

## Sol-Gel Preparation of PHFBMA/PFG/Silica Coatings with Durable Shortwave-band Antireflective Performance

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**Abstract:** A new silica shortwave-band antireflective (AR) coating with durable optical performance on fused silica substrate was prepared by a base-catalyzed Sol-Gel process using tetraethyl orthosilicate (TEOS) as a precursor. 1H, 1H, 12H, 12H-perfluoro-dodecane-1, 12-diol (simplified as PFG) was used to control the structure and size of the silica particles in the sols, and hence decreased the refractive indices of the coatings. After Poly (2, 2, 3, 4, 4, 4-hexafluorobutyl) methacrylate (PHFBMA) being introduced into the silica sols, the AR coatings could retain a transmission about 99.9% at about 300 nm. At the same time, the transmission stability of the coatings was improved significantly, which were tested in a moisture environment and an organic-containing vacuum chamber, respectively.

**Key words:** antireflective coating; Sol-Gel; shortwave-band; hydrophobicity; organic contamination

As a potential pollution-free high power tool, considerable interest has been given to the development of solid state lasers at ultraviolet (UV) band<sup>[1]</sup>. For this purpose, high peak power optics is in need of short wavelengths about 300 nm, especially 351 nm which is called third harmonics. And because of their excellent resistant performances to shortwave-band laser radiation, the Sol-Gel AR coatings have good applications in these high power laser systems<sup>[2-3]</sup>. Sol-Gel silica AR coatings consist of layers of silica particles which are randomly stacked on optics surfaces. However, with a percent of voids and a hydroxyl-covered surface, the silica Sol-Gel AR coatings are susceptible to environmental contaminants such as water vapor and volatile organics, thus the coatings always experience transmittance decline in usage<sup>[4-6]</sup>. There are many attempts to improve antireflective durability of the silica AR coatings by modification of silica sols<sup>[7-9]</sup>.

It is generally recognized that water and volatile organic compound repellency of a surface is attributed to the surface chemistry and surface roughness on multiple scales<sup>[10]</sup>. The aim of present work is to prepare a silica coating with durable shortwave-band AR performance, not only in moisture environment but also in organic-containing vacuum chamber, by combining the silica spheres with perfluoroalkyl methacrylic polymer. In order to obtain desirable transmission while bearing high concentration of PHFBMA in AR coating, PFG was introduced into the silica sol to control the stacking manner, size and porosity of the silica particles. Afterwards the silica sols were modified by employing the PHFBMA, AR coating with

transmission of 99.9% was obtained at about 300 nm, and the transmission stability of the coatings was enhanced greatly.

## 1 Experimental details

### 1.1 Preparation of silica sol

Colloidal silica sol was prepared by the hydrolysis and condensation of TEOS in deionized water and anhydrous ethanol catalyzed by ammonium hydroxide in an appropriate molar ratio. The final concentration of SiO<sub>2</sub> was 3.3wt%. Different amount of PFG was added into it. The ratio of PFG to SiO<sub>2</sub> was 0, 1wt%, 2wt%, 4wt% and 6wt%, respectively. Following stirring at room temperature for 6 h, the resultant sol was aged at 25°C for 10 d.

### 1.2 Modification of silica sol

PHFBMA was used as a modifier, and the number-average molecular weight of this polymer is about 29000. Assisted by ultrasonic, the PHFBMA was dissolved in ethanol in a few minutes. The ethanol solution of the polymer was then added into the silica sol and stirred for another 2 h. The ratio of PHFBMA to SiO<sub>2</sub> was 6.8wt%, 13.2wt% and 26.4wt%, respectively. Before coating application, all the sols were carefully filtered through 0.22 nm PVDF filters.

### 1.3 Preparation of AR coating

The fused silica substrates were cleaned by ultrasonication in acetone, and then wiped carefully with cleanroom wipers. Afterwards the modified silica sol was deposited on

these well cleaned fused silica substrates by dip-coating at the withdrawal rate of 70 mm/min. In order to obtain the refractive indices of the coatings before and after modification, the silica sol was deposited on well cleaned silicon substrates by dip-coating at the same withdrawal rate. All of the coatings were heated at 160°C for 24 h.

#### 1.4 Characterization of Sol-Gel derived silica coating

Fourier transform infrared (FTIR) absorption spectra of PFG/PHFBMA/silica, pure silica, PFG and PHFBMA were analyzed by Bruker Tensor 27. PFG/PHFBMA/silica and pure silica FTIR spectra were characterized from the pellet of the mixture of KBr powder and a small amount of silica xerogel, respectively. Viscosities of the sols were measured using a programmable rheometer (Brookfield, DV III ULTRA). The transmission spectra were measured with an UV-Vis spectrophotometer (Lambda 950). The water contact angles test of the AR coatings were carried out by a contact angle machine (Krüss DSA100L). The thickness and refractive index of the AR coatings was determined on the ellipsometry (SENTECH SE850 UV). Scanning electron microscope with focused ion double beam (FIB-SEM) (Helios Nanolab 650) was used to characterize the microcosmic structure and particle morphology of the AR silica coatings. Atomic force microscope (AFM) (MFP-3D) was employed to characterize the surface microstructure morphology of the AR coatings. The contour profile of the silica coatings were observed by contourgraph (WYKO RST-PLUS).

## 2 Result and discussion

### 2.1 Structure of sol particles characterized by IR spectroscopy

As shown in Fig. 1, the absorption peak revealed at 1745  $\text{cm}^{-1}$  are attributed to C=O asymmetric stretching mode of PHFBMA. The absorption band at 1101  $\text{cm}^{-1}$  and 1190  $\text{cm}^{-1}$  are assigned to asymmetric stretching and symmetric stretching mode of C–O of ester bond. For PHFBMA/PFG/silica, further absorption band were recorded at 1751  $\text{cm}^{-1}$ , 1172  $\text{cm}^{-1}$  and 1103  $\text{cm}^{-1}$ , corresponding to the existence of C=O and C–O in PHFBMA/PFG/silica particles.

In the IR spectra of PFG, PHFBMA and PHFBMA/PFG/silica, the strong absorption band at about 1290  $\text{cm}^{-1}$  corresponds to the stretching mode C–F<sup>[11-12]</sup>. The absorption bands at 1083  $\text{cm}^{-1}$  and 790  $\text{cm}^{-1}$  appeared in the spectra of pure silica and PHFBMA/PFG/silica, attributed to stretching mode of Si–O–Si bonds and Si–O bonds<sup>[13]</sup>.

### 2.2 Refractive index

To obtain AR coatings with excellent transmittance, the

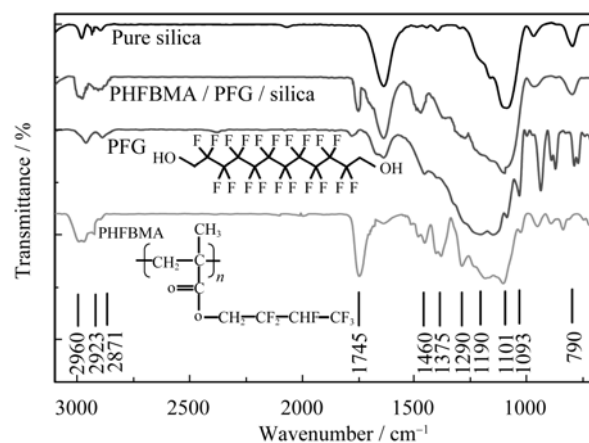


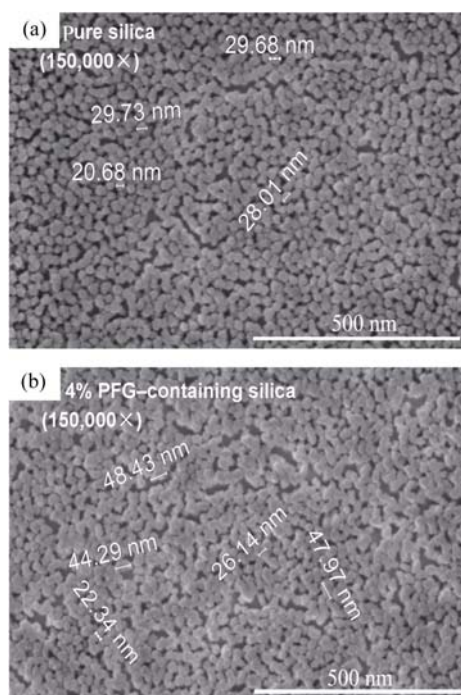
Fig. 1 FTIR absorption spectra of PFG/PHFBMA/silica xerogel, pure silica xerogel, PFG and PHFBMA

refractive index fitting between AR coating and substrate is very important. For the fused silica substrate with a refractive index of 1.475 at about 365 nm, the refractive index of a quarterwave AR coating close to 1.22 is desirable. The refractive index of modified AR coating is related to not only the connections between modifiers and silica particles, but also the stacking manner of the silica particles. As shown in Table 1, in the series of originally pure silica coating, by changing the ratio of PHFBMA to silica, refractive indices ranging from 1.245 to 1.271 were obtained. In order to obtain desirable transmission of AR coating bearing high content of PHFBMA, PFG was introduced into the silica sol. As shown in Table 1, as the PFG/silica ratio increasing, the refractive indices of the PFG/silica coatings were decreased from 1.212 to 1.177. This is attributed to the formation of PFG-containing silica, in which the characters such as particle size, aggregate mode between particles and stack manners lead to a more porous coating structure than pure silica systems. Therefore, PHFBMA modification is carried out after the PFG/silica sols being prepared. This allows us to prepare silica AR coatings with high PHFBMA loading and excellent transmission. It is shown in Table 1 that the PHFBMA/PFG/silica coatings only have a refractive index of 1.230 when the ratio of PHFBMA to silica is 26.4wt%, whereas the refractive index of PHFBMA/silica coating is 1.271. As we observed from Table 1, there is a close relationship between the coating thickness and sol viscosity. At the same withdraw rate in dip-coating, as the sol viscosity increases, the coating thickness shows a tendency of increasing.

We also tried to observe the structural status of the silica systems directly by FIB-SEM. As shown in Fig. 2, there are notable differences in particle size and morphology between silica coatings with and without PFG. In Fig. 2 (b), 4wt% PFG-containing silica shows a particle stacking

**Table 1** Refractive indices (at 365 nm) and thickness of the silica coatings and viscosity of the sols

Weight ratio of PFG to silica/%	Silica coatings		Viscosity of silica sols / ( $\times 10^{-3}$ , Pa·s)	Weight ratio of PHFBMA to silica/%	Silica coatings		Viscosity of silica sols / ( $\times 10^{-3}$ , Pa·s)
	Refractive index ( <i>n</i> )	Thickness /nm			Refractive index ( <i>n</i> )	Thickness /nm	
0	1.226	64.2	1.52	6.8	1.245	65.6	1.53
				13.2	1.263	67.6	1.53
				26.4	1.271	69.0	1.54
1	1.212	75.4	1.56				
2	1.204	86.1	1.66				
4	1.195	98.7	1.75	6.8	1.203	59.1	1.37
				13.2	1.210	61.4	1.44
				26.4	1.230	63.5	1.50
6	1.177	106.9	2.05				

**Fig. 2** FIB-SEM images of the coatings

(a) Pure silica coating with a magnification of 150,000; (b) 4wt% PFG-containing silica with a magnification of 150,000

pattern of “two-particle-team” which is obviously more porous than the single particle arranged pure silica coating as shown in Fig. 2 (a). This phenomenon is very interesting and worthy for further investigation.

Surface morphology of the coatings was investigated by AFM. As shown in Fig. 3 (a) and (b), silica coatings with PFG have a structure of higher porosity than those coatings prepared without PFG, and the situation is well consistent with the results observed by FIB-SEM. With the existence of a large number of hydroxyl groups in the pore and on the surface of silica particles, the solvent surface tension on silica gel network is considerable, which creates compressive forces around pores and results in gel contraction as the solvent evaporates. For PFG/silica gel, these hydroxyl groups were shielded by PFG compound,

and thus free energy of the solvent was lowered on it. Compared with pure silica, in the process of solvent evaporation and coating formation, PFG/silica gel contraction was restrained and the porosity could be retained. And with more nanopores in the coating structure, the PFG/silica coating has a lower refractive index.

According to Hansen solubility parameters, affinities between different polymers and affinities to surfaces can improve dispersion and adhesion. And it can be inferred from the group's contributions to solubility parameters that PHFBMA has similar solubility parameters with PFG. After modification by PFG, the surface of silica particles was covered by this compound. Then, with the addition of PHFBMA, the PFG/silica particles will mix homogeneously with the polymer. As is shown in Fig. 3(c), for PHFBMA /PFG/silica coating, the polymer molecules fill into the pores between silica particles and the particles are enwrapped and form big lumps. Thus, the porosity of the coatings is lowered to a certain degree. These results illustrate the comparative connections of the coatings refractive indices.

### 2.3 Optical properties

Figure 4 (a) shows the optical transmittance spectra of pure, 1wt%, 2wt%, 4wt% and 6wt% PFG-containing silica coatings on fused silica substrates, in which the silica content was 1.65wt%. The optical transmittances of the silica coatings, without and with different content of PFG, can be higher than 99.9% at certain wavelengths. With the ratio of PFG/silica increase from 0 to 6wt%, the maximum transmittance shifted to higher wavelength accordingly. As shown in Fig. 4(b), with the concentration of PHFBMA increasing from 6.8wt% to 26.4wt%, the maximum transmission of the PHFBMA/silica coatings decreased from 99.9% to 99.7%. And their maximum transmittance moved to long-wave. Figure 4(c) shows the transmittance of 4wt% PFG-containing sol modified by PHFBMA. As the concentration of PHFBMA increasing from 6.8wt% to 26.4wt%, the maximum transmittance

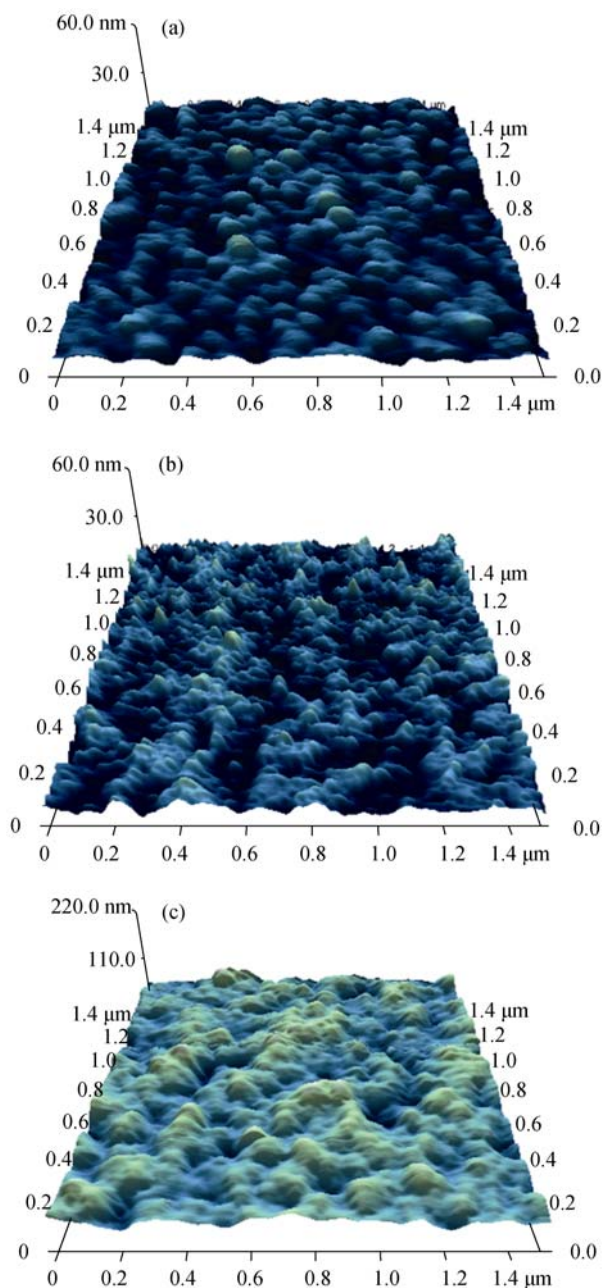


Fig. 3 Surface morphologies of coatings  
(a) Pure silica coating; (b) 4wt% PFG containing silica coating; (c) 4wt% PFG containing silica coating modified by 26.4wt% of PHFBMA

decreased and peak of the spectra shifted to a higher wavelength. Nevertheless, the maximum transmittances of PHFBMA/PFG/silica coatings can reach 99.9% at a certain wavelength.

As an important property of optics, the surface roughness of the coatings was measured. As shown in Fig. 5, the surface roughness of pure silica coatings, PHFBMA/silica coatings and PHFBMA/PFG/silica coatings are about 0.6 nm. With such a smooth surface, the scatter losses of these silica coatings are nearly neglectable.

## 2.4 Effect of PFG and PHFBMA on hydrophobicity of AR coating

Kim, *et al* suggested that AR durability of AR coatings

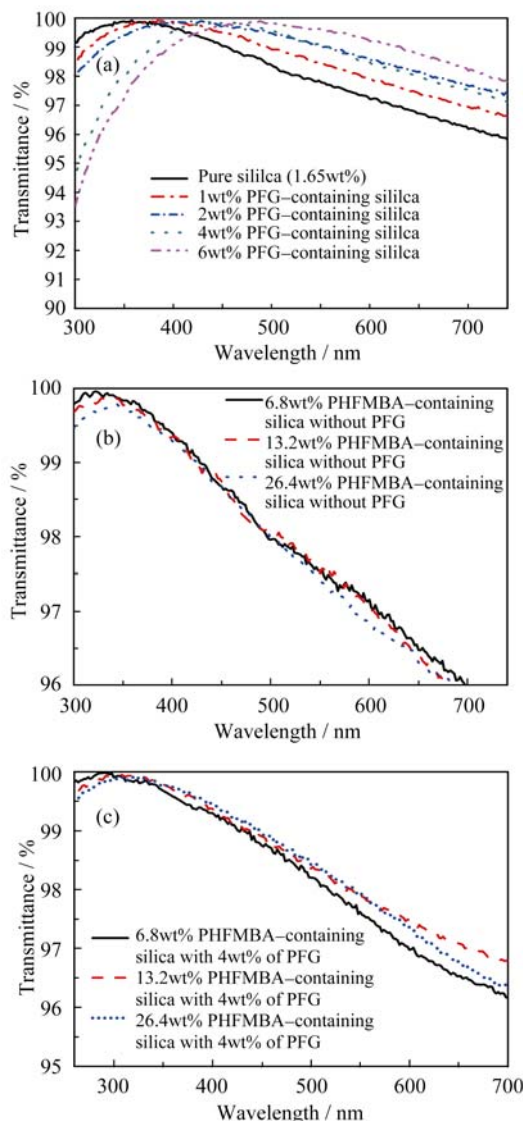


Fig. 4 Transmittance spectra of AR coatings  
(a) Pure silica (1.65wt%) and silica with different content of PFG; (b) Pure silica (1.65wt%) with different content of PHFBMA; (c) 4wt% PFG containing silica with different content of PHFBMA

is closely related to their hydrophobic character<sup>[14]</sup>. Figure 6 shows the water contact angles of the coatings. While the water contact angles of pure silica coating is about 36°, that of the silica coating with 4wt% PFG reaches 71°. This increase is caused by the existence of a certain amount of  $-\text{CF}_2$  in the coatings, which lowers the surface energy of the coating surfaces. While the concentration of PHFBMA in 4wt% PFG-containing sol increases from 0 to 26.4wt%, the water contact angles of the coatings increase from 71° to 116°. In the respects of water contact angle, surface hydrophobicity is determined mainly by molecules on the material surfaces, and this effect can be strengthened to a certain degree by the details of surface morphology<sup>[15]</sup>. In this case, with such a smooth surface of surface roughness about 0.6 nm, coating's surface morphology would influence water repellency to what extent needs further research.



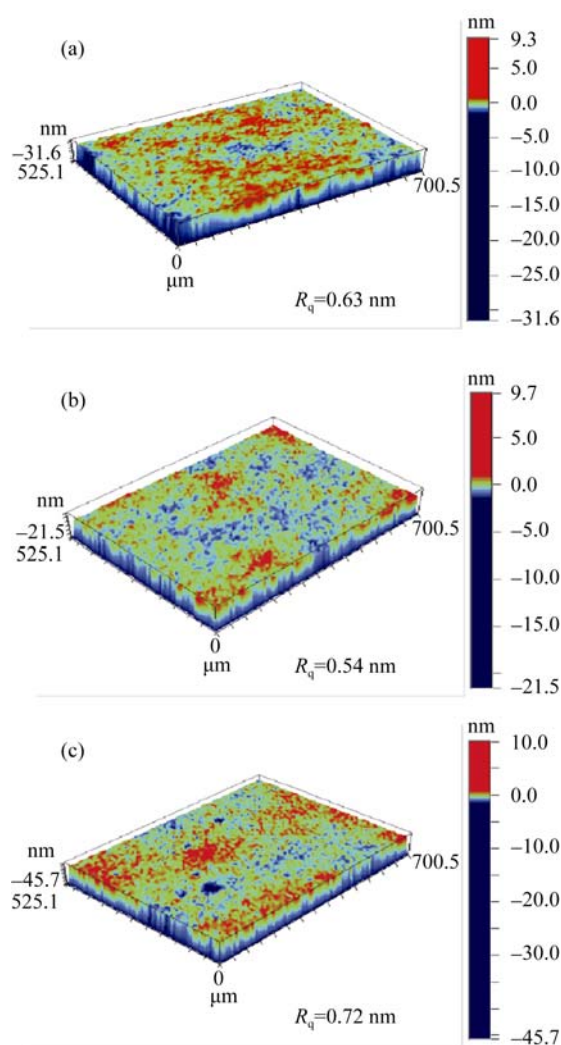


Fig. 5 Surface roughness of the coatings

(a) Pure silica; (b) 26.4wt% PHFBMA-containing silica; (c) 26.4wt% PHFBMA-containing silica with PFG

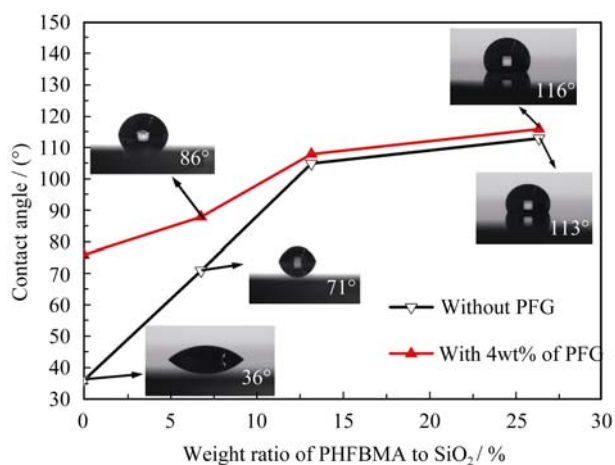


Fig. 6 Water contact angle values of silica coatings without and with 4wt% of PFG vs PHFBMA concentration

## 2.5 Transmission stability of AR coating

AR durability in moisture is an important property for AR coatings. Figure 7(a) shows the maximum transmi-

ttance of pure silica, 4wt% PFG-containing silica and 4wt% PFG-containing silica with 26.4wt% of PHFBMA, as a function of test time in a closed container with 75% relative humidity at 25°C. It is obvious that the moisture resistant ability is improved after the introduction of PHFBMA. The maximum transmittance of the PHFBMA/PFG/silica coating decreases from 99.9% to 99.6%, while that of pure silica coating decreases from 99.9% to 99.3% after being tested for 7 d.

The fused silica samples coated with modified and pure silica were kept in a vacuum chamber of 0.15 MPa for 10 d. The evolution of the peak transmission due to contamination is shown in Fig. 7(b). The transmittance of pure silica coatings decreased dramatically from 99.9% to 97.7% during the contamination exposure, while that of the 4wt% PFG and 26.4wt% PHFBMA containing silica coatings changed from 99.9% to 99.0%. The organic contaminants in this vacuum chamber were characterized by GC-MS, and the result showed that there are a certain concentration of cyclohexane, cyclopentane, alkanes and alkenes in the vacuum chamber. The decrease of maximum transmittance of the silica coatings in vacuum chamber was due to the absorption of those organic contaminants, which were volatilized from vacuum pump oil.

The incorporation of PHFBMA and PFG significantly

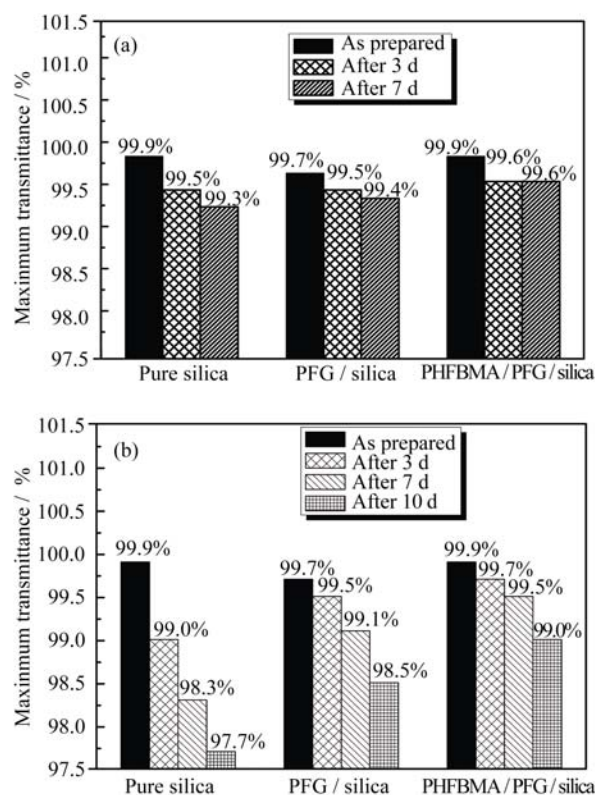


Fig. 7 Changes in maximum transmittance as function of test time

(a) In a closed container with 75% relative humidity at 25°C; (b) In a vacuum chamber of 0.15 MPa

improves the hydrophobicity and oleophobicity of AR coatings, which prevent the adsorption of water and organic contamination in the pore of the coating, affording a much better transmission stability in wet environments and coarse vacuum. This is mainly because of the lowered porosity and surface energy while containing higher PHFBMA content in silica AR coatings.

### 3 Conclusions

As a new shortwave-band AR coating, PHFBMA/PFG/silica coating is prepared by a base-catalyzed Sol-Gel process using TEOS as precursor. By adding PFG into the silica sol, the particle structure and size of the silica are successfully controlled, and hence decrease the refractive indices of the coating. Modification with PHFBMA can decrease porosity and lower the surface energy of the coatings. Consequently, introduction of PHFBMA into 4wt%-PFG silica increases the hydrophobicity and hence the transmission stability of the coatings maintains in wet environments. At the same time, by reducing the adsorption of organic contaminants, the stability of AR properties in a coarse vacuum environment is improved greatly. After being incorporated with PHFBMA and PFG, the silica AR coatings retain high transmission of up to 99.9% at about 300 nm, and possess an improved repellent ability to water vapor and volatile organics.

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## 溶胶-凝胶法制备 PHFBMA/PFG/SiO<sub>2</sub> 短波长长效增透膜

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**摘要:** 在碱性催化条件下, 以正硅酸乙酯为前驱体, 制备了一种新的、光谱性能长效的短波长减反膜。溶胶制备中, 采用 20 氟基-1, 12-十二醇 (PFG) 控制了二氧化硅颗粒的结构和尺寸, 从而一定程度地减小了薄膜的折射率。以 PFG 修饰的二氧化硅为基础, 再采用甲基丙烯酸六氟丁酯的聚合物(PHFBMA)对溶胶进行改性, 得到了适用于熔石英基底的 PHFBMA/PFG/SiO<sub>2</sub> 减反膜。该改性减反膜在 300 nm 左右可以达到 99.9% 的透过率, 并且一定湿度条件下和含有机污染物的真空腔室内的考察结果表明, 该改性膜层的透过率稳定性获得了显著提升。

**关键词:** 减反膜; 溶胶-凝胶; 短波; 疏水性; 有机污染物

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