR coating and an experimental and modeled double-wavelength AR coating.

tends to absorb contamination, such as water or polar organic molecules, from the environment. The contaminants absorbed into the pores of the AR coating will not only increase the refractive index, and hence decrease the transmittance, but also decrease the laser damage threshold. The adsorption of contamination can be hindered by replacement of polar hydroxyl groups on silica particles with nonpolar groups. In high-powered fusion laser system, HMDS surface modification was carried out to improve the environment-resistance of silica AR coatings by exposing these coatings to HMDS vapor.[13] Here, the HMDS surface modification of silica particles is accomplished before film deposition, and silica thin film with excellent hydrophobicity can be conveniently obtained. As shown in Figure 1, the water contact angle of unmodified silica film is hydrophilic with a water contact angle of 23.4°. After surface modification with HDMS concentration of more than 70%, the silica film shows superhydrophobic property, the water contact angles are more than 160° and 150° with a droplet volume of 3 μL and 6 μL, respectively. In fact, the hydroxyl groups on silica particles may be totally replaced by hydrophobic $-Si(CH_3)_3$ groups in optimal condition. The superhydrophobicity of the top layer can afford the double-layers broadband AR coating more environmental resistance.

3. Conclusions

A double-layer double-wavelength AR coating, which has nearly 100% transmittance at both 1064 nm and 532 nm, can be designed using thin-film design software (TFCalc) and the sol-gel process consists of a good experimental method to achieve this design. Superhydrophobic ORMOSIL thin film with an ultralow refractive index for the top layer was deposited from surface-modified silica particles by HMDS. The surface modification of silica particles decreased the refractive index of silica thin film from 1.23 to 1.13 and significantly increased the hydrophobicity of silica thin film. This double-wavelength silica AR coating prepared by sol-gel process can find applications in high power laser system.

4. Experimental Section

Materials: Tetraethylorthoxylsilicane (TEOS) was purchased from Sigma-Aldrich. HMDS was purchased from Alfa-Aesar. The water was deionized. Ethanol and ammonia water were purchased from Kelong Chemical Reagents Factory (Chengdu, China). All chemicals were used without further purification.

Preparation of Base-Catalyzed Pure Silica Sol: The base-catalyzed silica sols were typically prepared using the Stöber method, as previously reported.[14,15] Tetraethylorthoxylsilicane (164 g) was mixed with anhydrous ethanol (1385 g), ammonia water (25%–28%, 8.7 g), and deionized water (40 g). The solution was left in a closed glass container and stirred at 30 °C for 2 h and aged at 25 °C for 2 weeks to obtain silica particles with diameter of about 15 nm. This sol was named base-catalyzed pure silica sol.

Surface Modification of Silica Particles: HMDS was added into the base-catalyzed pure silica sol and aged at 25 °C for more than 7 days to guarantee the surface modification of silica particles being carried out conveniently. The weight ratio of HMDS to silica was varied from 0% to 300%.

Preparation of Acid-Catalyzed Silica Sol: Tetraethyl silicate (104 g) was mixed with anhydrous ethanol (860 g) and water (36 g) that contained concentrated hydrochloric acid (0.2 g). The solution was left in a closed glass container and stirred at 30 °C for 2 h and aged at 25 °C for 2 weeks.

Preparation of Base- and Acid-Catalyzed Mixed Silica Sol: Before mixing, the base-catalyzed silica sol was refluxed for more than 24 h to remove ammonia. Then the base-catalyzed silica sol and acid-catalyzed silica sol were mixed in different proportions to give silica thin films with refractive index varying from 1.22 to 1.44.

Film Preparation: BK-7 substrates were cleaned by ultrasonication in acetone for 10 min and wiped carefully before dip-coating. The sols were deposited on the well-cleaned BK-7 substrates by dip coating at a desired withdraw rate. To prepare double-layer double-wavelength AR coating, the withdraw rates for top and bottom layers were both about 195 mm/min and the weight ratio of acid-catalyzed silica sol to base-catalyzed silica sol in the mixed silica sol was about 25.3%. The film thickness of silica thin film from sol-gel process was related to the room temperature and humidity, so the withdraw rate during preparation of double-wavelength AR coating could be very different if the room temperature and humidity was different. Finally, the as-deposited film was heat treated at 160 °C for 2 h.

Characterization: The refractive indices of AR coatings were determined using an ellipsometer (SENTECH SE850 UV). Contact angles were measured on a Krüss DSA100 (Germany). The transmission spectra were measured with an UV-Vis spectrophotometer (Mapada, UV-3100PC). SEM was performed using a JSM-5900LV high-resolution SEM at an acceleration voltage of 30 kV. The double-wavelength AR coating was coated on a silicon wafer and then coated with Au prior to SEM imaging.

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[1] B. G. Prevo, E. W. Hon, O. D. Velev, *J. Mater. Chem.* **2007**, *17*, 791.
[2] H. P. Ye, X. X. Zhang, Y. L. Zhang, L. Q. Ye, B. Xiao, H. B. Lv, B. Jiang, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2347.
[3] A. L. Pénard, T. Gacoin, J. P. Boilot, *Acc. Chem. Res.* **2007**, *40*, 895.
[4] P. Prené, J. J. Priotton, L. Beaurain, P. Belleville, *J. Sol-Gel Sci. Technol.* **2000**, *19*, 533.
[5] P. K. Whitman, S. C. Frieders, J. Fair, I. M. Thomas, R. Aboud, C. B. Thorsness, A. K. Burnham, *ICF Quarterly Report*, **1999**, *9*, 163.
[6] I. M. Thomas, *Proc. SPIE* **1997**, *3136*, 215.

[7] J. Q. Xi, J. K. Kim, E. F. Schubert, *Nano Lett.* **2005**, *5*, 1385.
[8] J. Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. Chen, S. Lin, W. Liu, J. A. Smart, *Nat. Photonics* **2007**, *1*, 176.
[9] P. Falcaro, L. Malfatti, T. Kidchob, G. Giannini, A. Falqui, M. F. Casula, H. Amenitsch, B. Marmiroli, G. Grenci, *Chem. Mater.* **2009**, *21*, 2055.
[10] M. Yamaguchi, H. Nakayama, K. Yamada, H. Imai, *Opt. Lett.* **2009**, *34*, 2060.
[11] H. Hattori, *Adv. Mater.* **2001**, *12*, 51.
[12] I. M. Thomas, *Appl. Opt.* **1992**, *31*, 6145.
[13] I. M. Thomas, A. K. Burnham, J. R. Ertel, S. C. Frieders, *Proc. SPIE* **1999**, *3492*, 220.
[14] X. X. Zhang, H. P. Ye, B. Xiao, L. H. Yan, H. B. Lv, B. Jiang, *J. Phys. Chem. C* **2010**, *114*, 19979.
[15] X. X. Zhang, B. B. Xia, H. P. Ye, Y. L. Zhang, B. Xiao, L. H. Yan, H. B. Lv, B. Jiang, *J. Mater. Chem.* **2012**, *22*, 13132.